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J. Stöhr H.C. Siegmann

Magnetism

From Fundamentals to Nanoscale Dynamics

With 325 Figures and 39 Tables



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To my three favorite women, my mother Marga, my wife Linda and my daughter Megan, who have taught me much more than science and given me the most important gift of all, love.

J. Stöhr

To my collaborators and students who, through their inspiration and company, have made my life as a physicist a joyful adventure.

H.C. Siegmann

Preface

This book emerged from a close collaboration of the authors which started in the fall of 2000. Early that year one of us (J.S.) had joined the Stanford faculty after spending nearly 15 years at the IBM Almaden Research Center and the other (H.C.S.) had just retired from a chair at the ETH Zürich and come to Stanford as a visiting professor. Together we organized magnetism meetings of a small group of scientists which oscillated weekly between the Stanford Synchrotron Radiation Laboratory (SSRL) and the Advanced Light Source (ALS) in nearby Berkeley. We also organized annual winter workshops at Lake Tahoe where all participants reported on their research – of course we snuck in a few ski runs, as well. These meetings were great fun and some seemed to go on forever because there was so much interest and enthusiasm and so much to discuss... The participants varied over the years and consisted of students, postdocs, Stanford and Berkeley scientists, visiting scientists and participants from industry. In alphabetical order, some of the people involved were Yves Acremann, Scott Andrews, Andreas Bauer, Mark Burkhardt, Venkatesh Chembrolu, Kang Chen, Sug-Bong Choe, Bruce Clemens, Alexander Dobin, Thomas Eimüller, Stefan Eisebitt, Sara Gamble, Alexander Kashuba, Marcus Lörgen, Jan Lüning, Gereon Meyer, Hendrik Ohldag, Howard Padmore, Ramon Rick, Andreas Scherz, Bill Schlotter, Andreas Scholl, Christian Stamm, John Paul Strachan, Jan Thiele, Ioan Tudosa, Ashwin Tulapurkar, Shan Wang and Xiaowei Yu. All this would have been impossible without support from the Office of Basic Energy Sciences of the US Department of Energy (DOE), and we gratefully acknowledge DOE's support of our research program.

We have also greatly benefitted from discussions with colleagues and from material they have provided, and we would especially like to thank Elke Arenholz, Sam Bader, Carl Bennemann, Matthias Bode, Patrick Bruno, John Clendenin, Markus Donath, Olle Eriksson, Jürgen Kirschner, Peter Oppeneer, Jürg Osterwalder, Stuart Parkin, Danilo Pescia, Dan Pierce, Theo Rasing, Andrei Rogalev, Kai Starke, Dieter Weller and Ruqian Wu.

With the present book we intend to give an account of the historical development, the physical foundations and the continuing research underlying

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the field of magnetism, one of the oldest and still vital field of physics. Our book is written as a text book for students on the late undergraduate and the graduate levels. It should also be of interest to scientists in academia and research laboratories.

Throughout history, magnetism has played an important role in the development of civilization, starting with the loadstone compass. Our modern society would be unthinkable without the generation and utilization of electricity, wireless communication at the speed of light and the modern hightech magnetic devices used in information technology. Despite the existence of many books on the topic, we felt the need for a text book that reviews the fundamental physical concepts and uses them in a coherent fashion to explain some of the forefront problems and applications today. Besides covering the classical concepts of magnetism we give a thorough review of the quantum aspects of magnetism, starting with the discovery of the spin in the 1920s. We discuss the exciting developments in magnetism research and technology spawned by the computer revolution in the late 1950s and the more recent paradigm shift starting around 1990 associated with spin-based electronics or "spintronics". The field of spintronics was largely triggered by the discovery of the giant magnetoresistance or GMR effect around 1988. It utilizes the electron spin to sense, carry or manipulate information and has thus moved the quantum mechanical concept of the electron spin from its discovery in the 1920s to a cornerstone of modern technology.

These historical and modern developments in magnetism are discussed against the background of the development and utilization of spin-polarized electron techniques and polarized photon techniques, the specialties of the authors. It is believed that the technological application of magnetism will continue with a growth rate close to Moore's law for years to come. Interestingly, the magnetic technology goals of "smaller and faster" are matched by "brighter and faster" X-ray sources, which are increasingly used in contemporary magnetism research. Novel ultra-bright X-ray sources with femtosecond pulse lengths will provide us with snapshots of the invisible ultrafast magnetic nanoworld. These exciting developments are another reason for the present book.

Last not least, this book is born out of our passion for the subjects discussed in it. In the process we had to get to the bottom of many things and understand them better or for the first time. This process took a deep commitment and much time, with "the book" often preoccupying our minds. The process was greatly aided by discussions with our colleagues and students and we would like to thank them at this place. In particular, we need to thank Ioan Tudosa for his critical comments and for helping us with numerous illustrations. In this book we give an account of the field of magnetism that is colored by personal taste and our way of looking at things. We hope that you will enjoy the result.

Stanford, CA January 2006 Joachim Stöhr Hans Christoph Siegmann

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Magnetes Geheimnis, erklär mir das! Kein gröβer Geheimnis als Lieb' und Hass. The magnet's mystery, explain that to me! No greater mystery but love and hate.¹

Johann Wolfgang von Goethe (1749–1832)

1.1 Magnetism: Magical yet Practical

What is magnetism? This question has fascinated people ever since Thales of Miletus (about 634–546 BC) first described the phenomenon as the attraction of iron by "lodestone", the naturally occurring mineral magnetite, Fe₃O₄. Over the last 2,500 years we have not only extensively used the phenomenon for navigation, power production, and "high tech" applications but we have also come a long way in exploring its origin. Yet, even today, it is extremely difficult to answer the simple question why magnets attract. In fact, the term "magnetic" has acquired such a fundamental and familiar meaning that, following Thales of Miletus, "magnetic" and "attractive" (or repulsive) are used synonymously, and this association still serves to "explain" the phenomenon. Any deeper scientific explanation sooner or later runs into "mysteries". An example is the very concept of spin which magically emerged from Dirac's relativistic treatment of an electron in an external electromagnetic field. Today we simply accept this concept and base our understanding of magnetism on the elementary concepts of spin, giving rise to the spin magnetic moment, and the motion of electronic charges and the associated orbital magnetic moment.

Of the four forces of nature that form the pillars of contemporary physics, the electromagnetic force is arguably of greatest importance in our everyday lives because we can easily manipulate it and hence utilize it for our needs. We truly live in an electromagnetic world and electromagnetic phenomena form the basis of the modern industrialized society. This fact alone gives the old topic of magnetism a modern day vitality. The importance of magnetism

1

¹For Goethe the magnet constitutes a fundamental phenomenon (Urphänomen) that cannot be further explained. It incorporates the polarity (like love and hate) which became the essence of Goethe's "Weltanschauung". In this "natural philosophy" only pairwise opposites (e.g., love-hate, north-south) constitute a "whole". It is interesting that this philosophy agrees with our modern knowledge of magnetism, i.e., that no magnetic monopoles have been found.

is enhanced by the fact that the field still undergoes dynamic developments. Ever new magnetic phenomena continue to be discovered in conjunction with our ability to atomically engineer new materials.

As throughout history, today's magnetism research remains closely tied to applications. It is therefore no surprise that some of the forefront research areas in magnetism today are driven by the "smaller and faster" mantra of advanced technology. The goal to develop, understand, and control the ultrafast magnetic nanoworld is furthermore accompanied by the development of new experimental techniques, that offer capabilities not afforded by conventional techniques. We shall see below that polarized electrons and X-rays provide us with unprecedented opportunities to get to the bottom of long standing and novel problems. At the brink of the 21st century we find ourselves in a situation where the old field of magnetism is full of vitality, life, and excitement and this fact constitutes the basis for our book.

Because magnetism is one of the oldest scientific topics there is of course (too) much to write about. It is therefore not easy to find the right emphasis on the many concepts, definitions, laws and the experimental and theoretical developments of this old and broad field. Our book aims at discussing fundamental concepts and modern applications of magnetism and we have selected topics based on three main principles. First, they were chosen to be the fundamental pillars of magnetism. Second, we emphasized those fundamentals with applications in modern magnetism research and technology. Third, we emphasized topics where new experimental approaches such as polarized electron beam and X-ray experiments, the specialties of the authors, have led to new insights and promise further breakthroughs in the future. In many cases we have chosen modern applications to illustrate the basic laws.

Rather than covering all aspects of magnetism, our book concentrates on magnetic phenomena that are the subject of modern conferences on magnetism and magnetic materials. Today's magnetism community is interested in the scientific understanding of magnetic phenomena and magnetic materials and, following the historical trend, is clearly motivated and influenced by the goal to utilize the acquired knowledge for technological advancement. Our treatment therefore does not cover other electron correlation phenomena which give rise to interesting charge and spin ordering effects, and may play an important role in high temperature superconductivity, for example. These phenomena deserve an extensive separate treatment since they are causing a paradigm shift in condensed matter physics.

It is only fitting that we start this book by taking a look at the historical development of the field. Some of the magnetism terminology used in this introduction is not explicitly defined but we shall come back to the important aspects later in this book. The following historical review is based on information from many sources. We found the books by Segrè [1,2], Verschuur [3] and Livingston [4] very valuable. In the age of the internet, much information was gathered and checked for consistency by means of searches and comparisons of sources on the world wide web.

1.2 History of Magnetism

The most primitive electrical and magnetic phenomena were no doubt observed before recorded history began, and they are perhaps the oldest topics in physics. According to Pliny the Elder's (23–79 AD) *Historia Naturalis* the name "magnet" came from a shepherd called Magnes, who found his ironnailed shoes or iron-tipped cane stuck to the ground.² It seems more likely that the name originates from Magnetes, the inhabitants of a town called Magnesia, located in Asia Minor (part of the Greek Empire), who knew about ore in the area nearby that was naturally magnetic. Since around 1500 AD, the name *lodestone* ("lode" being old English for "lead") has been used to describe such magnetic ore because of its use in navigation. Today we more specifically associate lodestone with the spinel magnetite, Fe_3O_4 , which is magnetically aligned in nature, most likely by the earth's magnetic field during the cooling process of hot lava.

Local alignment may also occur by the strong magnetic field of a lightning bolt that leaves a characteristic circular pattern around the point of impact as shown in Fig. 1.1 [5–8]. A lightning bolt contains a current of the order of 100

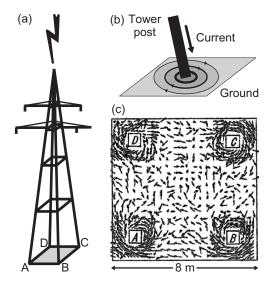


Fig. 1.1. Imprint of the magnetic field caused by a lightning current in the ironoxide containing ground at the foot of a transmission-line tower. (a) shows the geometry of the transmission-line tower, (b) the direction of current (positive charge) flow and the associated magnetic field lines, and (c) the measured magnetization around the four feet of the transmission-line tower labelled A, B, C, and D [5]. The magnetization (arrows) in the iron-oxide rock is seen to follow the circular magnetic field around the four points

²The smelting of iron was developed already around 1200 BC.



Fig. 1.2. Working model of the first instrument known to be a compass, called Si Nan (the south governor) by the Chinese. The spoon is of magnetic lodestone, and the plate is of bronze [10]

kA with a typical current density of 10^5 A/m^2 in a flash of a few microseconds duration. The current direction (flow of positive charge) is typically from the ground to the clouds, i.e., is in the opposite direction as that observed in the case shown in Fig. 1.1.

The first definite statement on magnetism is attributed to Thales of Miletus (about 634–546 BC) who said that lodestone attracts iron. Starting with the Chinese writer Guanzhong (died 645 BC) the Chinese literature in later centuries is also full of references to lodestone, called *ci shi*, the "loving stone" because of its ability to attract iron [9]. It is believed that the first direction pointers were made during the Qin dynasty (221–206 BC) by balancing a piece of lodestone. The lodestone was ground into the shape of a serving spoon that was placed on a bronze plate as shown in Fig. 1.2. Its handle miraculously pointed to the south.

Rather than navigation, these simple direction pointers were likely used for $feng \ shui^{3}$ or geomancy, the technique of achieving harmony with the forces of nature by properly aligning buildings and placing of objects. In particular, feng shui seeks to optimize the attractive and repulsive forces of magnetic fields that according to ancient Chinese philosophy surrounds all objects. In the context of magnetic energy it is interesting that much later, around 1780, Franz Anton Mesmer formulated a healing method on the belief that living bodies could be magnetized and healed – "mesmerized" – by magnetic fields [4]. His influence

³Feng shui (also fung shui), which translates literally as "wind water", is an ancient Chinese philosophy and practice based on the principle that all living things in the universe are subject to the control of the environment. It is still widely practiced today and tries to achieve harmony with the eight elements of nature – heaven, earth, hills, wind, fire, thunder, rain, and ocean. Also important are energies such as the air or "chi" and the magnetic energy, as are the spirits of yin (female-passive) and yang (male-active).

was so strong that his name has passed into the English language, an honor accorded to few. 4

The development of civilization has been defined by mastering the production and use of materials. To our knowledge, magnetic direction pointers or compasses were first used for navigation in China in the late 11th or early 12th century and the compass became known in Europe sometime later in the 12th century. Without magnetic materials in the form of a compass, the great voyages of discovery may not have taken place and the history of the world might have evolved differently!

The first scholarly treatment of magnetism is attributed to the French crusader and scholar Peter Peregrinus (Pierre Pèlerin de Maricourt) who in 1269 wrote an extended letter, an *epistola*, that described facts known about loadstones and discussed how to make instruments with them [3]. Three centuries later William Gilbert (1540–1603), a medical doctor and gentleman scientist, built on this work and conducted a truly systematic study of magnetism, summarized in his famous treatise *De Magnete*, published in 1600. He proposed that the earth itself is a giant magnet, with a field similar to that of a bar magnet. He also suggested that the magnetic poles do not coincide with the geographic ones defined by the earth's axis of rotation. This explained earlier observations of navigators like Columbus, who noted discrepancies between the direction of a compass needle and directions indicated by the stars. The earth's field was modeled in detail later around 1835 by Carl Friedrich Gauss (1777–1855).⁵

Until 1819 only one kind of magnetism was known, the one produced by lodestones or by iron compasses that had been magnetized by lodestones.⁶ Over the following years the world of magnetism was revolutionized by the work of four people.

In 1819 Hans Christian Ørsted (often spelled Oersted) (1777–1851) observed the magnetic force exerted on a magnetic needle by the electric current in a nearby wire. A year later the French scientists Jean-Baptiste Biot (1774– 1862) and Felix Savart (1791–1841) derived the magnetic field around a current carrying wire and during 1820–1825 André Marie Ampère (1775–1836) considered the forces between current carrying wires. This led to the famous laws named after the discoverers.

⁴Mesmer's teachings were based on earlier claims by Paracelsus (1493–1541) that magnets could be used for healing. In addition, Mesmer claimed that *animal magnetism* was residing in humans, and that healing could proceed by exchange of a "universal fluid" between him and his patients, without the explicit use of magnets.

⁵The origin of the earth's magnetic field is not well understood but is attributed to turbulent motions within electrically conductive liquid Fe in the earth's core (see Fig. 3.2).

⁶It is interesting to note that compass needles were typically made of iron which has a larger saturation magnetization than lodestone. However, because Fe has a much smaller coercivity than lodestone the needle often had to be remagnetized by a lodestone that was carried on board of ships [4].

Classical electromagnetism peaked with the work of two of the greatest physicists of the 19th century, the experimentalist Michael Faraday (1791– 1867) and the theorist James Clerk Maxwell (1831–1879) [1]. In 1831 Faraday discovered electromagnetic induction, and in 1845 he discovered a direct connection between magnetism and light: the magneto-optical or Faraday effect [11]. The magneto-optical Faraday effect is the change of light polarization in *transmission* through a magnetized material. The same effect in *reflection* was discovered in 1876 by the Scottish physicist John Kerr (1824–1907), and is called the magneto-optical Kerr effect in his honor. Faraday's ideas developed in his book *Experimental Researches in Electricity*, and in particular, his discoveries of electric motors, generators, and transformers, have become the foundation of the industrialized society. We shall come back to this point at the end of this section, in conjunction with the importance of strong permanent magnets.

Maxwell placed Faraday's notion of a connection between electricity and magnetism on a firm mathematical footing, developed in his book *Treatise* on *Electricity and Magnetism*. This constituted the birth of electromagnetism and the electromagnetic field. Today the concept of a "field" is a cornerstone of physics. In 1855 Wilhelm Eduard Weber (1804–1891) had derived a value $1/\sqrt{\mu_0\epsilon_0} = 3.1074 \times 10^8$ m/s in laboratory based experiments but could not understand why this was close to the speed of light. This connection was made by Maxwell who through studies of the equations describing electric and magnetic fields was led to the value $c = 1/\sqrt{\epsilon_0\mu_0}$. Maxwell concluded that light is a form of electromagnetic wave. The connection between magnetism and light had been established. Even today we still marvel at the power of Maxwell's equations and our continued struggle to comprehend their full content makes it even more remarkable that they were derived as early as 1864 – they are one of the truly great achievements in physics!⁷

Maxwell's theories and their experimental verification by Heinrich Hertz (1857–1894) in Germany, who discovered radio waves in 1888, today are the basis for global communications at the speed of light. It is fair to say that Maxwell's theory became accessible mostly through Hertz and the theoretical teachings of Henri Poincaré (1854–1912) in France. The 19th century development of magnetism concluded with Pieter Zeeman's (1865–1943) discovery in 1896 of the effect named after him. The century was crowned by the discovery of the electron by Joseph John Thomson (1856–1940) in 1897, and independently around the same time by Emil Wiechert (1861–1928) [13].

The understanding of magnetic phenomena in the 20th century largely concentrated on the development of an atom-based picture [2]. While correspondence between Augustin Jean Fresnel (1788–1827) and Ampère already mentioned the idea of microscopic currents as the origin of magnetism, a for-

 $^{^7}$ Maxwell's work was already deeply appreciated during his lifetime. For example, Ludwig Boltzmann wrote full of admiration "Was it a God who wrote these symbols ...?" [12]

1.2 History of Magnetism 7

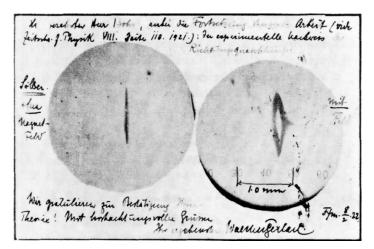


Fig. 1.3. Postcard sent by Walther Gerlach to Niels Bohr on February 8, 1922. In translation it says "Honorable Mr. Bohr, here [is] the continuation of longer work (see Z. Phys. 8, 110 (1921)). The experimental proof of directional quantization. We congratulate [you] on the confirmation of your theory! With respectful greetings, yours truly, Walther Gerlach." From [15]

mal treatment was not developed until 1907 when Pierre Weiss (1865–1940) introduced a theory of ferromagnetism based on a molecular field concept [14]. His theory, combined with that of Paul Langevin (1872–1946), explained the ferromagnetic–paramagnetic transition observed by Pierre Curie (1859–1906) at the so-called Curie temperature.

In 1913 Niels Bohr (1885–1962) first postulated that the angular momentum of electrons is quantized and that orbital magnetic moments are associated with orbiting electron currents. An elegant experiment by Otto Stern (1888–1969) and Walther Gerlach (1889–1979) in 1921 showed the splitting of a beam of Ag atoms upon traversing a nonuniform magnetic field due to quantized spin orientation. The important experiment is discussed in detail in Sect. 3.5.1. A postcard sent by Walther Gerlach to Niels Bohr on February 8, 1922, showing the refined results of the original experiment is shown in Fig. 1.3. The postcard shows photographs of the recorded pattern of Ag atoms without (left) and in the presence of (right) a magnetic field. It is interesting that the observed splitting into a doublet was incorrectly interpreted as arising from an orbital magnetic moment with l = 1 and $m = \pm 1$, as evident from Gerlach's note on the postcard in Fig. 1.3. He believed his experiment to confirm Bohr's theory of orbital angular momentum. At the time, the concept of spin was still unknown. The proper explanation of the splitting is due to the fact that Ag atoms have a single electron in their outer shell with s = 1/2, and so the splitting is actually due to the states $m_s = \pm 1/2$.

In order to account for the observed splitting of the emission lines of alkali atoms in magnetic fields, called the "anomalous Zeeman effect" (see

Sect. 6.6.1), Wolfgang Pauli (1900–1958) asserted in January 1925 that no two electrons may occupy the same states and cannot be described by the same set of quantum numbers, the famous principle later named by Dirac the *Pauli* exclusion principle. It is remarkable that at the time of Pauli's paper [16] the electron spin had not yet been discovered. Instead of today's quantum numbers n, l, m_l, m_s , Pauli's paper used a different, not easy to understand, set of quantum numbers. He realized that a satisfactory explanation of the anomalous Zeeman effect required more than the three quantum numbers n, l, m_l and called this a "Zweideutigkeit" (two-valuedness) of the quantum properties of the electron without specifying its origin [17]. The important step of identifying the "Zweideutigkeit" with the electron spin was taken by Uhlenbeck and Goudsmit later that year, in October 1925 [18–20] (see later).

The three year period 1925–1928 constituted a quantum jump in physics. It saw the development of quantum mechanics by Werner Heisenberg (1901– 1976) and Erwin Schrödinger (1887–1961) and the introduction of the electron spin. The idea of a "spinning electron" was mentioned for the first time by Arthur Holly Compton (1892–1962) in 1921 for reasons that were wrong and unconvincing [20]. Unaware of Compton's suggestion, George E. Uhlenbeck (1900–1988) and Sam A. Goudsmit (1902–1978) in 1925 used the fine structure (spin–orbit splitting) in atomic spectra to hypothesize the existence of the electron spin [18–20]. The revolutionary idea was the fact that the electronic spin had only half, $\hbar/2$, of the natural integer unit of angular momentum. The spin had independently been proposed in early 1925 by Ralph de Laer Kronig (1904–1995) [2] who told Pauli about it. Pauli objected to Kronig's suggestion of a half integer spin because it led to a discrepancy of a factor of 2 in the calculation of the fine structure splitting. Kronig did not publish his idea owing to Pauli's objection, as evidenced by the letter in Fig. 1.4.

In contrast, when Uhlenbeck and Goudsmit showed their idea to their mentor Paul Ehrenfest (1880–1933), he encouraged them to proceed with publication. For Uhlenbeck and Goudsmit, ignorance was bliss since they were unaware of the factor-of-2 problem. They worried more about the fact that it did not make sense to associate the spin with a classically rotating charged electron. The factor of 2 pointed out by Pauli was explained by a celebrated calculation of Llewellyn Hilleth Thomas (1903–1992) [20, 21] who in 1926 showed it to be due to a reference frame effect. Uhlenbeck and Goudsmit had been right after all!⁸

The concept of the spin with half-integer angular momentum is indeed quite amazing and even today its origin is not easily understandable. It naturally fell out of the celebrated relativistic theory of Paul Dirac (1902–1984), who in 1928 treated an electron in an external electromagnetic field, with-

⁸Much has been written about the discovery of the spin and the fact that Uhlenbeck and Goudsmit (or Kronig) did not receive the Nobel Prize. For a more detailed account and more references the reader is referred to the Pauli biography by Charles P. Enz [22], especially Chap. 5.

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Fig. 1.4. Part of a letter sent by Thomas to Goudsmit on March 26, 1926 [20]. It chronicles some of the events associated with the discovery of the spin. It reads as follows. "I think you and Uhlenbeck have been very lucky to get your spinning electron published and talked about before Pauli heard of it. It appears that more than a year ago Kronig believed in the spinning electron and worked out something; the first person he showed it to was Pauli. Pauli ridiculed the whole thing so much that the first person became also the last and no one else heard anything of it. Which all goes to show that the infallibility of the Deity does not extend to his self-styled vicar on earth."

out explicitly introducing the electron spin [23,24]. Dirac's quantum electrodynamics (QED) theory correctly described the magnetic properties of the electron and its antiparticle, the positron, but it proved difficult to calculate specific physical quantities such as the mass and charge of the particles. This was overcome in the late 1940s when Sin-Itiro Tomonaga (1906–1979), Julian Schwinger (1918–1994), and Richard P. Feynman (1918–1988) independently refined and fully developed QED⁹. An important feature of QED is that charged particles interact by emitting and absorbing photons, so that photons are the carriers of the electromagnetic force.

⁹The theories by Tomonaga, Schwinger, and Feynman were later shown to be equivalent by Freeman J. Dyson (b. 1923).

In 1928, the year of Dirac's QED theory, there was another important breakthrough in the history of magnetism with Heisenberg's formulation of a spin-dependent model for the exchange interaction [25]. The molecular field postulated by Weiss could now be interpreted as having its origin in the exchange interaction. The introduction of the strong, short-range exchange interaction constituted the birth of modern magnetism theory, which has its roots in, both, quantum theory and relativity. In a series of papers starting in 1932, Louis Néel (1904–2000) developed the concept of antiferromagnetism [26]. Néel's ideas of antiferromagnetic and ferrimagnetic spin alignments were later verified by neutron diffraction, pioneered by Clifford G. Shull (1915–2001). In the mid 1930s, band theory was first applied to magnetic systems by Neville F. Mott (1905–1996) [27], John C. Slater (1900–1976) [28, 29] and Edmund C. Stoner (1899–1968) [30, 31]. Today further developments of this theory are a cornerstone of modern magnetism, explaining the noninteger values of magnetic moments.

While research in magnetism today is largely driven by the fast moving pace of information technology, especially data storage and memory applications, one cannot forget that from a world-wide economic and societal point of view another more mundane application of magnetic materials may be more important. It is the use of high energy product permanent magnets that underlie the generation and use of electricity. Under the term "high energy product magnets" one understands magnets which exhibit a magnetization loop that is both wide (maximum coercive field) and high (maximum magnetization) [32]. Such magnets facilitate the reduction of the size and the weight of a device made from them, for example, electric motors and audio speakers. The historical increase of the energy product, formally defined as the product of the applied field and the magnetic induction $(H B)_{max}$, is illustrated in Fig. 1.5.

Today the strongest commercial magnet is Nd₂Fe₁₄B, developed in 1984 by Croat et al. [34] and Sagawa et al. [35]. Permanent magnets are key components of electrical generators.¹⁰ On a global scale, it is well established that the economic output of nations today is strongly correlated with their use of electricity since electrification makes an economy more efficient [36]. For example, today about half of the US energy is consumed as electricity and the US electricity retail sales amount to about 250 billion dollars per year, or about 2.5% of the US gross domestic product (GDP). It is therefore important to keep in mind the future development of improved permanent magnets. Such work was given new impetus by the suggestion of spring magnets by Kneller and Hawig in 1991 [37] and Stromski and Coey in 1993 [38]. Recent research on spring magnets has been reviewed by Bader [39]. More information on the properties of magnetic materials can be found in O'Handley's book [40].

¹⁰They have also revolutionized accelerator technology, allowing the construction of permanent magnet wigglers and undulators at third generation synchrotron radiation sources.

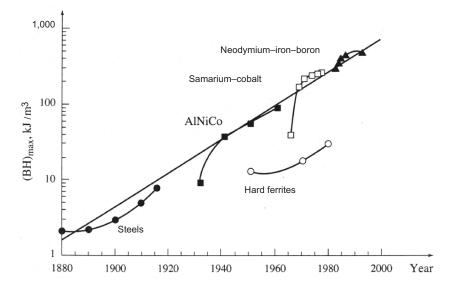


Fig. 1.5. Historical evolution of the performance of permanent magnets, defined by their energy product $(HB)_{\text{max}}$. Shown are five principal industrial magnet families. Note that the ordinate has a logarithmic scale. Figure taken from [33] after [32]

The most advanced applications of magnetism today are closely related to the technology underlying magnetic storage and memory [41,42]. As early as 1888 magnetic recording was proposed by Oberlin Smith and the first successful magnetic recording device, the telegraphone, was patented by Valdemar Poulsen in 1894 [41,43]. In 1949, physicist An Wang at Harvard created a device based on small ferrite rings, so-called "cores", that could be switched by current flow through wires that penetrated the rings, as illustrated in Fig. 1.6. In the 1950s this led to the development of nonvolatile *magnetic core memories* which became the dominant computer memories in the early 1960s but were replaced by semiconductor memories in the 1970s.¹¹

For the last 40 years magnetism has been used to store information in computers. This 50 billion dollars per year industry is based and dependent on fast developing concepts. It has fuelled a renaissance in magnetism research based on artificially engineered thin film structures [44, 45]. Nonvolatile magnetic memory is also making a comeback as so-called MRAM for magnetic random access memory [46]. From a science point of view the last 15 years have been particularly exciting and these developments and envisioned future concepts and technologies will be extensively discussed in this book.

¹¹Wang's patent was not granted until 1955, and by this time core memory was already in use. This started a long series of lawsuits, which eventually ended when IBM paid Wang several million dollars to buy the patent outright.

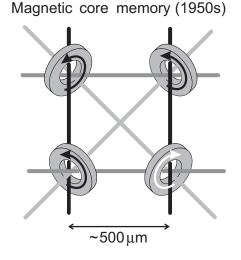


Fig. 1.6. Schematic of magnetic core memory used in computers in the 1960s. Currents through two wires were used for writing "bits", i.e., opposite magnetization states shown as white and black arrows, in small ferrite ceramic rings. The third wire was used for reading changes in magnetization through induction

1.3 Magnetism, Neutrons, Polarized Electrons, and X-rays

Early experiments to elucidate magnetic phenomena and materials were based on the measurement of forces and torques exerted on "samples" placed into magnetic fields produced by current flow through wires. Later experiments involved measurements of the magneto-optical Faraday (transmission) and Kerr (reflection) effects. Today the Kerr effect forms the basis of the magnetooptical recording technology by utilizing powerful yet small semiconductor lasers. The laser was proposed by Arthur L. Schawlow and Charles H. Townes in 1958 [47] and the first laser, made out of synthetic ruby, was built by Theodore H. Maiman in 1960. It is a powerful research tool for the study of modern magnetic materials, typically in the form of thin films, and scanning and imaging Kerr microscopy gives microscopic information with a resolution near the diffraction limit of light (about 200 nm). This diffraction limit is one of the Achilles' heals of visible light (and lasers) for the study of matter. The other one is the strong absorption of visible light by matter, making it difficult to look into or through many bulk materials. In principle, these limitations were overcome by Wilhelm Conrad Röntgen's (1845–1923) discovery of X-rays in 1895 [48] but the use of X-ray for the study of magnetic materials had to wait for nearly another century, as discussed later.

With the development of neutron diffraction and spectroscopy techniques in the 1940s and 1950s it was finally possible to determine the spin structure on

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an atomic level. The seminal contribution of neutron techniques to magnetism is reflected by the October 1994 press release by the Royal Swedish Academy of Sciences on the 1994 Nobel Prize in Physics, won by Bertram N. Brockhouse (1918–2003) and Clifford G. Shull (1915–2001), "Neutrons are small magnets, as are the atoms of a magnetic material. When a neutron beam strikes such material, the neutrons can therefore change direction through magnetic interaction with the atoms of the material. This gives rise to a new type of neutron diffraction which can be used to study the relative orientations of the small atomic magnets. Here, too, the X-ray method has been powerless and in this field of application neutron diffraction has since assumed an entirely dominant position. It is hard to imagine modern research into magnetism without this aid."

At the time of this press release efforts were already underway to change the role of X-rays in magnetism. This relatively recent and important development will be discussed later. The last 30 years have seen another important development, the generation and manipulation of spin polarized electrons [45]. This development has culminated in phenomena like giant magnetoresistance and "spintronics". We shall see later that studies by means of polarized electrons and X-rays have provided important new information. Today one could rephrase the last sentence of the above quote by the Nobel Prize Committee: It is hard to imagine modern research into magnetism without polarized electron and X-ray probes.

Within this book we shall not discuss the technique and applications of neutron scattering for the study of magnetic materials. This has been done extensively by others such as Bacon [49], Squires [50], Balcar and Lovesey [51], or more recently by Fitzsimmons et al. [52] and in the book on magnetism techniques by Zhu [53]. Another reason is that in today's magnetism research, materials with nanoscale dimensions and phenomena associated with surfaces, thin films, and interfaces are of prime importance. This has led to an increased demand for techniques with high sensitivity to small amounts of magnetic material or a small number of magnetic atoms. The *atomic sensitivity* of different techniques based on neutrons, electrons or X-rays may be expressed by a *figure of merit per atom per second* (FOM), defined by the product of the respective atomic interaction cross-section, the available incident flux, and the square of the magnetic contrast, as done in Table 1.3.

In the Table we have assumed that we can use samples as large as $10 \text{ mm} \times 10 \text{ mm}$ so that we list the incident flux per cm². For smaller samples the neutron flux and FOM would be reduced proportional to the area while the electron and photon flux remains unchanged down to sample areas of mm² or less. The Table shows that the use of neutrons with a small FOM is unfavorable for nanoscale magnetism research where the quest is for tools that can image small magnetic structures in short observation times. Neutron techniques have been and remain important for studies of bulk materials where the small FOM per atom is overcome by the large number of contributing atoms. In contrast, electron, resonant X-ray, and optical techniques offer a

Table 1.1. Comparison of factors determining the interactions of neutrons, low energy (< 10 eV) electrons, X-rays, and optical photons with magnetic materials such as the ferromagnets Fe, Co, and Ni. For neutrons and X-rays, the listed elastic scattering cross-sections σ refer to the magnetic cross sections per atom, for all other cases we list the combined charge and magnetic cross sections and indicate the magnetic contribution through a fractional value for the magnetic contrast P. We also list the incident monochromatic flux per appropriate experimental bandwidth Φ , and the relative figure of merit per atom per second, defined as $\sigma \Phi P^2$. The true magnetic signal for a given sample will depend on the probed number of magnetic atoms in the beam. For a given lateral sample size the number of atoms can be increased by making the sample thicker but the maximum number of probed atoms is inversely proportional to the cross-section. Therefore neutron techniques can overcome the limited scattering signal per atom by use of large and thick samples

	technique	atomic cross-	magnetic	incident	figure of merit
		section σ	contrast P	flux Φ^{b}	$10^{-7}\sigma\Phi P^2$
		$[barn/atom]^{a}$		$[\mathrm{s}^{-1}\mathrm{cm}^{-2}\mathrm{BW}^{-1}]$	
neutrons	El. Scatt. ^c	1	1	1×10^7	1
electrons	El. Scatt	1×10^8	0.5	1×10^{10}	2.5×10^{10}
X-rays	El. Scatt.	5×10^{-2}	1	1×10^{12}	5×10^3
	Res. El. Scatt. ^d	5×10^3	0.5	1×10^{12}	1.25×10^8
	Res. Abs. ^d	5×10^6	0.3	1×10^{12}	4.5×10^{10}
light	Kerr Effect	5×10^6	0.01	1×10^{16}	5×10^{11}
	04 0				

 $^{a}1 \text{ barn} = 10^{-24} \text{ cm}^{2}$

^b We have used monochromatic fluxes with appropriate experimental bandwidths (BW). The BWs are 1% for neutrons and 0.1% for electrons and photons ^c The nuclear and magnetic neutron cross sections are about the same

^d Total resonant cross-section at 3*d* transition metal L-edge

large sensitivity per atom and are well suited for the studies of surfaces, thin films and nanostructures.

Of the various techniques the magneto-optical Kerr effect (MOKE) has a very high FOM and the technique is relatively simple in practice [54,55]. Consequently, it is the technique that enjoys the greatest popularity, particularly for the study of ultrafast magnetization dynamics where the availability of short and intense laser pulses is a great asset [56, 57]. The main drawback of the Kerr technique is its limited spatial resolution which arises from the relatively long wavelength of near-visible light. This makes MOKE unsuited for imaging the magnetic structure of nanoscale magnetic elements. It is therefore expected that in the future the use of X-ray techniques will increase, especially for the study of nanoscale dynamics as discussed in Chap. 15.

In the following we shall discuss the developments of electron and X-ray techniques.

1.3.1 Spin Polarized Electrons and Magnetism

Quantum theory as well as the discovery of electron-spin resonance in 1945 by Evgeny Konstantinovich Zavoisky (b. 1907) [58] had made it clear that the magnetization in Fe, Co, and Ni must be predominantly generated by the spin polarization of the metallic electrons. However, for a long time it appeared impossible to extract spin polarized electrons from metals into vacuum by field emission or photoemission techniques despite expectations that the spin should be conserved in these emission processes. The problems were not due to the lack of a method to detect the spin polarization since "Mott detectors" were already used by H. Frauenfelder [59] in 1957 to detect the spin polarization of the electrons emitted in β -decay, verifying parity violation in weak interactions as suggested by Lee and Yang in 1956 [60]. Mott scattering is based on the spin–orbit coupling in the Coulomb scattering of electrons from heavy nuclei such as Au, discussed in Sect. 3.5.2. In the end, the inability to extract spin polarized electrons from ferromagnetic cathodes proved to be mainly due to improper surface preparation.

In 1969 Siegmann and collaborators [61,62] showed that once atomically clean surfaces of the magnetic metals are prepared, photoelectrons emitted from all kinds of ferromagnets exhibit sizeable spin polarization. Figure 1.7 shows a congratulatory postcard sent to H. C. Siegmann by Walther Gerlach in March 1969. Over the last thirty-plus years Spin-polarized photo-emission spectroscopy (SPES) has been developed into a powerful tool for the determination of the occupied spin polarized band structure of magnetic solids, particularly near or at the surface. The surface sensitivity arises from the very short mean free path of electrons in metals, which is of order 1 nm. SPES provides a rigorous test of our understanding of magnetism and the connection between electron emission and the electronic structure.

Spin polarized electron spectroscopies in their various forms were essential in the development of surface and thin film magnetism, an area that has provided the basis for a renaissance in magnetism research and enabled the development of innovative magnetic technologies over the last 15 years. The new structures of interest have nanoscale sizes in at least one direction so that interfacial and surface properties often dominate their static magnetic structure and transport behavior (see Chap. 13). The power of SPES techniques lies in their sensitivity to the spin polarized band structure of magnetic solids, be it in the form of insulators, metals, or the exotic half-metallic ferromagnets, distinguished by their complete spin polarization at the Fermi-level $E_{\rm F}$.

As an example of the insight that can be obtained by measurement of the spin polarization of photoelectrons, we show in Fig. 1.8 results for the oldest magnetic material, magnetite Fe_3O_4 , obtained in 1975 by Alvarado et al. [63] with natural crystals found in a dry river bed close to Zermatt, Switzerland. For a long time, the electronic structure of the ferrites was a subject of speculation [64] due to the ambiguities of spectroscopies without spin analysis. The Fe_3O_4 -spectra are complex due to the coexistence of 3 different Fe-ions and the

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Fig. 1.7. Postcard sent by Walther Gerlach to H. C. Siegmann on March 28, 1969. In translation it says "My dear Siegmann, Thank you very much and congratulations on the nice work. It pleases me very much. I wish you much success in the future – first of all happy holidays for your wife and you. Always, yours Walther Gerlach. Please also extend my greetings to Mr. Busch. Munich, 28. 3. 69"

oxygen 2*p*-bands. The ambiguities in the interpretation are overcome by spin analysis. The negative spin polarization at photoelectric threshold shows that the highest lying levels are occupied with minority spins. This confirms the famous model for the metal/insulator or Verwey-transition at 119 K in Fe₃O₄ put forward by Mott [64] that the electrical conduction at $E_{\rm F}$ is generated by hopping of minority spins. The data shown in Fig. 1.8 also provide evidence that magnetite is a *half-metallic oxide*, i.e., that conduction occurs in one spin channel only. We shall discuss the electronic structure and magnetism of magnetite in more detail in Sect. 7.7.4.

While conventional magnetism techniques typically measure the magnetic signal of the bulk of a ferromagnet or the combined signal from different layers in sandwich-like structure, SPES can probe the surface magnetism indepen-

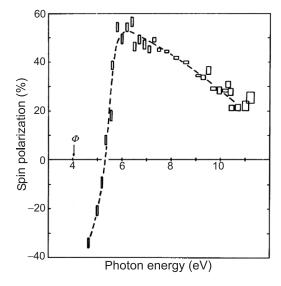


Fig. 1.8. Spin polarization of photoelectrons as a function of photon energy from single crystal magnetite, Fe₃O₄, measured by Alvarado et al. in 1975 [63]. The energy dependence of the spin polarization P supports the half-metallic character. The high value of P suggests that the energy of the oxygen 2p-bands lies below that of the Fe 3d-levels (see Sect. 7.7.4)

dent of the magnetic properties of the underlying material because of its small probing depth. Photoemission spectra from the elemental ferromagnetic metals Fe, Co, and Ni are complex because the 3d-states are not separated from the 4s, p-states as in magnetite. Additionally, a rich mixture of surface resonances and surface states is superimposed onto the bulk states [65]. Initially, it was difficult to understand the observations of SPES even in the simplest case of threshold photoelectrons. The difficulties in the interpretation arose because threshold photoemission was in fact the first manifestation of the unexpectedly strong preferential scattering of minority spins in ferromagnetic metals, today often called the "spin filter effect" [66], as discussed in Sect. 12.6.1.

The low energy secondary electrons emerging from the ferromagnetic metals exhibit as much as a threefold enhancement of the degree of spin polarization over that expected from the magnetic moment. This again is due to the spin dependence of the electron scattering generating the low energy electron cascade. The high polarization of the low energy cascade is used in scanning electron microscopy with polarization analysis (SEMPA), pioneered by Koike and Hayakawa in 1984 [67] and developed in the following years mostly by Unguris, Pierce, and Celotta [68], to produce stunning high resolution images of magnetic structures at surfaces with a spatial resolution of ~ 10 nm. Figure 1.9 shows a particularly beautiful SEMPA image which pictures the

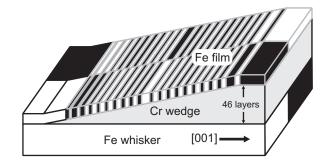


Fig. 1.9. Magnetic image, recorded by scanning electron microscopy with polarization analysis (SEMPA), of a thin Fe film, separated by a wedge-shaped Cr spacer layer from a single crystal Fe whisker [69]. The indirect magnetic coupling between Fe oscillates as a function of the Cr-spacer layer thickness from ferromagnetic (aligned Fe magnetizations) to antiferromagnetic (opposed Fe magnetizations). The actual data are shown superimposed on a schematic of the wedge structure. Black and white contrasts in the image correspond to opposite in-plane magnetization directions

oscillatory magnetization pattern in a thin Fe film that is coupled via a Cr wedge to a single domain Fe substrate [69].

In contrast to photoemission, field emission of electrons from the metals into vacuum yields mostly weakly polarized electrons. The initial results with field emitted electrons were nonreproducible due to improper measurement of the small spin polarizations in the presence of a magnetic field at the fieldemission cathode. However, Meservey and Tedrow discovered in 1971 that high spin polarization similar to the one observed in photoemission or secondary emission occurs also in tunneling of electrons from the ferromagnetic metals into super-conducting Al [70]. The interpretation of the sign and magnitude of the spin polarization observed in tunneling constituted a problem as documented by the letter shown in Fig. 1.10, and it is still a challenge today. Spin polarized magnetic tunneling spectroscopy holds many promises for the future.

Spin polarized photoelectrons may also be extracted from nonmagnetic materials if circularly polarized light is used for the excitation of the photoelectrons and if spin-orbit coupling is large. Such nonmagnetic photocathodes are more convenient than ferromagnetic ones since no magnetic field is present at the cathode that can disturb the electron-optics. The spin can simply be switched from up to down by switching from right- to left-circularly polarized light in the excitation of the electrons. For this reason GaAs-type photocathodes, first proposed and demonstrated in 1974 by Garwin, Pierce, and Siegmann [72, 73] are now the most common sources of polarized electrons, delivering intense, highly monochromatic, and almost completely polarized electron beams in which the spin direction can be chosen at will without affecting other beam characteristics. The possibility to flip the spin separates the scattering due to the spin from the dominant scattering due to the Coulomb

UNIVERSITY OF CAMBRIDGE DEPARTMENT OF PHYSICS

From PROFESSOR SIR NEVILL MOTT, F.R.3. CAVENDISH LABORATORY FREE SCHOOL LANE CAMBRIDGE, CB2 3RQ Telephone : 0223-54481

26th March, 1971.

Dear Dr. Siegmann,

Thank you for your letter of 15th March. I have indeed seen the paper on spin-dependent tunnelling into nickel.

I assume that Phil Anderson has sent you his note, but I think that in view of this tunnelling work what he says cannot give the answer and I confess that I am quite at a loss to explain these fascinating results. If we have any further ideas, I will certainly write to you again.

Yours sincerely,

D.F. Wort.

Dr. H. Ch. Siegmann, Laboratorium für Festkörperphysik, CH-8049 Zürich, Hönggerberg, Switzerland.

Fig. 1.10. Letter by Sir Neville Mott about spin polarized electron experiments on Ni by means of photoemission [62] and tunneling [70]. It indicates the problems associated with the interpretation of the sign of the spin polarization observed in these experiments. Mott refers to Phil Anderson's paper [71]

interaction. Over the years, spin modulated electron beams have been extensively used to probe magnetism. In fact, spin modulated electrons have been called "surface neutrons" because they are as important in surface magnetism as neutrons are in bulk magnetism.

A number of striking experiments can be done with the GaAs source. In inverse photo-emission spectroscopy (IPES), the Bremsstrahlung is measured when incident electrons with spin parallel or antiparallel to the magnetization recombine with the solid. It is thus possible to measure the spin polarized unoccupied band structure and to detect magnetism in the various surface states. When an electron beam with spin at an angle to the magnetization traverses a magnetic solid or when it is reflected from a magnetic surface, the spin of the electron precesses at a very fast rate due to the exchange interaction. It also rotates into the direction of the magnetization due to inelastic scattering. Both, precession and rotation can be separately measured by observing the position of the spin polarization vector after the interaction. This directly determines the exchange interaction as it depends on electron momentum and energy as well as the inelastic scattering events that are es-

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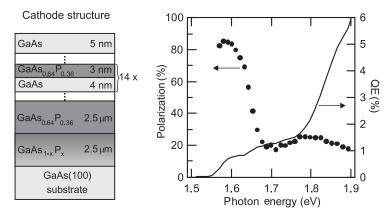


Fig. 1.11. Strained GaAs/GaAsP superlattice cathode developed at the Stanford Linear Accelerator Center (SLAC) for the creation of spin polarized relativistic electron beams. The structure of the cathode is shown on the left and the polarization and quantum efficiency (QE) as a function of laser excitation energy are shown on the right. The cathode is taken from a 2-inch diameter substrate wafer onto which layers are grown by gas-phase molecular beam epitaxy. The lattice of these layers is distorted from cubic symmetry which increases the electron polarization created by incident circularly polarized light. To avoid depolarization, the cathode is Be-doped with a low concentration, except in the top 5 nm the concentration is increased to $5 \times 10^{19} \,\mathrm{cm}^{-3}$ to improve the QE [77]

sential in many magnetic phenomena. In yet another application of the GaAs source, called spin polarized low energy electron diffraction (SPLEED), the magnetic structure can be observed superimposed on the crystallographic one. In spin polarized low energy electron microscopy (SPLEEM), very low energy spin polarized electrons are reflected from the magnetic surface yielding dynamic information on magnetic processes at surfaces at video frequencies and at $\sim 10 \text{ nm}$ spatial resolution [74].

GaAs sources are also used to create polarized relativistic electron beams for high energy physics experiments. For example, an early version of the source shown in Fig. 1.11 was used in a famous experiment in 1978 at the Stanford Linear Accelerator Center (SLAC) which revealed a very small but consequential spin dependence of 10^{-5} in the scattering of electrons with energies around 20 GeV on deuterium and hydrogen [75,76]. The electron spin was oriented parallel to the beam direction to separate the electromagnetic from the weak interaction. The experiment constituted an important step toward the confirmation of the Weinberg–Salam gauge theory of the weak and electromagnetic interactions, underlying the "Standard-Model" in which the two interactions are unified.

Today the concepts underlying the production of spin polarized electrons by laser excitation of GaAs are used in semiconductor based spintronics re-

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search. In this case the electrons are excited with circularly polarized light from the valence to the conduction band with an energy that is insufficient for photoemission from the sample. The excited conduction band electrons are spin-polarized and may be manipulated or probed by a well defined second laser pulse [78].

In 1988, Albert Fert and collaborators in Paris [79] and Peter Grünberg and collaborators in Jülich [80,81] independently¹² discovered that spin selective scattering is observed in multilayered magnetic structures as well, generating the phenomenon of giant magneto-resistance (GMR). In 1990 Stuart Parkin et al. [82,83] demonstrated that GMR is present not only in single crystal materials but also in sputtered multilayers that are compatible with manufacturing techniques and that through thickness control of the nonmagnetic spacer layer the coupling may be changed from ferromagnetic to antiferromagnetic. These discoveries have transformed magnetism, and GMR has become an important component of high speed, high-density magnetic recording.

More recently, John Slonczewski [84] and Luc Berger [85] proposed that spin polarized electron currents can transport angular momentum from one ferromagnet to another and excite spin waves or even switch the magnetization. As discussed in Sect. 14.2, this idea has been verified in experiments and attracted much attention. It combines interesting scientific questions related to the dynamics of the exchange coupled spins with the promise of applications in high density magnetic recording and storage. All-solid-state spin polarized electron physics and spin electronics, so called "spintronics", have become an important topic in magnetism.

Yet another basic capability of magnetometry with spin polarized electron spectroscopy includes *time resolution*. As will be discussed in detail in Chap. 15, photoemission of electrons is a very fast process that occurs on a time scale of less than 10^{-15} s for kinetic energies larger than a few eV. If combined with pulsed lasers or photon pulses from synchrotron sources, it can be used to generate a short pulse of photoelectrons. The spin polarization of the photoelectron pulse can be measured. It is proportional to the magnetization of the initial electron states from which the electrons were emitted. These initial electron states can be selected by choosing the photon energy or by selecting the energy of the photoelectrons. In this way, the time scale and the mode on which the magnetization reestablishes itself after an excitation, e.g., by the generation of electron-hole pairs, can be studied [86]. The spin dependence of the lifetime of electrons that have been excited to states above the Fermi-energy has been observed, as well [87], providing direct evidence for the preferred scattering of minority spins in the time domain.

¹²Note that in contrast to the publication dates, the Grünberg paper was submitted to Physical Review on May 31, 1988 while the Fert paper was submitted to Physical Review Letters on August 24, 1988.

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1.3.2 Polarized X-rays and Magnetism

Despite the power of optical techniques for magnetic studies, we have already mentioned limitations set by the wavelength and energy of light. Today's most powerful applications of X-rays in magnetism utilize fully polarized, tuneable synchrotron radiation, where the X-ray energy is tuned to the absorption edge of a magnetic atom [88]. This was first suggested by Erskine and Stern [89] in 1975 by considering an extension of the magneto-optical Faraday and Kerr effects into the ultraviolet/soft X-ray region. The principles underlying optical and X-ray effects are illustrated and compared in Fig. 1.12. Optical methods rely on spin dependent transitions between valence band states at certain wave-vector (k) points in the Brillouin zone. In contrast, X-ray techniques utilize core to valence transitions. The resonant X-ray signal is element and even chemical state specific since core level binding energies depend on the atomic number and chemical state. In addition, the measured resonant X-ray intensity is quantitatively linked by sum rules with the spin and orbital magnetic moments since it measures wave-vector integrated properties of the valence shell, in contrast to optical methods which measure specific wave-vector dependent transitions. Finally, as dimensions enter the nanoscale, typically identified with dimensions below 100 nm, visible light becomes "blind" and one needs shorter wavelength X-rays to see the magnetic nanoworld.

Following the pioneering use of X-rays for magnetic studies by de Bergevin and Brunel [90] in 1972, important new developments occurred in the mid

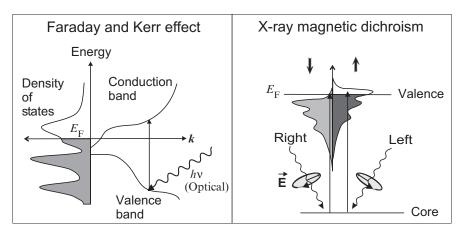


Fig. 1.12. Comparison of the processes underlying the Faraday and Kerr effects in the visible spectral range and the processes in X-ray magnetic circular dichroism (XMCD). In the visible one typically uses linearly polarized light and measures the polarization rotation and ellipticity of the transmitted or reflected light. In XMCD one measures the difference of the absorption spectra obtained with left and right circularly polarized X-rays

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1980s. In 1985, Blume first pointed out the advantage of performing magnetic scattering experiments by tuning to an absorption edge, so-called *resonant magnetic scattering*, and developed its theory. The effect was first observed in the same year by Namikawa et al. using tuneable synchrotron radiation [91]. Later work by Gibbs et al. in 1988 [92] clearly showed the advantage of using the large cross-section enhancements associated with absorption edges and this work established X-rays as a viable alternative to neutrons for the study of magnetic structure.

In the same time period, two other developments took place which were based on X-ray absorption spectroscopy instead of X-ray scattering. In 1985, Thole, van der Laan, and Sawatzky [93] predicted the occurrence of a linear X-ray magnetic dichroism effect in near-edge X-ray absorption spectra which was observed by van der Laan et al. in 1986 [94]. Another breakthrough came in 1987 when Schütz et al. [95] demonstrated a circular magnetic dichroism effects in X-ray absorption. By the late 1980s the stage was set for exploring and refining X-ray techniques for magnetic studies.

In the 1990s it became clear that soft X-rays play a particular important role for magnetic studies [98,99]. The power of soft X-rays arises from the fact that the most important absorption edges for resonant magnetic studies, the L-edges (2p core shell) of Fe, Co, and Ni and the M-edges (3d core shell) of the rare earths fall into the 700–1,500 eV range. These absorption edges exhibit large magnetic effects and through dipole allowed $2p \rightarrow 3d$ and $3d \rightarrow 4f$ transitions provide access to the magnetic properties of the important 3d and 4f valence electrons which dominate the magnetic properties of transition metals and rare earths, respectively. Figure 1.13 illustrates the relative size of the magnetic dichroism effect, defined as the difference in absorption between right and left circularly polarized X-rays, near the Co K-edge and the L-edges. The effect is seen to be larger at the soft X-ray L-edge by a remarkable factor of 2,000.

The experimental soft X-ray studies triggered theoretical work on the information content of the experimental spectra, leading to fundamental sum rules linking the measured dichroic intensities to spin and orbital magnetic moments and their anisotropy [100–102]. The importance of the sum rules lies in the fact that they allow the use of X-rays for quantitative magnetometry. The final important developments were the demonstrations that X-rays can be used for domain imaging in ferromagnets in 1993 [103]¹³ and antiferromagnets in 1999 [105–107]¹⁴. With the beginning of the new millennium versatile experimental soft X-ray tools were in place to tackle problems in the field of magnetism.

¹³An independent yet later paper in 1993 published by Schneider et al. [104] also demonstrated magnetic imaging with X-rays. It used Auger electron detection, in contrast to total or secondary electron yield detection employed by Stöhr et al. [103].

¹⁴Following first attempts by Spanke et al. in 1998 [108] the first clear images of antiferromagnetic structure were obtained by Stöhr et al. in a series of experiments starting in 1999 [105–107].

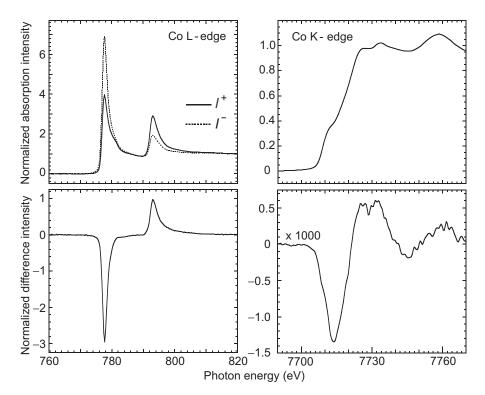


Fig. 1.13. The top row shows absorption spectra near the L-edge (left) [96] and K-edge (right) [97] of magnetized Co metal with magnetization and photon angular momentum parallel and antiparallel, respectively. For the Co K-edge the two spectra are indistinguishable on the plotted scale. In both cases the spectra have been normalized to the same average edge jump, which was set to 1. Underneath are shown the XMCD specta, defined as the difference spectra of the polarization dependent absorption spectra. Comparison of the size of the XMCD effect reveals that the L-edge XMCD effect is larger by a factor of 2,000

An illustrative example of the development of X-ray science in the first 100 years is shown in Fig. 1.14. The figure compares one of the first X-ray images recorded by Röntgen with the first magnetic image recorded by Stöhr et al. with soft X-rays in 1993 [103]. The figure illustrates several important general points. X-rays can be used for electron density as well as for magnetic imaging. While high energy X-rays are most suitable for imaging of bulk objects, soft X-rays are particularly well suited for imaging the structure of thin films, e.g., magnetic domains. Kortright et al. [44] have discussed the opportunities in the study of magnetic materials and phenomena by means of X-rays.

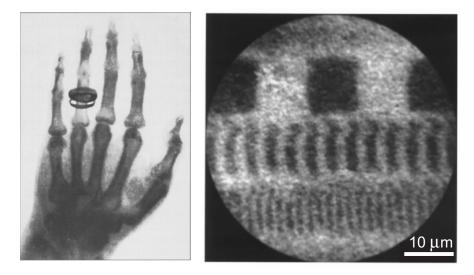


Fig. 1.14. 100 years of X-ray imaging. The left X-ray image is one of the first pictures taken by Röntgen, recorded in November 1895, possibly of his wife's hand. The right image shows the magnetic bit structure of a CoPtCr magnetic recording disk, recorded in 1993 using the Co L-edge X-ray magnetic circular dichroism [103]. Note that the field of view is smaller by a factor of about 10^4 in the right image, and the contrast is of magnetic origin

1.4 Developments in the Second Half of the 20th Century

It is quite fascinating that after about 1960 independent revolutions occurred in the utilization of X-rays and magnetism. On the X-ray side this revolution was triggered by the advent of synchrotron radiation sources. A fundamental measure of the properties of a photon source and good measure for its usefulness for materials science research is its brightness, the number of photons emitted per source size, angular emission cone, and energy bandwidth [109]. Figure 1.15 shows a plot of the increase in average source brightness through 3rd generation synchrotron sources and the anticipated increase in *peak* brightness by X-ray free electron lasers in the near future (black curve). The average brightness increase is a remarkable factor of 10^{13} over the 40 year period 1960–2000 with an anticipated growth of peak brightness of about 10 orders of magnitude in the future. These growth rates significantly exceed the well known Moore's law [110] of chip density growth, shown as a dotted curve.

One may argue that the modern era of magnetism dawned around 1957 with the first hard disk storage drive, the IBM RAMAC (for random access method of accounting and control) [111]. We have seen above that throughout history magnetism has had important practical applications. Even today, a close link exists between scientific research and technological applications. The

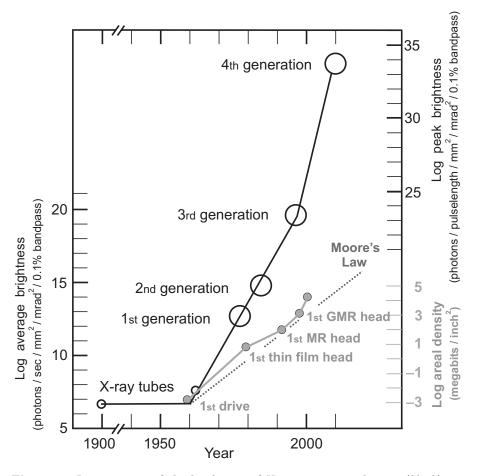


Fig. 1.15. Improvement of the brightness of X-ray sources with time (black) in comparison to the development of the areal magnetic storage density in computers (gray). Moore's law [110], representing the doubling of the transistor density on an electronic chip every two years, is shown as a dotted curve. The X-ray brightness is plotted as an average brightness on the left and has been aligned to the right scale of peak X-ray brightness at the point representing 3rd generation synchrotron radiation sources

topics at modern magnetism conferences are greatly influenced and fueled by existing and future applications of magnetic phenomena, and often empirical developments precede a thorough scientific understanding. It is for this reason that the growth curve of lateral magnetic storage density shown in Fig. 1.15 is quite representative of the developments in modern magnetism. Indicated in the figure are milestones in this development when innovations have driven technological progress. Examples, which are marked in the figure, are the developments of new read heads that can sense ever weaker signals from the decreasing magnetic bits. The overall growth rate is seen to be close to that of Moore's law.

The science and technology of magnetic materials is largely fuelled by the 50 billion dollars per year magnetic storage industry. Of interest are sandwiched magnetic sensors or "read heads", such as spin valves, and magnetic "media" consisting of ferromagnetic thin films and multilayers that can store information in nanosized "bits". On the horizon are nanoscale magnetic memory structures that are read out by their tunneling magnetoresistance which depends on the relative orientation of the magnetization in different layers. Some of the structures of interest are shown in Fig. 1.16.

It is apparent from Fig. 1.16 that today's magnetic materials are not the bulk materials of old, but atomically engineered thin film and multilayer structures that often have lateral dimensions on the nanometer scale [44–46,112]. The study and understanding of such materials requires the use of better experimental and theoretical techniques that can give reliable information for the new low-dimensional materials. The growth of magnetic technologies shown in Fig. 1.15 is due to scientific and technological developments in three key areas (1) the development of new magnetic materials, (2) the progress in

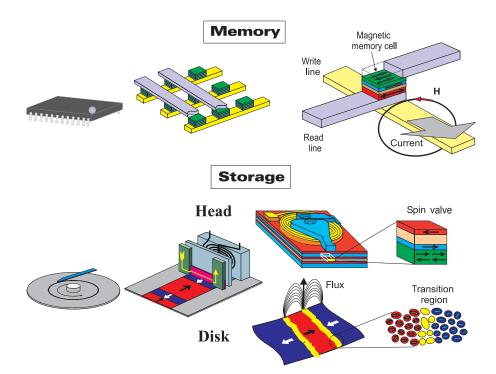


Fig. 1.16. Illustration of various structures used for magnetic memory and storage applications. They form the first generation of spintronics devices, as discussed in the text

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theoretical developments, and (3) the developments of new experimental techniques. We have already touched on area (3) and described the developments of spin polarized electron and X-ray techniques. We shall now briefly discuss areas (2) and (1).

It is widely recognized today that part of the unfolding of a new scientific revolution is based on the development of electronic structure theory. This has formally been acknowledged with the award of a Nobel Prize for density functional theory to Walter Kohn in 1998. Computational modeling and simulation of real materials problems has been made possible by utilizing the continued explosive growth of computer power. Simulations of ever-increasing complexity on more and more realistic models has become possible through the introduction of massively parallel computer platforms. These simulations now serve to fill the increasingly urgent demands of scientists and engineers. Some examples that demonstrate the power of modern theory of magnetism include the following:

- The success of density functional theory in the local spin density approximation to account for many of the magnetic properties of the bulk ferromagnetic metals.
- The calculation of the strong enhancements of both spin and orbital moments in thin films and at surfaces.
- The prediction of the existence of magnetism in thin films of metals such as Cu that are nonmagnetic in the bulk, when they are adjacent to a ferromagnet.
- The ab initio calculation of surface and interface magnetic anisotropies despite their small value of only 10^{-4} – 10^{-5} eV.
- The first principles calculation of the magneto-optical response in both the visible and X-ray range.

Despite all the successes of electronic structure calculations it needs to be recognized, however, that it is valid only in certain limits, namely small correlation effects and zero temperature. As reviewed by Albert et al. [113] insights into finite temperature magnetism have only been gained on the basis of some form of mean field theory, with small fluctuations taken into account within a linear approximation. This approximation is known to break down in the vicinity of the critical point of a ferromagnet, so that the ab initio description of finite temperature magnetism remains one of the grand challenges of the future.

We now come to the most important development – new materials. The various applications shown in Fig. 1.16 require magnetic materials that at room temperature possess a sizeable equilibrium magnetization, a preferred magnetization direction (anisotropy) and a well defined coercivity.

In practice, the materials used for high-tech applications contain the magnetic metals Fe, Co, Ni with rare earths playing a relatively minor role. Scientific investigations are concerned with the origin of magnetic coupling and spin transport across interfaces and the time dependence of magnetic reversal

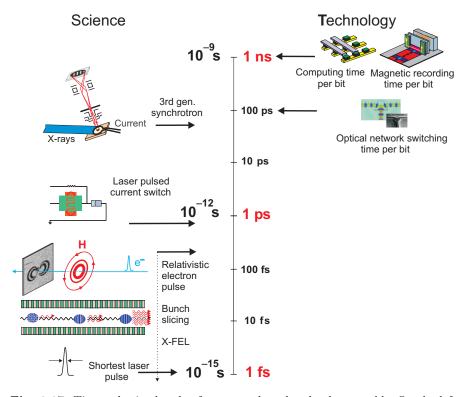
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processes. In today's devices magnetic switching times are about one nanosecond. In advanced recording studies times as short as 100 picoseconds have been achieved. The future of the magnetic storage and memory technology is dependent on new materials that are patterned or can self-assemble on the nanoscale and are magnetically stable at room temperature, on new materials and structures that at room temperature exhibit large magnetoresistance changes in small external fields, and on the development of methods to manipulate the magnetization on the subnanosecond time scale. An important challenge is the understanding of the size and speed limits of magnetic technologies. We shall specifically discuss the existence of a speed limit for precessional magnetic switching in Chap. 15.

One may refer to the structures shown in Fig. 1.16 as the first generation of spintronics devices [112]. They are based on ferro- and antiferromagnetic materials containing atoms with sizable magnetic moments, typically transition metals and oxides. A second generation, which aims to couple such magnetic materials with semiconductors is rapidly gaining importance today [114,115]. Such a combination of semiconductor and magnetic materials would allow a seamless integration of magnetic, electronic, and optoelectronic functionality in a single device that offers additional degrees of freedom, and therefore may offer enhanced performance. We will discuss an example of such a hybrid structure, a novel spin-based transistor, proposed by Datta and Das in 1989 [116] in Sect. 14.3.

Semiconductor based spintronics research has been fueled by two important discoveries, the existence of magnetic semiconductors such as Mn doped GaAs with Curie temperatures as high as 120 K, and the existence of long-lived nonequilibrium magnetization densities in nonmagnetic semiconductors [117]. In the latter systems, the magnetization is produced by spin-dependent laser excitations from the valence to the conduction band or through spin injection from an adjacent ferromagnet. The remarkably long spin lifetime of nanoseconds in semiconductors, corresponding to a spin flip or coherence length of tens of microns, raises the possibility of manipulating and probing spins states in small devices. The spins may be manipulated by external fields, optical excitation and even through the hyperfine interaction, and this forms the basis of the futuristic concept of quantum computing.

It is important to realize that the nonequilibrium magnetization densities in semiconductors are tiny compared to the equilibrium magnetization densities in conventional magnetic materials. Because of the weak magnetization densities, it appears that the field of semiconductor based spintronics, at present, is limited by the nonexistence of a spin current amplifier, as discussed in Sect. 14.4. Despite their great potential we shall not treat magnetic semiconductors and semiconductor based spintronics in this book but refer the interested reader to the book by Awschalom, Loss and Samarth [78] or the review by Žutić, Fabian and Das Sarma [115].



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Fig. 1.17. Timescales in the ultrafast research and technology worlds. On the left side we show the capabilities of various ultrafast methods, with the benchmark set by 1 fs laser pulses. Third generation storage rings typically produce X-ray pulses of about 50 ps length. Today we can envision various concepts to reach pulse lengths shorter than 100 fs, such as "slicing" of an electron bunch with a laser or bunch compression in X-ray free electron lasers (X-FELs, see Sect. 4.4.2). Note the lack of technological or man-made applications below about 100 ps, indicating great research opportunities to help explore and develop faster technologies

1.5 Some Thoughts about the Future

It is obvious from Figs. 1.15 and 1.16 that the future of the magnetic data storage and memory technology is concerned with cramming information into smaller and smaller bits and manipulating these bits faster and faster. To-morrow's magnetic bit sizes will lie in the range of tens of nanometers and processing times will be in the picosecond (ps) range. Typical length scales and timescales in the ultra-small and ultra-fast worlds are illustrated in Fig. 1.17. The figure clearly reveals a general technology gap, not limited to magnetic technologies, in the ultrafast domain below about 100 ps.

In present day devices, the magnetic system responds to external magnetic field pulses on the nanosecond time-scale. The main challenge in magnetism

today is the development of new methods of magnetization control that overcome the limits imposed by classical electromagnetism such as the long range and slow spatial decay of regular magnetic fields and their limited rise- and decay-time imposed by the induction laws. The goal is to develop new methods of magnetization control on the nanometer length scale and the picosecond or even femtosecond (fs) time scale. These efforts involve conventional magnetic materials such as transition metals and rare earths but also novel materials such as semiconductors.

Of particular interest is the utilization of the strong, short range quantum mechanical exchange interaction for magnetic switching. This effect naturally matches the nanoscale of future devices and requires the use of spin currents, where the switching is mediated by the exchange interaction and angular momentum transfer between the injected spin polarized "itinerant" electrons and "localized" moments in the ferromagnet. This mechanism is not fully understood. In fact, it goes to the very origin of transition metal magnetism which is often envisioned to involve exchange of "itinerant" and "localized" electrons.

X-rays can play an important role in this development. They facilitate ultrafast imaging on the magnetic nanoscale. Present facilities offer pulses as short as 50 ps. Careful inspection of Fig. 1.15 reveals that the revolutionary development and growth is all but over. On the X-ray horizon are developments that boggle the mind – leading to an X-ray free electron laser (X-FEL) within the next five years. Such a source has a peak brightness that is a factor of about 10^{10} larger than that of present 3rd generation X-ray sources. The factor of 10^{10} arises from a 10^7 times larger flux per pulse and a 10^3 times shorter pulse length than for present sources. Today's 3rd generation synchrotron sources deliver an average photon flux per second that originates from about 10^6 electron bunches that each radiate about 10^6 photons with a pulse length of about 100 picoseconds. With this intensity of about 10^{12} X-rays per second we can typically record a diffraction image in one second. In the future, a soft X-ray FEL will emit about 10^{13} X-rays in a single ultrafast burst of about 100 femtoseconds. That means we will be able to record complete diffraction images with a single shot and see how things move with a resolution of 100 femtoseconds. Advanced X-ray FEL schemes even promise shorter pulses down to about 1 femtosecond or even into the attosecond (10^{-18} s) range. This time scale corresponds to a characteristic energy of about 1 eV (see footnote 15) and therefore may allow us to take a closer look at the ultimate problem in magnetism – the understanding of the exchange interaction itself.

¹⁵As discussed in Sect. 3.7, it is often useful to correlate a characteristic energy E of a system with a time of change Δt . Using the relationship $E = h\nu = h/\Delta t$, where Δt corresponds to a complete cycle time (see Sect. 3.7) we get $E\Delta t = h = 4.136 \text{ eV}$ fs, so that 1 eV corresponds to about 4 fs.

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1.6 About the Present Book

It is apparent that there is much excitement in the field of magnetism and its past and projected future growth provides much material to write about. Our book aims to form a bridge between fundamental and advanced concepts. We try to accomplish this by dividing the book into *five major parts* positioned between the Introduction, Chapter 1, and appendices gathered in Chapter 16 or Chap. A.

Part 1 deals with static electric and magnetic fields, magnetic moments, and the concepts of time-dependent fields, with emphasis on electromagnetic waves and their polarization.

In *Chap. 2* we start with a review of the origin and basic concepts underlying electric and magnetic fields and discuss how the fields change inside materials. We emphasize fundamental differences in the symmetry properties of electric and magnetic fields.

In *Chap. 3* we discuss the origin and concepts of magnetic moments and their basic interactions with magnetic fields, their energy in a magnetic field, the force experienced in inhomogeneous fields and the important concept of torque. We use the concept of magnetic force in conjunction with the Stern-Gerlach experiment to introduce the quantum mechanical concept of the spin. The concept of torque is linked to the fast temporal evolution of the magnetization, described by the precession and damping terms in the Landau-Lifshitz-Gilbert equation, and probed by magnetic resonance. We explicitly discuss how the dynamics can be probed in either time or frequency (energy) space and the origin of this important energy-time correlation.

Chapter 4 extends the concepts of static electric and magnetic fields to time-dependent fields. In particular, we discuss fields created by relativistic electrons because of the importance of such fields in ultrafast magnetism research. After a brief review of relativistic concepts we discuss *velocity fields*, defined as fields that remain attached to the generating charge, and point out how ultra-short and ultra-strong field pulses can be created by relativistic electron beams. We then discuss the more familiar acceleration fields, i.e., electromagnetic (EM) radiation, emitted by relativistic charges that are accelerated or decelerated. In particular, we review the concepts underlying synchrotron and X-ray free electron laser radiation.

Chapter 5 is devoted to the discussion of EM waves, which are shown to naturally emerge from Maxwell's equations. In particular, we discuss the nature of polarized EM waves and, by use of the example of circularly polarized waves, emphasize the difference between the important concepts of angular momentum and chirality. We end with a brief illustration of these concepts by discussing the transmission of EM waves through magnetic and chiral media.

Part 2 consists of two extensive Chapters on the historical development and modern description of the fundamental magnetic interactions in atoms, molecules and solids.

1.6 About the Present Book 33

In Chap. 6 we review the history and the concepts underlying the three magnetic interactions: the exchange, spin-orbit, and Zeeman interactions. Our goal is to provide a history of the quantum mechanical concepts of magnetism. We review the seminal role played by early atomic and molecular spectroscopy, and by the quantum theory that was developed to explain the spectra. The major part of the Chapter deals with the important exchange interaction. We discuss how the concept of electron correlation, manifested in the Coulomb and exchange integrals, and the Pauli principle emerged from the study of the helium atom and the hydrogen molecule. We discuss the famous Heitler-London calculation for the hydrogen molecule, why it forms the basis for our modern view of electron "localization", and how it links magnetism with the formation of the chemical bond. We also discuss the origin of the independent electron model which emphasizes the "delocalized" or itinerant (meaning traveling) character of electrons. We then discuss the important Heisenberg and Hubbard models. We point out that, despite their great importance in modern magnetism research, they are not ab initio methods, but were constructed to circumvent the difficulties encountered in treating correlation in systems that contain more than two electrons. The discussion of exchange is followed by a treatment of the spin-orbit and Zeeman interactions. Both were first observed in atomic spectra and were readily explained once quantum theory and the concept of spin had been introduced. We also discuss Hund's three rules which postulate the favored orientations between spins, between orbital moments, and between spin and orbital moments.

Chapter 7 deals with the concepts underlying the description of electronic and magnetic interactions in solids. We start by discussing the basic concepts of localized versus delocalized electronic states and link them to the existence of centrifugal barriers in the atomic potential. These concepts lead to the interplay between band-like and localized behavior and the relative size of the major electronic interactions in 3d and 4f compounds. Next we introduce the band model of electronic structure, starting with the Stoner model, followed by a more general discussion of band theory and its practical implementation in terms of density functional theory in the local spin density approximation (LSDA). The ligand field approach is discussed next, both in terms of an independent electron and correlated electron or multiplet approach. We then discuss the origin of correlation effects and link them to a proper description of excited states which are associated with electron conduction. In this context we touch upon computational schemes such as the Hubbard and LDA + Umethods. We then link the concept of excited states in transition metal oxides to the existence of ferromagnetism and antiferromagnetism in such systems. Specific subsections deal with the concepts of superexchange, double exchange, the origin of the colossal magnetoresistance effect and the magnetism of magnetite, the oldest yet still interesting magnetic material. The following section deals with another form of indirect exchange, the RKKY interaction, and its existence in diluted magnetic impurity systems and multilayers. The final section deals with the spin-orbit interaction in solids. We present a particularly simple model, the so-called Bruno model, that links the magnetocrystalline

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anisotropy with the anisotropy of the orbital magnetic moment. In support of this model, we present a model calculation and direct measurements of the anisotropy of the orbital moment by XMCD.

Part 3 discusses polarized electron and X-ray techniques for the study of magnetic materials, the specialty of the authors.

In *Chap. 8* we discuss the generation of polarized electrons by laser excitation of GaAs, give experimental concepts of polarized electron experiments, and present the formal description of individual spin polarized electrons in terms of the quantum mechanical Pauli spinor formalism and the spin polarization vector. This concept is then extended to spin polarized beams. We discuss the interactions of polarized electrons with magnetic materials in terms of spin filtering, "spin-flip" excitations and spin "de-phasing". By extending the Pauli spinor formalism by concepts due to Poincaré we show how to describe the transmission of a spin polarized beam through a magnetic material, the equivalent of the Faraday effect. The same formalism is then shown to be usable for both spin polarized electrons and polarized photons. As an example, we present experimental measurements of the X-ray Faraday effect and describe it within our formalism.

Chapter 9 provides a semiclassical and quantum mechanical description of the interaction of EM radiation with matter. We link the concept of the refractive index, historically used in the optical regime, with that of the scattering factors (including resonant effects), commonly used for the description of X-ray interactions with matter. We then discuss the relationship between the general concept of "scattering" (including reflectivity) with the more specific concept of "absorption" and present the important Kramers-Kronig relations. In the remaining Sections we introduce the quantum theory underlying polarization dependent X-ray absorption spectroscopy and resonant magnetic scattering, which is based on the calculation of polarization dependent transition matrix elements. In particular, we discuss the physics behind X-ray natural linear dichroism (XNLD), X-ray magnetic linear dichroism (XMLD) and X-ray magnetic circular dichroism (XMCD). In the process we take a look at the famous sum rules that make X-ray magnetic circular dichroism into a powerful quantitative magnetometry tool.

Chapter 10 is devoted to experimental concepts and results of X-ray dichroism spectroscopy and microscopy. After a general introduction of nomenclature, i.e., the distinction between "natural" and "magnetic" dichroism, we concentrate on three dichroism techniques, XNLD, XMLD, and XMCD. We present the experimental concepts and details of polarization dependent spectroscopy, discuss the quantitative analysis of experimental spectra and present the spectra of important materials such as the elemental ferromagnetic metals Fe, Co, Ni, and Gd, and the various transition metal oxides. Using the spectra of small metal clusters as an example, we then explain the information content of the measured resonance intensities and derive important information on the orbital magnetization of these systems. We also discuss the determination of extremely small magnetic moments, and as an example present XMCD measurements of Pauli paramagnetism in Pd metal. We then extend the spectroscopy concepts to those used in X-ray magnetic microscopy. We discuss four microscopy methods, three based on direct imaging in real space and one on inverting reciprocal space scattering intensities into real space. We finish with selected microscopy results for ferromagnetic and antiferromagnetic thin films and multilayers.

Part 4 covers the general description of ferromagnetism and then more specifically deals with the fundamental properties of the ferromagnetic metals which form the basis for most magnetic devices today.

In *Chap. 11* we discuss fundamental aspects of ferromagnetism, such as the origin of the spontaneous magnetization, the description of its temperature dependence and the Curie temperature, and give a discussion of the meaning of "exchange" in the Weiss, Heisenberg, and Stoner models. We specifically discuss spin waves and critical phenomena. We continue with a discussion of the origin of magnetic anisotropy and distinguish the shape anisotropy from the magnetocrystalline anisotropy. We finish with a discussion of aspects of magnetic micro- and nanostructures such as magnetic domains, the origin of hysteresis loops and the magnetism in small particles.

Chapter 12 treats the magnetism in the elemental ferromagnetic metals Fe, Co, Ni, and Gd. Our emphasis reflects the important role these materials have played in the development and testing of our scientific understanding of ferromagnetism and the utilization of magnetism in modern technology. The overriding goals of this Chapter are our present day understanding of two topics, the phenomenon of metallic ferromagnetism and the electrical and spin transport in such materials, which are discussed in turn. Results of band structure calculations for the elemental ferromagnetic metals are compared to experimental results by spin resolved photoemission and inverse photoemission. The rest of the Chapter deals with spin transport in metals. We first discuss the all-important two current model, based on separate conduction channels for up and down spins, which underlies our modern thinking. We then briefly discuss the phenomenon of anisotropic magnetoresistance. In the two following sections we differentiate between two fundamental scattering channels in spin transport and spin polarized beam experiments, namely, spin-conserving and spin nonconserving scattering. We show that spin-conserving scattering events determine the electron mean free paths in the two separate spin channels, and that they dominate over spin nonconserving, often called "spin flip", scattering events. This fact constitutes the physical basis for the two current model. Several experimental results are presented that demonstrate the dominance of spin-conserving scattering. We also show the experimental detection of the much weaker "spin-flip" channel. At the end of the Chapter we briefly comment on remaining challenges in our understanding of the phenomenon of ferromagnetism.

Part 5 deals with three important topics in contemporary magnetism research: surfaces and interfaces, spin transport, and ultrafast magnetization dynamics.

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Chapter 13 builds on the revolution in magnetism ushered in by our ability to prepare well defined surfaces and interfaces, in particular "spin engineered" magnetic multilayers. It first discusses the study of magnetic surfaces by spin polarized techniques such as photoemission and spin polarized tunneling microscopy. It then reviews studies of the reflection of spin polarized electron beams from surfaces. The last section discusses various coupling phenomena in multilayer structures that are engineered from ferromagnetic, paramagnetic, and antiferromagnetic layers. We show how modern magnetism techniques have led to an improved understanding of interface phenomena like exchange bias, the existence of induced magnetic moments in atoms like Cu and C, and the exchange coupling of ferromagnets across a non-magnet.

Chapter 14 is devoted to the discussion of spin transport. It presents the basic theory underlying electron and spin transport across an interface between a ferromagnet and a nonmagnet. By introducing concepts like the spin dependent chemical potential and spin dependent diffusion, we are led to important new effects associated with interfaces like the spin accumulation voltage, the boundary resistance, and spin diffusion lengths and times. These allow us to explain the origin of the giant magnetoresistance effect. In the second half of the Chapter we deal with the topic of spin injection into a ferromagnet. We discuss the detailed mechanisms underlying the transfer of angular momentum from the spin polarized current to the magnetization of a ferromagnet. Starting from the master equation of conservation of the total angular momentum, we derive the torques acting on the injected spins and on the magnetization. We also present experimental results for switching the magnetization of a ferromagnet by spin currents. At the end of the Chapter we compare spin transport in metals and semiconductors and discuss the concept of a spin current amplifier.

Chapter 15 treats the topic of magnetization dynamics. We restrict ourselves to the interesting "ultrafast" time regime below 100 picoseconds, defined by the present limits of technology and the spin–lattice relaxation time. We start with a general overview of the exchange of energy and angular momentum between the three fundamental physical reservoirs: the electronic system, the lattice (phonons) and the magnetization system. We then present state-ofthe-art studies of the magnetization dynamics following ultrafast excitations, triggered by lasers (electronic excitations) and electron pulses (magnetic excitations). We then address the specific problem of reliably switching the magnetization on ultrafast time scales. We discuss various schemes, precessional switching by conventional field pulses, switching by spin injection, and finally the possibility of all-optical switching.

Several *Appendices*, gathered in Chap. A, contain tables of important constants, equations, and functions.

Before we get started we point out that within this book we use the units and definitions of the système international (SI). It is based on the fundamental units: Volt [V], Ampère [A], meter [m], second [s], as summarized in App. A.1.

Electric Fields, Currents, and Magnetic Fields

2.1 Signs and Units in Magnetism

 $\mathbf{2}$

In our world, electrons play a more important role than the positrons of the antiworld. The historical choices that the electron has a negative charge q = -e (we shall always assume that $e = 1.602 \times 10^{-19}$ C is a positive number) and the definition that the current I reflects the motion of positive charges is somewhat of a nuisance because the electrons move against the direction of the electric current. Another consequence of the negative charge of the electron is that the most important quantity of magnetism, the magnetic moment of the electron, is directed antiparallel to its intrinsic angular momentum, the spin. In this chapter we will define and discuss two basic quantities of magnetism, the static electric and magnetic fields.

The long history and international development of magnetism has generated yet another nuisance, possibly the largest of all, namely the various systems employed to measure magnetic quantities.

We shall use exclusively the units and definitions of the système international (S.I.) which all nations have, in principle, agreed on.

Unfortunately, this is not always practiced. More important than small possible advantages of one system over the other is the common use and teaching of one and the same system. Once one has understood the fundamentals of magnetism, it is easy to switch from one system to the other, but for the novice, the various systems that are in use can be disturbing and easily lead to errors. When in doubt, consult the Appendix A.1.

2.2 The Electric Field

An electric charge gives rise to an electric field. The historical sign convention is that the electric field originates on a *positive* charge. Two simple cases of

40 2 Electric Fields, Currents, and Magnetic Fields

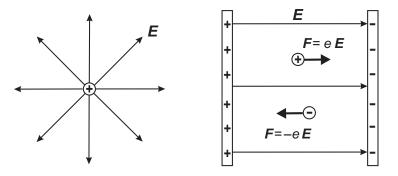


Fig. 2.1. Examples of electric fields, illustrating the sign convention. The electric fields originate on positive and terminate on negative charges. In the case of the field between two charged condenser plates we have also indicated the force on a positive and negative charge, defining the direction of motion

electric fields are shown in Fig. 2.1. The electron charge is measured in units of Coulomb, with $q = -e = -1.602 \times 10^{-19}$ C. For a point charge q the electric field is given by

$$\boldsymbol{E} = \frac{q}{4\pi\,\epsilon_0\,r^2}\,\boldsymbol{r}_0\;,\tag{2.1}$$

where $\epsilon_0 = 8.86 \times 10^{-12} \text{ A s V}^{-1} \text{m}^{-1}$ is the dielectric constant of the vacuum and r_0 is a unit vector pointing away from the origin of the charge. With the conversion 1 C = 1 A s, the electric field has units of $[\text{V m}^{-1}]$.

The electric field \boldsymbol{E} is measured in units of $[V m^{-1}]$.

As shown in Fig. 2.1, a charge in an electric field is subject to a force

$$\boldsymbol{F} = q \, \boldsymbol{E} \;, \tag{2.2}$$

that leads to a motion of the charge.

2.3 The Electric Current and its Magnetic Field

As soon as electric charges move we say that there is an electric current. Steady electric currents may flow by injecting charge carriers into vacuum or by applying a voltage to a conductor such as a metal. The strength of the electric current I is defined as the charge q that flows per time interval Δt through a cross section, $I = q/\Delta t$, and is measured in units of Ampère [A]. 1 A corresponds to the motion of the charge q = 1 C, corresponding to $1/e = (1/1.6) \times 10^{19}$ elementary charges, through a surface in $\Delta t = 1$ s. The direction of the electric current is defined as the direction in which a *positive* charge moves.

In vacuum, and in superconductors, electric currents may persist without the presence of an electric field while in matter, an electric field \boldsymbol{E} must be applied to sustain the current. The force $\boldsymbol{F} = q\boldsymbol{E}$ generated by the electric field compensates for the frictional force acting on the charge carriers moving in matter.

The current density j is a vector pointing in the same direction as the current but of magnitude j = I/S, where I is the electric current flowing through the surface S. Hence j is measured in $[A m^{-2}]$. It follows that $j = \rho v$ is proportional to the volume density of the electric charges $\rho = q/V$ and to the velocity v with which the electric charge moves. The velocity reverses when the time runs backwards, i.e., in a time reversal transformation $t \to -t$. Hence the current density j changes sign upon time reversal.

In 1820 Hans Christian Oersted discovered with the help of a ship's compass that an electric current generates a magnetic field. If we assume that a straight current I flows in the z direction, the magnetic field vector \boldsymbol{H} is found to lie in the x-y plane. The strength of \boldsymbol{H} is given by the *Biot-Savart* law

$$H = \frac{I}{2 \pi r} , \qquad (2.3)$$

where r is the distance from the center of the current. This defines the units of the magnetic field.

The magnetic field \boldsymbol{H} is measured in $[\mathrm{A m}^{-1}]$. The often used units of Oersted [Oe] are defined as $1\mathrm{Oe} = (1,000/4\pi) \mathrm{A m}^{-1} = 79.59 \mathrm{A m}^{-1}$.

It turns out that the magnetic field lines are closed generating a curl of the magnetic field around the current as shown in Fig. 2.2. The magnetic field lines can be made visible with a number of small compasses or iron particles arranged in the x-y plane around the current. The corresponding magnetic pattern produced by the current of a lightning strike at the foot of a transmission line tower is shown in Fig. 1.1. The magnetic particles are iron oxide occurring naturally in the earth and we have here an example of magnetic recording as it occurs without human interference. If the electric current flows in a closed loop, then it generates a magnetic field H in the

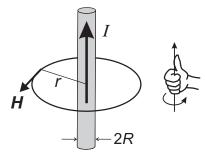


Fig. 2.2. Magnetic field H around a straight tube or wire with radius R carrying an electric current I. The direction of the magnetic field is obtained by the *right hand rule*. When the thumb of the right hand is pointed into the direction of the current, defined as the flow of *positive* charges, the fingers will indicate the direction of the magnetic field

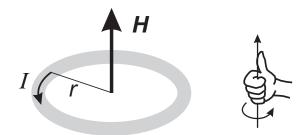


Fig. 2.3. The direction of the magnetic field H defines the sense of rotation of the current. The right hand rule illustrated on the right applies to determine the sense of rotation. Therefore one says that H has a handedness

center of the loop that is perpendicular to the plane in which the current flows. The direction of this magnetic field can again be determined with the right hand rule as illustrated in Fig. 2.3 and in the center of the loop has the magnitude

$$H = \frac{I}{2r} . (2.4)$$

The basic discovery of Oersted, and the further development by Ampère and by Biot and Savart, thus tells us the units in which a magnetic field is measured. However, it additionally shows the two fundamental symmetry properties of the magnetic field. First, \boldsymbol{H} is a so-called axial vector (see Sect. 2.5), because it defines a handedness or chirality. Second, it changes sign when the current reverses, that is, it depends on the sign of the parameter time. More generally, the current density \boldsymbol{j} (in $[A m^{-2}]$) and the magnetic field \boldsymbol{H} (in $[A m^{-1}]$) are related by *Ampère's law*

$$\boldsymbol{j} = \nabla \times \boldsymbol{H} \;, \tag{2.5}$$

where ∇ is the gradient or Nabla-operator $\nabla = \{\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\}$. To calculate magnetic fields from (2.5), one makes use of *Stokes' theorem* [118].

Stokes' theorem links the integral of any vector field \boldsymbol{H} around a closed loop L that bounds an arbitrary surface S to the component $(\nabla \times \boldsymbol{H})_n$ normal to the surface according to

$$\lim_{S \to 0} \frac{1}{S} \oint_{L} \boldsymbol{H} \cdot d\boldsymbol{l} = (\nabla \times \boldsymbol{H})_{n} \quad \text{or} \quad \oint_{L} \boldsymbol{H} \cdot d\boldsymbol{l} = \iint_{S} (\nabla \times \boldsymbol{H})_{n} \, dS \,. \tag{2.6}$$

For instance, let us calculate the magnetic field of a current flowing in the z direction in a cylindrical tube with radius R, centered at x = y = 0, as shown in Fig. 2.2. To obtain the field outside the tube we choose the closed

integration path to be a circle of radius $r \ge R$ in the x-y plane. Then $S = \pi r^2$ and $L = 2r\pi$, and we obtain from (2.6) $H2\pi r = j\pi R^2$, or with $I = j\pi R^2$ we recover (2.3) or $H = I/(2\pi r)$.

To calculate the magnetic field inside the tube (r < R) we assume a uniform current density $j = I/\pi R^2$ = constant inside the tube and choose an integration path with r < R. We get $H2\pi r = j\pi r^2$ and inserting the constant current density we obtain

$$H_{\rm i} = \frac{I}{2\pi R^2} \ r \ . \tag{2.7}$$

We see that the magnetic field strength H_i inside the current carrying tube is zero in the center and increases linearly with the distance r from the center. The maximum field strength $H = I/2\pi R$ is reached at the edge r = R of the wire.

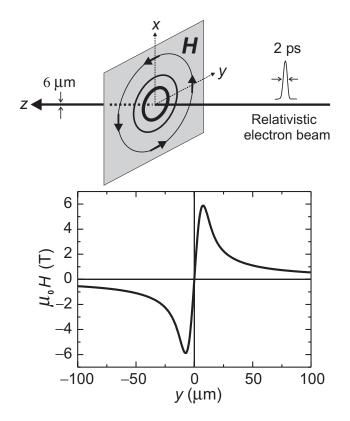
The magnetic induction \boldsymbol{B} is another quantity used to describe magnetic fields. It relates to the production of magnetic fields by electromagnetic induction according to Faraday's induction law $\nabla \times \boldsymbol{E} = -\boldsymbol{B}$ where $\boldsymbol{B} = \partial \boldsymbol{B}/\partial t$. In vacuum and to a very good approximation also in gases at normal conditions, the magnetic field \boldsymbol{H} and the magnetic induction \boldsymbol{B} are related by $\boldsymbol{B} = \mu_0 \boldsymbol{H}$.

In vacuum the magnetic induction B is given by

$$\boldsymbol{B} = \mu_0 \, \boldsymbol{H} \; . \tag{2.8}$$

The units of \boldsymbol{B} are $[V \text{ sm}^{-2}]$, where $1 \text{ V sm}^{-2} = 1 \text{ T}$. $\mu_0 = 4\pi \times 10^{-7} \text{ V s} \text{ A}^{-1} \text{ m}^{-1}$ is the magnetic permeability of the vacuum. In vacuum, B = 1 T corresponds to $H = 10^4 \text{ Oe}$.

The laws expressed by (2.5) and (2.7) have a host of important applications. One contemporary of them is the large magnetic field surrounding a "bunch" of charged particles that are accelerated to nearly the speed of light in electron accelerators, illustrated in Fig. 2.4. We will come back to the origin and applications of such fields in more detail in Sect. 4.3.2 and Chap. 15. Such electron bunches may carry about 1 nC of charge or about 10^{10} electrons and have very high current densities because of their short duration. For the experimental geometry shown in Fig. 2.4 with the electron beam traveling in the z direction the actual current density across the electron beam can be measured with fine carbon wires spanned in the x and y directions. The current density in the beam has a Gaussian shape centered at x = y = 0. The lower part of Fig. 2.4 shows the calculated magnetic induction $B = \mu_0 H$ in units of Tesla for such a Gaussian distribution of the current density as a function of the distance x or y from the beam center. In the frame of an observer or a stationary sample the magnetic field direction resembles that of a current carrying wire and is shown in the upper part of the figure. As for the calculation with a uniform current density according to (2.7), the mag-



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Fig. 2.4. Geometry and calculated magnetic field for a Gaussian shaped "bunch" of 1.2×10^{10} electrons and a lateral size of $6\,\mu\text{m}$ moving nearly at the speed of light. In the laboratory frame of reference, the pulse width is assumed to be 2×10^{-12} s, so that the corresponding peak current is 960 A. Note that the maximum field strength is reached near the edge of the beam (see (4.27))

netic field is zero in the center of the current and decays with 1/y at large distances. The maximum field strength is reached at the "edge" of the beam, corresponding to the steepest drop of the Gaussian current density distribution. The distance-dependent expression for the field strength is given by (4.27).

The conventional way of generating magnetic fields is, of course, with current carrying wires wound into a coil. Equation (2.5) yields for the magnetic field of a long and thin coil

$$H = \frac{n\,I}{L} \,\,, \tag{2.9}$$

where I is the electric current, n the number of windings, and L the length of the coil. In practice, it is difficult to reach large field strengths with a coil because of the heat generated by the current in the wire. Without cooling,

Table 2.1. Some values of magnetic field strengths

where?	mag. field	duration
	(Tesla)	
brain activity	10^{-13}	milliseconds
heart activity	10^{-11}	milliseconds
$MilkyWay^a$	10^{-9}	average
Earth-dipole	$\sim 5 \times 10^{-5}$	average
Sun-dipole	$\sim 5 \times 10^{-3}$	average
Sun-spot	~ 0.5	min-hours
perm. magnets	~ 1	average
relat. e-bunch	$\sim 10^2$	$\sim 10^{-13} {\rm s}$
pulsed coils	$\sim 10^3$	$\sim 10^{-6} \mathrm{s}$
exchange field ^b	$\sim 10^4$	average
neutron star	$\sim 10^7$	average

 $^{\rm a}$ For cosmological magnetic fields see P. P. Kornberg, Phys. Today, Dec. 2002, p. 40 $^{\rm b}$ This is not a true field but acts like one on the electron spin

coils typically produce only fields of 10 mT. Higher fields of up to 20 T are now routinely produced with coils made of superconducting wire [119]. Table 2.1 lists the size of some magnetic fields found in the Universe. The spectacular image shown in Fig. 2.5 of the sun arises from the X-ray emission of hot plasmas by electrons and ions that also create magnetic fields.

2.4 High Current Densities

It is instructive and important for contemporary magnetism to examine the current densities that exist in nature or may be produced with new technologies available today.

The current densities existing naturally in some of the stationary electronic states of atoms are actually surprisingly high. In Bohr's model of the atom, the electron moves in a circle of radius $a_0 = 0.5 \times 10^{-10}$ m at a circular frequency $\omega = 2\pi\nu$ around the atomic nucleus. This establishes an electric current of $I = \nu e$ where -e is the charge of the electron. For an electron that circles with the Rydberg frequency of $\nu \approx 3 \times 10^{15} \text{s}^{-1}$ we obtain a current of $\sim 0.5 \text{ mA}$ and a current density of $j = I/a_0^2 \pi \approx 1 \times 10^{17} \text{ Am}^{-2}$. The only limitation to the current density in the atom is Pauli's exclusion principle which does not allow more than one electron in the same state. One could imagine that the atoms shrink in size due to the magnetic field produced by the electrons whereby sufficient electrostatic energy would be gained to compensate for the energy necessary to produce the magnetic field. This would then destabilize the atoms. However, it has been shown that matter is stable in arbitrarily strong magnetic fields due to the Pauli principle [120].

If one wanted to produce the current density existing in atoms in a Cu-wire of 1 mm^2 cross-section, one would have to inject 10^{11} A. This is larger than

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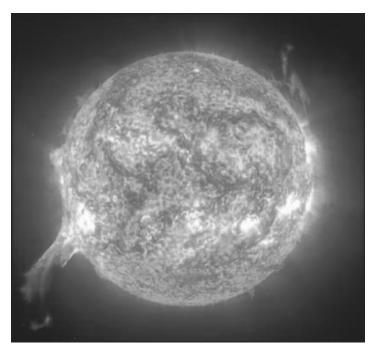


Fig. 2.5. X-ray image of the sun taken by NASA's SoHo satellite. Magnetic fields are at the root of virtually all of the features we see on and above the Sun. The magnetic fields are produced on the Sun by the convective flow of electrically charged ions and electrons and can be readily probed by the Zeeman splitting of the atomic levels discussed in Sect. 6.6.1. Sunspots are places where very intense magnetic lines of force break through the Sun's surface. The sunspot cycle results from the recycling of magnetic fields by the flow of material in the interior. The loops above the surface, known as prominences, are rarely as big as the one seen on the lower left. The sun also has a smaller dipolar field (see Table 2.1) which changes polarity once about every 11 years for reasons that are not well understood. The earth's magnetic field is shown in Fig. 3.2

what can be done by about 10 orders of magnitude. There are two obstacles to attaining high current density. In solids it is the scattering of the charge carriers producing heat, and in vacuum it is the electrostatic repulsion in the space charge that counteracts high electron densities. Both obstacles may be overcome to a large extent.

In metals, the electrostatic repulsion of the electrons is reduced greatly because the charge of the electrons is compensated by the charge of the atom cores, and furthermore, any Coulomb field is screened by the conduction electrons reducing the range of all electrostatic interactions significantly. Hence the space charge is not a problem but the scattering must be avoided if high current densities are to be reached. The most obvious way to avoid scattering is to use superconductors. However, Oersted's magnetic field associated with the current breaks the superconducting pairs if the currents are large. Another way to reduce scattering is to reduce the length of the pathway of the electrons in the material to below the scattering length. This is achieved in nanoscopic constrictions. In tunneling microscopy, for instance, a very fine point contact is produced when the tunneling tip approaches a surface and all the current passes through the last atom on the tip. Current densities of 10^{13} A m⁻² have been reported between a nickel tip and a nickel surface and between a silver tip and Co/Cu multilayer without inducing any permanent damage in the tip or the surface [121, 122]. When such current densities flow through a ferromagnet a large spin polarized current can be created which may be used to manipulate the state of the magnetization in another magnetic layer into which it is injected. This exciting new concept of *spin injection* will be discussed later in Sect. 14.2.

We have already seen in connection with Fig. 2.4 that high current densities can also be produced in vacuum, although we did not explain how this fascinating and useful effect is possible despite the large Coulomb repulsion between the charges. In order to understand it, we need to first discuss relativistic effects, which is done in Sect. 4.2.2. High current densities in electron beams will then be explained in Sect. 4.3.2.

2.5 Magnetic and Electric Fields inside Materials

In Sect. 2.3 we have seen that the magnetic field \boldsymbol{H} and the magnetic induction \boldsymbol{B} are related by $\boldsymbol{B} = \mu_0 \boldsymbol{H}$. This strictly applies only in vacuum. In order to describe the fields existing in matter as well, a third field vector is introduced, the magnetization \boldsymbol{M} . The magnitude of \boldsymbol{M} is defined as the volume density of magnetic moments.¹

The three magnetic field vectors are related according to	
$oldsymbol{B}=\mu_0oldsymbol{H}+oldsymbol{M}$.	(2.10)
M is measured in the same $[V s m^{-2}]$ or $[T]$ units as B .	

We shall see later that the magnetization is an important property of magnetic materials. For example, it determines the maximum magnetic field that can be generated by a fully magnetized body. The magnetizations for the three important ferromagnetic metals Fe, Co, and Ni are listed in Table 2.2.

All three magnetic field vectors must have the same symmetry because they occur as a sum in the same equation (2.10). That is \boldsymbol{B} , \boldsymbol{H} , and \boldsymbol{M} each define a sense of rotation, and as discussed later, are therefore called *axial* vectors. They also change sign upon time reversal. The symmetry properties

¹Magnetic moments are discussed in Chap. 3.

Table 2.2. Saturation magnetizations for the ferromagnetic elemental metals Fe, Co, and Ni at 4.2 K in [Tesla] [123]

metal	M [T]
Fe (bcc)	2.199
Co (hcp)	1.834
Ni (fcc)	0.665

of the magnetic field vectors are based on experimental observation. We shall discuss this point in more detail later.

In isotropic *paramagnetic* and *diamagnetic* substances we have the simple linear relationship

$$\boldsymbol{B} = \mu \,\mu_0 \,\boldsymbol{H} \;, \tag{2.11}$$

where μ is called the *relative magnetic permeability*. It is dimensionless and >1 for paramagnetic but <1 for diamagnetic media. It typically differs from unity by a factor of about 10^{-5} .

The relation between the magnetization M and the magnetic field H defines the often quoted magnetic susceptibility χ according to

$$\boldsymbol{M} = \chi \,\mu_0 \,\boldsymbol{H}.\tag{2.12}$$

The magnetic susceptibility is dimensionless. From (2.10) and (2.12) one obtains a relation between the magnetic parameters: $\mu = 1 + \chi$. Thus, with *paramagnetic* media $\chi > 0$ and with *diamagnetic* media $\chi < 0$.

For the case of the electric field vector \boldsymbol{E} and the dielectric field or *dielectric displacement* \boldsymbol{D} , analogous equations exist. In vacuum and in many materials of interest here we have $\boldsymbol{D} = \epsilon_0 \boldsymbol{E}$, where $\epsilon_0 = 8.86 \times 10^{-12} \text{A s V}^{-1} \text{m}^{-1}$ is the dielectric constant of the vacuum. To generally describe the electric fields in matter, the *dielectric polarization* \boldsymbol{P} is introduced which is the density of electric dipoles.

The three electric vectors are related by the equation

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P},\tag{2.13}$$

D has units $[A s m^{-2}]$, and $\epsilon_0 = 8.86 \times 10^{-12} A s V^{-1} m^{-1}$ is the dielectric constant of the vacuum.

In isotropic substances we have the linear relationship

$$\boldsymbol{D} = \epsilon \, \epsilon_0 \boldsymbol{E} \;, \tag{2.14}$$

where ϵ is the dimensionless relative electric permittivity and ϵ_0 is the dielectric constant.

In contrast to the magnetic field vectors, the electric field vectors do not indicate a sense of rotation, they only define a direction and do not change sign when the time is inverted (see later). The electric field vectors are therefore called *polar vectors*.

2.6 The Relation of the Three Magnetic Vectors in Magnetic Materials

To understand the nature of the three magnetic vectors \boldsymbol{B} , \boldsymbol{H} , and \boldsymbol{M} discussed in Sect. 2.5 we take a closer look at relation (2.10) that links them. We use the example of a flat ferromagnetic disk that has been perpendicularly magnetized, as shown in Fig. 2.6 by an external magnetic field. After this process the external magnetic field has been turned off, so that we consider only the field generated by the ferromagnetic disk itself. Such magnetized disks can nowadays be made from materials that exhibit anisotropic atomic structure to favor an out-of-plane magnetization direction. Examples are given in Sect. 11.2.

We can now write down expressions for the magnetic field H in the interior of the disk and outside the disk by use of (2.10). The field inside the disk is

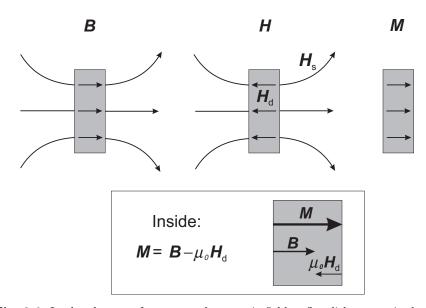


Fig. 2.6. In the absence of an external magnetic field, a flat disk magnetized perpendicular to the surface is characterized by the three magnetic vectors B, H, and M, as shown. The magnetic field inside the magnetic material is called the *demagnetizing field* H_d because it is oriented opposite to the magnetization M, thus tending to destroy it. The field outside the material is called the *stray field* H_s and it loops around in space. Note the opposite relative orientations of H_d and H_s near the sample. In the lower part of the figure we show the directions and an example of the relative magnitudes of the three vectors

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given by

$$\boldsymbol{H}_{\rm d} = \frac{1}{\mu_0} (\boldsymbol{B} - \boldsymbol{M}) , \qquad (2.15)$$

and the field outside of the magnetic material is

$$\boldsymbol{H}_{\rm s} = \frac{1}{\mu_0} \boldsymbol{B} \;. \tag{2.16}$$

We have chosen specific indices for the fields inside and outside the disk which reflect their common names.

The magnetic field inside a magnetic material is called the *demagnetization field*, that outside the magnetic material the *stray field*.

In order to more clearly see the nature of the two fields we choose a closed integration path that follows the \boldsymbol{B} field in Fig. 2.6. Since there are no currents flowing through the area bordered by the integration path, we conclude from (2.5) that

$$\oint \boldsymbol{H} \cdot \mathrm{d}\boldsymbol{l} = 0 \ . \tag{2.17}$$

This can only be the case if $H_{\rm d}$ is directed opposite to the field $H_{\rm s}$. Hence inside the disk the *demagnetization field* $H_{\rm d}$ must be directed opposite to the magnetization M. The directions of the M, B, and H fields are illustrated in Fig. 2.6.

When the magnetization direction of a material is turned, the demagnetization field also changes direction. In fact, the case of perpendicular magnetization shown in Fig. 2.6, is actually unusual for a thin film. In most thin film materials it is favorable for the magnetization to lie in the plane of the film. The demagnetization field is then oriented parallel to the film surface. Clearly, the demagnetizing field depends on the shape of the magnetic body and is generally not homogeneous over the whole sample volume.

Let us take a closer look at the implications of the connection between the fields illustrated in Fig. 2.6. We can obtain insight on the magnetic induction \boldsymbol{B} by combining the fundamental Maxwell equation governing magnetostatics (see (5.2))

$$\nabla \cdot \boldsymbol{B} = 0, \tag{2.18}$$

with Gauss' theorem [118].

Gauss' theorem states that the outward flux $\iint_S \boldsymbol{B} \cdot \boldsymbol{n} \, \mathrm{d}S$ of any field \boldsymbol{B} through a surface S that encloses a volume V is related to the divergence of the field $\nabla \cdot \boldsymbol{B}$ inside the volume V by

$$\lim_{V \to 0} \frac{1}{V} \iint_{S} \boldsymbol{B} \cdot \boldsymbol{n} \, \mathrm{d}S = \nabla \cdot \boldsymbol{B} \quad \text{or} \quad \iint_{S} \boldsymbol{B} \cdot \boldsymbol{n} \, \mathrm{d}S = \iiint_{V} \nabla \cdot \boldsymbol{B} \, \mathrm{d}V \; . \tag{2.19}$$

2.6 The Relation of the Three Magnetic Vectors in Magnetic Materials 51

By combining (2.18) and (2.19) we see that the total flux of the magnetic induction emerging from a closed surface must be zero. Isolated magnetic poles would generate a nonvanishing total flux and therefore cannot exist. We can state this result in a complementary way as a conservation law for the magnetic induction \boldsymbol{B} that enters into and emerges from any volume Vsurrounded by a closed surface S. Since there cannot be a magnetic source inside any volume that adds to or subtracts from the incoming flux we see that "what goes in must come out." An example of his law is seen in Fig. 2.6 where the flux of \boldsymbol{B} that enters into the gray sample volume on one side comes out on the other. Note that this conservation law does not hold for \boldsymbol{H} and \boldsymbol{M} , individually, but since $\boldsymbol{B} = \boldsymbol{M} + \mu_0 \boldsymbol{H}$ it holds for the sum. We shall make use of this next.

We can use the relation $\nabla \cdot \boldsymbol{B} = \nabla \cdot [\mu_0 \boldsymbol{H} + \boldsymbol{M}] = 0$ to define the *stray* field as the field which is generated by the magnetization \boldsymbol{M} . The sinks and sources of the magnetization act like positive and negative "magnetic charges" or "magnetic poles" for the stray field \boldsymbol{H}_s , as illustrated in Fig. 2.7. In analogy with the electric field, the magnetic field originates on positive charges, as shown. In contrast to electric charges, magnetic charges or poles never appear isolated but are always balanced by opposite charges or poles. By definition, the positive magnetic pole of a body is taken to be the north pole (see Sect. 3.1, below), so that magnetic fields point from the north pole to the south pole.

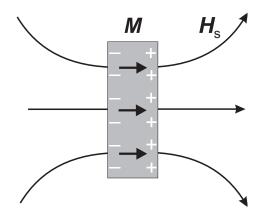


Fig. 2.7. The stray field H_s of a flat sample magnetized perpendicular to the surface can be viewed as arising from positive and negative "magnetic charges" or "magnetic poles" that act as the sinks and sources of the magnetization M. Note that by definition the field H_s originates on positive "magnetic" charges, also identified with the "north pole" of the material

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The sinks and sources of M act like positive and negative poles for the field H according to,

$$\mu_0 \nabla \cdot \boldsymbol{H} = -\nabla \cdot \boldsymbol{M} \ . \tag{2.20}$$

The field H is called H_d inside and H_s outside the material. The magnetic stray field H_s generated by a magnetic body contains energy. The total energy E_d is given by

$$E_{\rm d} = \frac{\mu_0}{2} \iiint_{\rm space} \boldsymbol{H}^2 \, \mathrm{d}V = -\frac{1}{2} \iiint_{\rm sample} \boldsymbol{H}_{\rm d} \, \boldsymbol{M} \, \mathrm{d}V \;. \tag{2.21}$$

The energy E_d connected to the stray field is always positive. The second integral in (2.21), expressing the energy of the field H_d inside the sample is often easier to evaluate since it extends only over the volume of the magnetic sample. H_d has a negative sign because it is opposed to M. The factor 1/2is introduced to avoid double-counting the interactions between two magnetic dipoles, as explained in detail in the book by Aharoni [124].

2.6.1 Stray and Demagnetizing Fields of Thin Films

In modern magnetism research, magnetic thin films are of key importance and in such systems the magnetization may have two extreme directions, either in the film plane or perpendicular to it. We will now take a look at the stray and demagnetizing fields for these two cases.

To do so we make use of the concept of virtual magnetic surface charges as illustrated in Fig. 2.7. In this model the magnetic charges are located in an arbitrarily thin sheet at the surface, neglecting the atomic structure. The stray field will not change if one locates the sheet with the poles either inside the magnetized body or just outside of it in the vacuum.

In order to explore this concept we shall now calculate the stray field inside an extended slit-like cavity inside a homogeneously magnetized material. The result will also apply for the opposite case where the cavity is filled with magnetic material but outside of it is vacuum, i.e., the case of a magnetic thin film. The sheet with the surface charges is the same in both cases, hence it produces the identical magnetic field, but in one case the field corresponds to the stray field H_s outside the magnetic material while in the other it reflects the demagnetizing field H_d inside the magnet. We only need to remember that in the two cases the fields have opposite signs.

We consider a homogeneously magnetized material with a two-dimensional thin slit cavity that is oriented either parallel or perpendicular to M as depicted schematically in Fig. 2.8. The field in the cavities arises from the shown

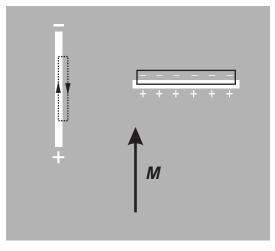


Fig. 2.8. A large homogeneously magnetized piece of material with a twodimensional thin slit cavity, oriented parallel or perpendicular to M. For the parallel orientation, we consider a line integration according to Stokes' theorem along the dotted line. For the perpendicular slit we use a surface integration around a volume, whose projection is indicated by a solid black line, according to Gauss' theorem

magnetic surface charges. According to our above reasoning, we can now calculate the field H_s inside the cavities and, apart from the sign, the result will also correspond to the demagnetizing field H_d inside a magnetic thin film that has the shape of the cavity.

The magnetic field \boldsymbol{H}_{s} inside the thin slit cavity oriented *parallel* to \boldsymbol{M} is obtained from Stokes' theorem (2.6) by choosing a line integration path along the dotted loop in Fig. 2.8. Since there are no currents, the closed loop integral $\oint \boldsymbol{H} \cdot d\boldsymbol{l}$ must be zero, according to (2.5). Inside the cavity we have a contribution $\int \boldsymbol{H}_{s} \cdot d\boldsymbol{l}$ to the integral around the whole loop and in the material we have a contribution $-\int \boldsymbol{H}_{d} \cdot d\boldsymbol{l}$, because the element $d\boldsymbol{l}$ has the opposite direction in the cavity and outside the cavity. The two path contributions perpendicular to the cavity–material interface vanish. This gives

$$\oint \boldsymbol{H} \cdot d\boldsymbol{l} = \int (\boldsymbol{H}_{s} - \boldsymbol{H}_{d}) \cdot d\boldsymbol{l} = 0 \qquad (2.22)$$

and therefore $H_s = H_d$. In our case the magnetic field component in the cavity points in the direction of M and it is *continuous* across the interface separating the cavity and the magnetic material! Additionally, we see that H_s inside the slit must also be very small because the surface charges that generate it are far apart. Because of the surface charge analogy discussed above, this means that the demagnetizing field H_d of a magnetic thin film magnetized along an in-plane direction is very small, as well.

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Now consider the slit-like cavity oriented perpendicular to \boldsymbol{M} . We make use of Gauss' theorem and put a closed surface in the shape of a rectangular "Gauss" box so that one side of the box is inside the cavity and the other side is inside the material, as shown in Fig. 2.8. With $\nabla \cdot \boldsymbol{B} = 0$ we have from $(2.19) \iint_{\boldsymbol{S}} \boldsymbol{B} \cdot \boldsymbol{n} \, \mathrm{d}\boldsymbol{S} = 0$ and the magnetic flux from inside to outside the box is zero. In the cavity we have an induction $\boldsymbol{B}_{\mathrm{c}}$ and in the material $\boldsymbol{B}_{\mathrm{m}}$ so that we have the following two nonvanishing contributions to the closed surface integral

$$\iint_{S} (\boldsymbol{B}_{c} - \boldsymbol{B}_{m}) \cdot \boldsymbol{n} \, \mathrm{d}S = 0$$
(2.23)

because the outward surface normal \boldsymbol{n} has opposite signs on both sides of the box. This gives $\boldsymbol{B}_{\rm c} = \boldsymbol{B}_{\rm m}$. The component \boldsymbol{B}_{\perp} is therefore *continuous* across the cavity-material interface, and therefore a large magnetic stray field $\boldsymbol{H}_{\rm s} = \boldsymbol{M}/\mu_0$ must exist inside the slit. One concludes that the demagnetizing field inside a thin film that is magnetized perpendicular to the surface has a maximum value $\boldsymbol{H}_{\rm d} = -\boldsymbol{M}/\mu_0$, and the demagnetizing field is opposed to \boldsymbol{M} of the sample. We can summarize as follows.

The magnitude of the demagnetizing field for a homogeneously magnetized thin film \mathbf{H}_{d} is nearly zero for *in-plane* magnetization. The demagnetizing field is largest for *out-of-plane* magnetization and its direction and magnitude is given by,

$$\boldsymbol{H}_{\rm d} = -\frac{\boldsymbol{M}}{\mu_0} \ . \tag{2.24}$$

2.6.2 Applications of Stray and Demagnetizing Fields

A ring magnetized along its circumference is equivalent to an infinitely long bar because the charges at the end-surfaces are neutralized if the bar is bent into a ring. Hence a ring-shaped sample has no demagnetizing field at all, and no field is generated on the outside according to (2.21). Closed magnetic rings or approximations of them are used in transformers where field leakage to the outside would generate losses. A ring can be magnetically saturated with a weak additional field produced by a coil wound around it, yet in the radial slit also called "the gap" there will be a sizeable field $H_{\rm s} \sim M/\mu_0$ because it corresponds to the perpendicular situation in Fig. 2.8. A magnetic core surrounded by a coil in the form of a ring with a small slit or "gap" is an *electromagnet* and finds many applications in the generation of magnetic fields. A "high-tech" application is a *magnetic recording* "head" that writes tiny magnetic domains, or "bits," into a *magnetic medium* that is deposited on a disk that spins underneath the head as shown in Fig. 2.9.

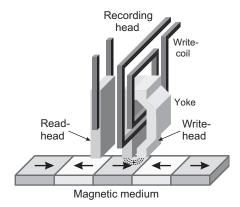


Fig. 2.9. A magnetic recording "head" is basically a tiny electromagnet that writes magnetic "bits" of different magnetization directions into a magnetic medium. The magnetic material in the head is shaped into a yoke with a gap at the bottom end. The gap is only a fraction of a μ m wide to write the small bits required in magnetic recording. A flat lithographically made coil produces a relatively small field that is sufficient to saturate the "soft" (i.e., easily saturated) magnetic yoke material, e.g., a CoFe-alloy with a high value of M. The field in the gap is remarkably large of order of ~1 T. The field used for writing is the stray field that protrudes out of the gap

The rate at which the write field polarity is changed determines the rate at which data can be written. With a macroscopic electromagnet, self-induction produces decay times of the magnetic field in the gap which are typically ~ 1 s. As self induction decreases proportional to the cross-section of the magnetic core, the miniaturized electromagnet allows one to change the magnetization in a time of $\sim 10^{-9}$ s. This makes possible the data rates in contemporary computers of $\sim 1 \text{ GHz}$. We see that miniaturization not only saves space and material, but also produces faster devices.

Spherical voids in magnets or magnetic samples with the shape of a sphere are of practical interest as well. Even without a detailed calculation it is plausible that a spherical void in a magnetic material will lie in between the two limiting cases of the parallel and perpendicular slits in Fig. 2.8. It turns out that for a spherical hollow $H_{\rm s} = (1/3) M/\mu_0$. Furthermore, the field inside a spherical or elliptical void is homogeneous, while the fields in voids of other shapes are generally inhomogeneous. Again, we conclude that the demagnetizing field inside a magnetic sphere is $H_{\rm d} = -(1/3) M/\mu_0$.

In general, we can write

$$\boldsymbol{H}_{\rm d} = -\frac{N}{\mu_0} \boldsymbol{M} , \qquad (2.25)$$

where N is called the *demagnetizing factor*. For a crystalline material, N is a tensor. For homogeneously magnetized isotropic materials we have the follow-

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ing values for three special cases: N = 0 for a long and thin bar, magnetized along its axis, or for an in-plane magnetized thin film; N = 1 for a thin film magnetized perpendicular to the surface, and N = 1/3 for a spherical particle.

In many applications, the demagnetizing field presents a problem because it tends to destroy the homogeneously magnetized state. As we shall see later, the magnetization has preferred directions in a solid where the energy is at a minimum. The demagnetizing field tends to twist M out of this "easy" direction. In the case of a material consisting of small particles, thermal fluctuations may then lead to the destruction of the homogeneously magnetized state. The bits recorded into magnetic recording media for instance tend to disappear with time due to the combined action of demagnetizing fields and thermal fluctuations. One dilemma of magnetic recording is that one would like to have a small demagnetizing field to ensure a long term stability yet, without a demagnetizing field, there would be no stray magnetic field, which is needed to read the magnetization direction of the bits.

The concept of "synthetic antiferromagnet media," illustrated in Fig. 2.10 tries to overcome this problem through an ingenious compromise [125]. The stray field extending below the magnetic bits is not necessary for the reading process of the bits. It is therefore short circuited by an antiparallel-coupled "slave layer" approximating a closed magnetic ring for the lower half of each bit and in this way helping to stabilize it. By making the slave layer only about half as thick as the main layer, the upper half of the magnetic flux needed for the readout process is still present.

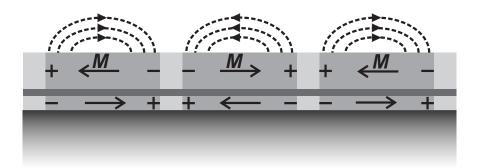


Fig. 2.10. Magnetic stray field for an in-plane magnetized thin film recording medium with an underlayer or "slave" layer that is coupled antiparallel to the main layer by a very thin ruthenium spacer layer. Such "synthetic antiferromagnet media" presently support the highest bit densities. The stray field above the thin film medium is still present and usable for read-out of the bits, while the stray field below is short-circuited by the antiferromagnetically coupled slave layer. As is common in magnetism, hypothetical magnetic charges are assumed from which the stray field seems to originate. Note, however, that isolated magnetic poles do not exist

2.7 Symmetry Properties of Electric and Magnetic Fields

Electromagnetic phenomena are guided by two fundamental symmetries,

- Parity, \mathcal{P} , or inversion of spatial coordinates about a chosen origin.
- Time reversal, $\boldsymbol{\mathcal{T}}$, or the reversal of the direction of motion.

These symmetries provide important guidelines for the prediction of experimental results and tests for the detection of anomalies and errors. They are particularly important in the context of electromagnetic interactions because, as we shall see later, electric and magnetic fields behave distinctly different with respect to spatial and time coordinates. Let us look at the two symmetry concepts in turn.

2.7.1 Parity

We start with the mathematical definition of the parity operation.

The <i>parity transformation</i> is defined by the replacement			
x ightarrow - x			
y ightarrow - y			
z ightarrow - z.	(2.26)		
By introducing the <i>parity operator</i> $\boldsymbol{\mathcal{P}}$ we say that a quantity A with			
$\mathcal{P}A = +A$	(2.27)		
is of $even$ or $ungerade$ (g) parity. When the operation changes the sign			

 $\mathcal{P}B = -B \tag{2.28}$

we say that B has odd or ungerade (u) parity. \mathcal{P} has eigenvalues ± 1 .

The above definition allows us to now take a look at the parity of the fields \boldsymbol{E} and \boldsymbol{H} . In order to see the properties of \boldsymbol{E} and \boldsymbol{H} on inversion we consider their origin and invert the field generating system, i.e., two oppositely charged plates for \boldsymbol{E} and a rotating charge for \boldsymbol{H} , about the origin O. This is illustrated in Fig. 2.11.

When the two charged plates are inverted at O the electric field E, which by definition points from the positive to the negative plate, is seen to invert sign. Since magnetic monopoles do not exist we cannot use hypothetical magnetic charges to generate H but use the well-known fact that a circling positive

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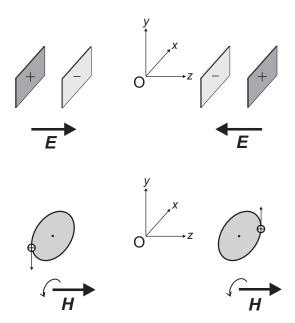


Fig. 2.11. Illustration of the concept of *axial* and *polar* vectors. The electric field vector E, like most common vectors, changes sign upon inversion of spatial coordinates. This is illustrated here by inversion of the system of charged plates that generates E about the origin O of a coordinate system. E is a *polar* vector. The magnetic field vector H, originating from a rotating positive charge q, remains invariant under the same inversion operation since the rotation direction is preserved. H is an *axial* vector

charge q produces a magnetic field H according to the right hand rule. We see that the rotation sense of the charge remains the same upon inversion and hence the H field is unchanged in direction by a parity transformation and is of even parity. The different behavior of H and E leads to the concept of *polar* and *axial* vectors. This is summarized as follows.

The electric field vector E is of *odd* parity and is called a *polar* vector. The magnetic vectors H, B, and M are all of *even* parity. They are called *axial* vectors.

$$\mathcal{P}f(\boldsymbol{E},\,\boldsymbol{H}) = f(-\boldsymbol{E},\,\boldsymbol{H}). \tag{2.29}$$

Like the electric field vector \boldsymbol{E} , most common vectors are *polar vectors*, such as the radial vector \boldsymbol{r} , the gradient vector ∇ , the force \boldsymbol{F} , the velocity \boldsymbol{v} and the related momentum \boldsymbol{p} , and wave \boldsymbol{k} vectors. Vectors that are related to a rotation, such as the magnetic vectors, the angular velocity $\boldsymbol{\omega}$, the torque \boldsymbol{T} , the orbital \boldsymbol{l} and spin \boldsymbol{s} angular momenta, and the photon angular momentum

are axial vectors. The cross product between two like vectors is an axial vector, and the cross product between two unlike vectors is a polar vector. We can summarize the parity transformation properties of some important quantities as follows.

$$\mathcal{P} f(t, r, H, E, l, v, F, T) = f(t, -r, H, -E, l, -v, -F, T)$$
 (2.30)

2.7.2 Time Reversal

Similar to the parity operator, we can define a time reversal operator \mathcal{T} .

<i>Time reversal</i> is defined by the operation	
t ightarrow - t .	(2.31)
By use of the time reversal operator ${oldsymbol {\mathcal T}}$ we say that the quantity A with	
${oldsymbol{\mathcal{T}}} A=+A$	(2.32)
is time-even, and that the quantity B with	
${oldsymbol{\mathcal{T}}} B=-B$	(2.33)
is time-odd. $\boldsymbol{\mathcal{T}}$ also has eigenvalues ± 1 .	

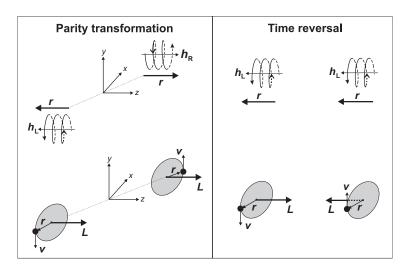


Fig. 2.12. Left: Parity transformation, consisting of inverting a system at the origin of a coordinate system. The position vector \boldsymbol{r} turns into $-\boldsymbol{r}$ and a right handed helix into a left handed one. Both quantities are parity-odd, while the angular momentum vector $L = m(r \times v)$ is parity-even. *Right*: The opposite is true under the timereversal operation, consisting of replacing t by -t. Now r and the helix are time-even and L is time-odd

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60 2 Electric Fields, Currents, and Magnetic Fields

It is now straightforward to determine the time-reversal properties of physical quantities of interest. All quantities that do not originate from timedependent process must be *time-even*, and all quantities that depend linearly on time or are first derivatives of time must be *time-odd*. We can readily write down the time reversal properties of the quantities in (2.30).

$$\mathcal{T} f(t, r, H, E, l, v, F, T) = f(-t, r, -H, E, -l, -v, F, T).$$
 (2.34)

Note that the velocity \boldsymbol{v} is odd in both parity and time, and the torque $\boldsymbol{T} = m \times H = \mathrm{d}\boldsymbol{l}/\mathrm{d}t$ is always even.

The parity and time-reversal properties of three important quantities, the position vector \mathbf{r} , a handed helix, denoted $\mathbf{h}_{\rm R}$ for right and $\mathbf{h}_{\rm L}$ for left handed, and the angular momentum \mathbf{L} are summarized in Fig. 2.12. We shall come back to the concepts of chirality and angular momentum later in this book.

3.1 The Classical Definition of the Magnetic Moment

In analogy with an electric dipole, we can imagine that a magnetic dipole is formed by a fictitious positive magnetic charge $p^+ = +p$ and a negative magnetic charge $p^- = -p$ of equal magnitude separated by a distance d, as shown in Fig. 3.1. In the spirit of the analogy to the electric field of a point charge given by (2.1), we then postulate that each point-like pole produces the magnetic field of strength p. The magnetic field H_D at a point with position vector r_1 from the positive and r_2 from the negative pole is then given by

$$\boldsymbol{H}_{\rm D} = \frac{p}{4\pi\mu_0 r_1^3} \boldsymbol{r}_1 - \frac{p}{4\pi\mu_0 r_2^3} \boldsymbol{r}_2 \;. \tag{3.1}$$

The magnetic fields generated by a dipole are the familiar fields of permanent magnets. The field lines seem to originate from a point source and disappear in a point-like sink. However, as discussed in conjunction with Fig. 2.11, it should be remembered that the magnetic dipole (like the other magnetic vectors \boldsymbol{H} , \boldsymbol{B} , and \boldsymbol{M}) is an axial vector. This is not evident from the historical definition of the dipole moment based on hypothetical magnetic poles but is evident from Fig. 2.11.

The magnetic dipole moment m points from the negative or south magnetic pole to the positive or north magnetic pole and has units of V s m. The magnetic field H points from the positive or north pole to the negative or south pole.

Equation (3.1) allows us to calculate the magnitude of the magnetic field $|\mathbf{H}_{\rm D}|$ at an average distance $\mathbf{r} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ from the center of the dipole as

$$|\boldsymbol{H}_{\rm D}| = \frac{|\boldsymbol{m}|}{4\pi\mu_0 r^3} \sqrt{1+3 \,\cos^2\varphi} \propto \frac{|\boldsymbol{m}|}{r^3} \,,$$
 (3.2)

3

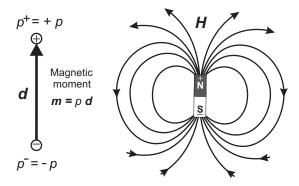


Fig. 3.1. Definition of the magnetic moment m based on imaginary magnetic charges p^+ and p^- , separated by a distance d. By definition, the dipole moment m = pd points from the negative to the positive magnetic pole. We also show the correlation of the "charges" with the magnetic poles and the direction of the field H

where φ is the angle between the dipole moment and the position vector \boldsymbol{r} . The important result to note is that $|\boldsymbol{H}_{\rm D}|$ decreases with distance r from the dipole according to r^{-3} .

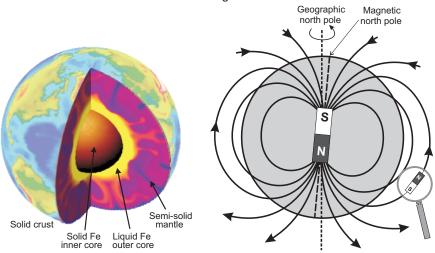
It turns out that any inhomogeneous magnetic field can be described by the superposition of the magnetic fields generated by an even number of magnetic poles. The higher poles are called quadrupoles, sextupoles, octopoles, etc. But the field strength from these higher multipoles naturally decreases even faster with distance r than for the dipole, namely with r^{-5} , r^{-7} , r^{-9} , etc. Consequently, at large distances, the field $H_{\rm D}$ from the dipole is the dominant contribution to the total magnetic field. Hence any magnetic field looks like the magnetic field of a dipole at large distances. This explains why magnetic dipoles are most important in magnetism.

We shall see later that the magnetic field of a closed current loop is identical to that of a dipole. Current loops exist wherever electric charges rotate. Examples are the current produced by orbiting atomic electrons which create orbital magnetic moments and contribute to atomic magnetic fields or the electric currents in the liquid iron outer core of the earth which create the earth's magnetic field as shown in Fig. 3.2. At large distances, the magnetic fields are always well described by the dipole-like form given by (3.2).

A macroscopic current loop may be realized with a current carrying wire as shown in Fig. 3.3. By comparing the field of the current loop with the field generated by a magnetized disk, one proves that the magnetic dipole moment of a current loop is given by

$$|\boldsymbol{m}| = \mu_0 \, I \, S, \tag{3.3}$$

where I is the current and S the area enclosed by the loop.



The Earth and its magnetic field

Fig. 3.2. Illustration of the geological structure of the earth (*left*) and its magnetic field (*right*). The earth's field resembles that of a magnetic dipole. It is believed to be produced mainly by electric currents in the outer core consisting of liquid Fe and changes direction every 500,000 years, on average. The geographic poles, defined by the rotation axis of the earth, differ from the magnetic poles. The earth field direction can be directly determined by a compass in form of a small bar magnet as shown on the bottom right. The end of the compass or bar magnet that points north is said to be its north pole. From Figs. 2.6 and 3.1 we then find that the magnetic north pole of the earth actually corresponds to the south pole if the earth is considered a bar magnet. Note that the magnetic field of the earth has nothing to do with ferromagnetism as the Fe inside the earth is in a nonmagnetic state

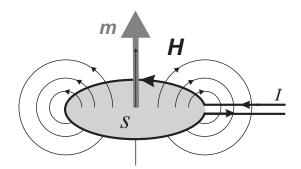


Fig. 3.3. Magnetic moment m and magnetic field H of a closed current (I) loop with area S. The magnetic field generated by the incoming leads is negligible because their fields cancel if the two wires are close together

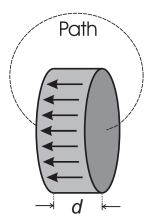


Fig. 3.4. A flat disk magnetized perpendicular to the surface produces a magnetic field similar to a current loop. The *arrows* indicate atomic magnetic dipole moments generating the magnetization M (compare Fig. 2.6). The disk has an area S and a thickness d, and the *dashed line* is the pathway of the integration

To prove (3.3), one considers a disk of very small thickness d magnetized in a direction perpendicular to the disk surface, as shown in Fig. 3.4. The fields of the disk have been discussed in Sect. 2.6 and from (2.17) we have

$$\oint \boldsymbol{H} \cdot d\boldsymbol{s} = \frac{1}{\mu_0} \oint \boldsymbol{B} d\boldsymbol{s} - \frac{1}{\mu_0} \int_0^d \boldsymbol{M} d\boldsymbol{s} = 0, \qquad (3.4)$$

which can only be the case if $\oint \mathbf{B} \cdot d\mathbf{s} = \int_0^d \mathbf{M} \cdot d\mathbf{s}$. This in turn means that

$$\frac{1}{\mu_0} \oint \boldsymbol{B} \cdot \mathrm{d}\boldsymbol{s} = \frac{1}{\mu_0} M d. \tag{3.5}$$

However, for the current loop, $I = \oint \mathbf{B} \, \mathrm{d}\mathbf{s}/\mu_0$ so that the current loop and magnet are identical if $I = M d/\mu_0$. With this result and the volume of the disk V = S d, we get for the magnetic moment of the macroscopic magnet disk $|\mathbf{m}| = M V = M S d = \mu_0 IS$. This last expression can then be taken to define the magnetic moment of a current loop, giving (3.3).

3.2 From Classical to Quantum Mechanical Magnetic Moments

In the historical development of the concepts of magnetism rotating electric charge distributions have played a crucial role. Before the discovery of the spin they were held solely responsible for the magnetic moments of atoms and the magnetization of solids. We have already derived the magnitude of the magnetic moment of a ring current given by (3.3). We can rewrite this equation in a more general form. The current is given by $I = q (\omega/2\pi)$, where ω is the angular frequency with which the charge q moves around the current loop, and the area of the loop is $S = r^2\pi$, so that we obtain $|\mathbf{m}| = \mu_0 q \omega r^2/2$ [V m s]. This equation can be written in vector form as

$$\boldsymbol{m} = \frac{q\mu_0}{2} r^2 \boldsymbol{\omega} , \qquad (3.6)$$

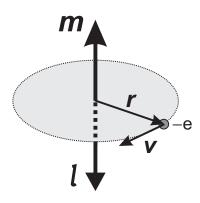


Fig. 3.5. Definition of the magnetic moment caused by an electron q = -e that orbits around a center at a distance r with a tangential velocity v and angular velocity ω . The classical angular momentum l of the rotating electron with mass $m_{\rm e}$ is also shown

or with the definition $v = \omega \times r$ we obtain the magnetic moment for a circulating electron with charge q = -e as

$$\boldsymbol{m} = -\frac{e\mu_0}{2} \left(\boldsymbol{r} \times \boldsymbol{v} \right). \tag{3.7}$$

The moment is perpendicular to the orbit of the circulating charge as shown in Fig. 3.5. The magnetic moment given by (3.6) or (3.7) is seen to have a similar form as the classical angular momentum l (units $[VAs^2]$) of a circulating electron with mass m_e (units $[VAs^3m^{-2}]$)¹

$$\boldsymbol{l} = m_{\rm e}(\boldsymbol{r} \times \boldsymbol{v}) = m_{\rm e} r^2 \boldsymbol{\omega} . \qquad (3.8)$$

Combining (3.7) and (3.8) we obtain an expression for the magnetic moment m of the electron with charge q = -e in terms of the *classical* angular momentum l of a orbiting electron with mass $m_{\rm e}$,

Classical relation:
$$\boldsymbol{m} = -\frac{e\mu_0}{2m_{\rm e}}\boldsymbol{l}$$
 (3.9)

The minus sign arises from the negative charge of the electron.

3.2.1 The Bohr Magneton

The classical expression (3.9) may be converted into a quantum mechanical one.² In doing so one has to realize that in quantum mechanics the expectation value of l cannot be observed but only the component along a quantization

¹Note that the electron mass m_e in S.I. units is given by $m_e = 9.109 \times 10^{-31} \mathrm{V \, A \, s^3 \, m^{-2}} = 9.109 \times 10^{-31} \mathrm{ \, kg}.$

²For historical reasons this is often done by use of Bohr's model of the atom and postulating that any wave function has to be unique. For an orbiting atomic electron the wave function then has to assume its starting value again after a full revolution. This can only happen if the angular momentum l is quantized and occurs in integer multiples of Planck's constant.

axis, say z, defined by an alignment field. Thus we can only observe the expectation value $\langle \boldsymbol{l}_z \rangle$, which for a single electron with wavefunction $|l, l_z, s, s_z \rangle$ is given by $\langle \boldsymbol{l}_z \rangle = \langle l, l_z, s, s_z | \boldsymbol{l}_z | l, l_z, s, s_z \rangle = \hbar l_z$. In the last expression we have specifically indicated that $\hbar l_z$ is the eigenvalue of the operator \boldsymbol{l}_z . The quantum mechanical expression for the measured magnetic moment along z is therefore

Quantum relation:
$$\langle \boldsymbol{m}^z \rangle = -\frac{e\mu_0}{2m_{\rm e}} \hbar l_z$$
 (3.10)

The unit $[VAs^2]$ of the classical angular momentum l is the same as that of the quantum mechanical quantity $\hbar l_z$ since l_z is a dimensionless integer and $\hbar = 1.055 \times 10^{-34} \text{ VAs}^2$.

The quantum mechanical relation (3.10) is used to define the so-called *Bohr magneton*, $\mu_{\rm B}$. It is commonly defined as $\mu_{\rm B} = e\hbar/2m_{\rm e}$. With this definition the Bohr magneton is given in units of [A m²], with a value $\mu_{\rm B} = 0.927 \times 10^{-23}$ A m². We prefer a different definition in [V m s] units which will be used throughout this book.³

The Bohr magneton is defined as,

$$\mu_{\rm B} = \frac{e\,\mu_0\hbar}{2m_{\rm e}} = 1.17 \times 10^{-29}\,{\rm V\,m\,s}~. \tag{3.11}$$

Since the magnetic moment $\langle \boldsymbol{m} \rangle$ also has [V m s] units, we can express it in units of Bohr magneton [$\mu_{\rm B}$], according to $1 \,\mathrm{Vm\,s} = 0.855 \times 10^{29} \mu_{\rm B}$.

3.2.2 Spin and Orbital Magnetic Moments

The quantum mechanical relation (3.10) describes the magnetic moment due to a circling electron, also called the orbital magnetic moment. By use of the Bohr magneton we may write in general,

$$\langle \boldsymbol{m}_{o}^{z} \rangle = -\frac{\mu_{\mathrm{B}}}{\hbar} \langle \boldsymbol{l}_{z} \rangle$$
 (3.12)

The orbital angular momentum is therefore given by the expectation value of the angular momentum operator, $\langle l_z \rangle$ (units [\hbar]). In solids, the expectation

³With our definition, both $\mu_{\rm B}$ and the magnetic moment \boldsymbol{m} have units of [V m s]. This leads to the simple relation $\boldsymbol{m} = \boldsymbol{M}V$, where V is the volume in m³, and the magnetization \boldsymbol{M} has units [V s m⁻²], according to (2.10). With these definitions the magnetic energy is written $E = -\boldsymbol{m} \cdot \boldsymbol{H}$ in order to have the proper [A V s] units in the S.I. system. If we had defined $\mu_{\rm B}$ and \boldsymbol{m} in units of [A m²], as is often done, we would have the awkward relation $\boldsymbol{m} = \mu_0 \boldsymbol{M}V$, or we would have to rewrite (2.10) as $\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$. Then \boldsymbol{H} and \boldsymbol{M} would have the same units [A m⁻¹]. The magnetic energy would be $E = -\boldsymbol{m} \cdot \boldsymbol{B}$ in order for E to have the units [A V s].

value $\langle l_z \rangle$ is calculated with the appropriate band or ligand field wavefunctions as discussed in Sect. 7.9.3 (in particular see (7.67)).

In addition, the electron itself has an *intrinsic* angular momentum or *spin* with half-integer *spin quantum number* $s = \hbar/2$ and observable projections $s_z = \pm \hbar/2$. This emerged from the study of optical transitions in atoms where the electron spin is conserved because it couples only weakly to the electromagnetic wave. Particles with half-integer angular momentum, such as the electron with $\hbar/2$, are called *Fermions*, in honor of Enrico Fermi, those with integer intrinsic spin are called *Bosons*, in honor of Satyendranath Bose.⁴

It is of key importance that the electron spin generates a *full* Bohr magneton with a spin of only $\hbar/2$. For the *spin magnetic moment* $\langle \mathbf{m}_s \rangle$ we can write a similar general expression as (3.12) for the orbital moment, namely

$$\langle \boldsymbol{m}_{s}^{z} \rangle = -2 \, \frac{\mu_{\mathrm{B}}}{\hbar} \, \langle \boldsymbol{s}_{z} \rangle \;.$$
 (3.13)

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Quantum mechanically, the measured value of m_s is again determined by the expectation value $\langle s_z \rangle$ along the quantization axis. In solids, the expectation value $\langle s_z \rangle$ is again calculated with the appropriate wavefunctions as discussed in Sect. 7.9.3 (in particular see (7.65)).

In actual fact, the spin generates a slightly larger moment, by a fraction of $\sim 10^{-3}\mu_{\rm B}$. This latter small increase of the magnetic moment is called the anomalous magnetic moment and is caused by the effect of the fields of the moving electron on itself. It was experimentally discovered in 1951 by Willis Lamb through a slight shift of a spectral line for H, the *Lamb shift*. When writing the magnetic moment in terms of a so-called g-factor as $\mathbf{m}_s = -g\,\mu_{\rm B}\,s/\hbar$ the small correction corresponds to g = 2.002319304386. It is important in quantum electrodynamics but not when discussing magnetism.

The total magnetic moment is given by the sum of the spin and orbital magnetic moments, and when neglecting the anomalous correction to the g-factor, it is given by

$$\langle \boldsymbol{m}_{\text{tot}}^{z} \rangle = -\frac{\mu_{\text{B}}}{\hbar} \left(2 \langle \boldsymbol{s}_{z} \rangle + \langle \boldsymbol{l}_{z} \rangle \right) = -\frac{\mu_{\text{B}}}{\hbar} \left(g_{s} \langle \boldsymbol{s}_{z} \rangle + g_{\ell} \langle \boldsymbol{l}_{z} \rangle \right) .$$
 (3.14)

Therefore we can associate a g-factor $g_s = 2$ with the spin moment and $g_{\ell} = 1$ with the orbital moment.

⁴It is one of the most mysterious phenomena that the famous Pauli exclusion principle applies to Fermions but not to Bosons. As discussed in Sect. 6.2.2, the Pauli exclusion principle together with the electric Coulomb interaction generates the coupling between the electron spins commonly called the exchange coupling that leads to the magnetization of solids in a fashion that is not rigorously understood up to now. The photon on the other hand is an example of a Boson. As discussed in Sect. 5.4.1, for photon propagation along the z quantization axis, a linearly polarized photon has an angular momentum component $\ell_z = 0$ and a circularly polarized photon an angular momentum of $\ell_z = \pm \hbar$, depending on its handedness. With photons, one can put as many of them as one wishes into the same state, which is realized in optical or X-ray lasers.

The nuclear magnetic moments $\mu_{\rm K}$ generated by the spin $\hbar/2$ of the nucleons are reduced compared to $\mu_{\rm B}$ by the ratio of the mass of the electron to the mass of the proton, that is by 1/1,836. Therefore nuclear magnetic moments do not contribute significantly to the magnetization of a solid. Larger nuclei also possess a complicated internal structure and the resulting nuclear g-factors can vary significantly.

We next look at the interaction of magnetic moments with the magnetic field.

3.3 Magnetic Dipole Moments in an External Magnetic Field

After our previous excursion into quantum mechanics, we now consider the behavior of classical magnetic moments, i.e., magnetic dipoles, in external magnetic fields. The interactions of magnetic moments with magnetic fields are basic to the understanding of all magnetic phenomena and may be applied in many ways. In the following, we will derive the energy, the force, and the torque that a magnetic dipole experiences in a magnetic field and mention some of the most important applications of each interaction.

In the applications, one uses the interactions to measure either the magnetic moment or the magnetic field existing at the site of the magnetic moment. Homogeneously magnetized solids also exhibit a magnetic moment, which for a given volume V is given by m = VM. If V is the atomic volume, then m is the magnetic moment per atom, if V is the volume of the the magnetic solid, m is the total magnetic moment of the body. The latter case is often called the "macrospin approximation." It assumes that the exchange coupling which extends over the magnetic solid can strongly couple all the individual electron spins to form one single giant spin or moment. Under these conditions, the equations given below are valid for solids as well, but we will confine the discussion for the time being mostly to noninteracting atomic magnetic moments. It should be remembered that the magnetic dipole moment m is an axial vector constructed to describe the interaction of current loops with the magnetic field, and that magnetic poles are fictitious, that is they do not exist in reality.

Conservation of energy is of course as important in magnetism as in all fields of physics. Yet typically, when applying magnetic energy equations, one cannot determine how fast the state of lowest energy is reached, and in fact it sometimes is reached only on the scale of years or perhaps never. Therefore, another conservation law is at the root of contemporary developments in magnetism, namely the conservation of angular momentum. The "two current model" and the spectroscopic observation of the magnetization to be discussed later are based on it, and it governs magnetization dynamics. Most notably, it also leads to the precession of the magnetic moment in a magnetic field

and to magnetic resonance from which in turn a wealth of new basic knowledge on magnetic moments and many applications such as magnetic resonance imaging in medicine or the atomic clock have emerged.

Conservation of angular momentum means that the vector \boldsymbol{L} of the angular momentum of a rotating inert mass must remain constant in magnitude and direction unless angular momentum is carried away. Our intuition of the motion of a magnetic dipole in a magnetic field is influenced by the oldest and most honorable magnetic experiment, seeing how a compass needle turns into the direction of the earth's magnetic field. This is only part of the story. What really happens is the following. When the magnetic needle is placed into a uniform magnetic field, e.g., the earth's field which is uniform over the size of the needle, the magnetization of the needle actually starts precessing about the field direction. The precession of the magnetization relative to the body of the compass needle induces a frictional or damping torque that forces the magnetization of the needle to turn into the magnetic field. Conservation of angular momentum and energy requires that the frictional torque be transferred from the magnetization to the body of the compass and then to the surrounding environment (compass mount and air). In the end the body of the compass aligns itself again with the magnetization in the north-south direction.

In fact, the detailed visualization of the entire precession and damping motion of a magnetic moment in a magnetic field has only been accomplished in recent times. It was made possible by using pulsed laser magneto-optics which allowed the observation of the detailed motion of the magnetization vector \boldsymbol{M} in a solid. The experiment required a time resolution of the order of 10^{-12} s combined with a spatial resolution of at least a few µm. In these experiments one detects how \boldsymbol{M} spirals into the direction of the magnetic field in a time of typically 10^{-9} s.

If suspended properly one could see that the compass needle does not just turn into the field direction but rotates when the angle between M and Hchanges, thus conserving angular momentum. The famous experiment of Einstein and de Haas has in fact verified that solids rotate when the magnetization direction is changed. The process that transfers the angular momentum from the spin magnetic moment to the solid crystal lattice is called spin–lattice relaxation. We shall see below that the magnetization dynamics is described by the so-called Landau–Lifshitz–Gilbert equation. But before we take a detailed look at this equation we need to first review the basic physics of a magnetic dipole in an external magnetic field.

3.4 The Energy of a Magnetic Dipole in a Magnetic Field

Our definitions of the units of the magnetic moment and the magnetic fields determines the form of the magnetic energy of a dipole in a magnetic field.

The *energy* of a dipole \boldsymbol{m} in a field \boldsymbol{H} is given by

$$E = -\boldsymbol{m} \cdot \boldsymbol{H}. \tag{3.15}$$

The units of energy are [V A s]. $1 \text{ V A s} = 1 \text{ J} = 0.624 \times 10^{19} \text{ eV}.$

To derive (3.15), one assumes a magnetic dipole as defined in Fig. 3.1, which is initially perpendicular to \boldsymbol{H} and is then turned into the direction of the magnetic field, as illustrated in Fig. 3.6. In doing so, one gains energy given by the force times length of the path travelled by the magnetic poles in the direction of the magnetic field. The forces are $\boldsymbol{F}^+ = p^+ \boldsymbol{H} = p \boldsymbol{H}$ and $\boldsymbol{F}^- = p^- \boldsymbol{H} = -p \boldsymbol{H}$ and by means of Fig. 3.6 we see that $\boldsymbol{H} \cdot d\boldsymbol{\ell} = H(d/2) \cos \phi \, d\phi$ and the energy gain is given by

$$E = 2 p \int \boldsymbol{H} \cdot d\boldsymbol{\ell} = p \, d \, H \int_{\pi/2}^{0} \cos \phi \, d\phi = -\boldsymbol{m} \cdot \boldsymbol{H} \; . \tag{3.16}$$

Here we have used the definition pd = m from Fig. 3.1. We see that the energy is a true scalar obtained by multiplying two axial vectors. A true scalar conserves parity. It is mandatory for the energy to be a true scalar.

Equation (3.15) shows that magnetic moments tend to align themselves parallel to the magnetic field. Thermal motion, on the other hand, tends to

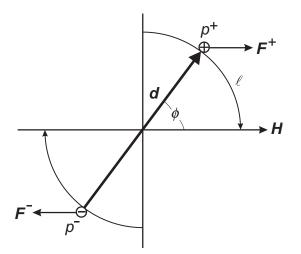


Fig. 3.6. A magnetic dipole m = pd initially perpendicular to the magnetic field direction is turned into its stable state parallel to the magnetic field. The energy gain is given by the forces $F^+ = p^+H = pH$ and $F^- = p^-H = -pH$ times the length of the path traveled by the poles p in the direction of the field. Note that the net force on the dipole is zero

destroy this alignment. This leads to an equilibrium magnetization that can be calculated with thermodynamics. This treatment is so common in all text books on solid state physics and magnetism that we shall for simplicity only treat the simple case s = 1/2 since it contains the important physics.

For a magnetic moment s=1/2 (in units of \hbar) there are only two levels corresponding to $s_z = \pm 1/2$. From (3.13) and (3.15) it follows that the energy levels in the magnetic field are $E = \pm \mu_{\rm B} H$. The saturation magnetization at T = 0 when all spins are aligned is $M(0) = N\mu_{\rm B}$ where N is the volume density of the spins. The Boltzmann factor e^x with $x = -\mu_{\rm B} H/k_{\rm B} T$ is proportional to the probability that the state with energy $\mu_{\rm B} H$ is occupied, where $k_{\rm B}$ is the Boltzmann constant. The magnetization of the two level system is then given by $e^x - e^{-x}$ divided by the sum of all probabilities which is $e^x + e^{-x}$. This yields the magnetization as a function of temperature T and magnetic field H, the so-called Brillouin function which for s = 1/2 is simply the tanh x function⁵

$$M(H,T) = N\mu_{\rm B} \frac{{\rm e}^x - {\rm e}^{-x}}{{\rm e}^x + {\rm e}^{-x}} = N\mu_{\rm B} \tanh(x) = M(0) \tanh(x) , \qquad (3.19)$$

The result (3.19), derived by L. Brillouin in 1927 assumes that the individual spins are quantized in two orientations $s_z = \pm 1/2$. An earlier theory derived by P. Langevin in 1905, based on a "macrospin" composed of classical magnetic moments with no direction quantization, yielded a quite similar function called the *Langevin function* $L(x) = \coth x - 1/x$ (see footnote 5 and Fig. 11.1).

Magnetic energies are generally small compared to the energy of thermal fluctuations. A moment of 1 $\mu_{\rm B}$ in a field of B = 1 T corresponding to $H = 7.96 \times 10^5$ A m⁻¹ yields a splitting between the spin up and the spin down levels of $2\mu_{\rm B}H = 1.86 \times 10^{-23}$ V A s $= 1.16 \times 10^{-4}$ eV. This splitting is about equal to the thermal energy at T = 1 K, since $1 \text{ eV}/k_{\rm B} = 1.16 \times 10^4$ K (see Appendix A.1). Therefore, $x \ll 1$ in most cases, and we can approximate e^{±x} by $1 \pm x$. This yields

$$M(H,T) = N\mu_{\rm B} x = \frac{N\mu_{\rm B}^2}{k_{\rm B}} \frac{H}{T} .$$
 (3.20)

⁵The general Brillouin function for angular momentum J is given by

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right).$$
(3.17)

For J = s = 1/2 one gets $B_{1/2}(x) = \tanh x$. In another limit $J \to \infty$ one obtains the Langevin function

$$B_{\infty}(x) = L(x) = \coth x - \frac{1}{x}.$$
 (3.18)

We recognize Pierre Curie's famous law for the temperature dependence of the magnetic susceptibility $\chi = M/\mu_0 H$,

$$\chi(T) = \frac{M(H,T)}{\mu_0 H} = \frac{N\mu_{\rm B}^2}{\mu_0 k_{\rm B}} \frac{1}{T} = \frac{\mu_{\rm B}}{\mu_0 k_{\rm B}} \frac{M(0)}{T} = \frac{C}{T}$$
(3.21)

where C is called the *Curie constant*, which in our case corresponds to s = 1/2. The Curie law is an approximation of the Brillouin function for small fields and/or large temperatures. Curie's law emerged from the study of the magnetization of oxygen gas. The oxygen molecule has a spin moment of $2\mu_{\rm B}$ generated by two parallel electron spins.

In the other limiting case $x \gg 1$, that is at low temperature or in high fields, we obtain from (3.19) $M = M(0) = N\mu_{\rm B}$. This "paramagnetic" saturation magnetization is reached asymptotically. Materials to which the theory applies are called *paramagnetic*.

In paramagnets the magnetization M(T) is generated by aligning preexisting magnetic dipoles in an external field. The average magnetization is always parallel to the field and varies with temperature as 1/T.

The condition for the applicability of the Brillouin function to a material is the absence of interactions between the magnetic moments. This applies in diluted systems. In cases where interactions exist, one may add an appropriately chosen effective field to the applied external field, as will be shown in Sect. 11.1.

Curie's law does not apply to the itinerant electrons in a metal. The magnetic susceptibility of the metal electrons is independent of temperature as explained later by W. Pauli in conjunction with the degeneracy of the Fermiongas as discussed in Sect. 15.3.

3.5 The Force on a Magnetic Dipole in an Inhomogeneous Field

Let us now consider a magnetic dipole in an inhomogeneous static magnetic field H(x, y, z). In general, the force F is given by the negative gradient of the energy

In general, the *force* on a dipole m in a field H is given by

$$\boldsymbol{F} = \nabla(\boldsymbol{m} \cdot \boldsymbol{H}). \tag{3.22}$$

The force F is a polar vector. It is the negative gradient of the energy and has units $[VAsm^{-1}]$, where $1VAsm^{-1} = 1N$.

We can expand the right side of (3.22) according to the gradient operator rules listed in Appendix A.2, and by assuming that the dipole is small we obtain

$$\boldsymbol{F} = (\boldsymbol{m} \cdot \nabla) \boldsymbol{H}. \tag{3.23}$$

As an example, let us consider the case illustrated in Fig. 3.7. We have an increasing magnetic field in the z direction of our coordinate system and, for simplicity, we have assumed that the magnetic dipole moment is already aligned along z. There is then a net force acting on the dipole to move it into the direction of the increasing field. According to (3.23) we have $\mathbf{F} = (\mathbf{m} \cdot \nabla) \mathbf{H}$ and neglecting the cylindrically symmetric force in the x-y plane which has no net effect on the dipole we have

$$F_z = (\boldsymbol{m} \cdot \boldsymbol{e}_z) \,\frac{\partial H_z}{\partial z} \,. \tag{3.24}$$

The same result is obtained from the simple argument presented in the caption of Fig. 3.7.

Generally it is helpful to remember that whenever a magnetic moment is parallel to the magnetic field such as is the case in paramagnetic materials where the magnetization is generated by alignment of preexisting magnetic moments, it experiences a force toward increasing field. Yet when the magnetization is antiparallel to the field such as in diamagnetic or superconducting materials, the force (3.22) pushes it toward the weaker field. The fact that the

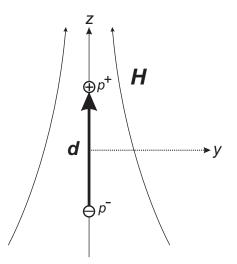


Fig. 3.7. A magnetic dipole is aligned in a cylindrically symmetric inhomogeneous magnetic field along the z-axis. Since any field gradient perpendicular to z is cylindrically symmetric, the net force on the dipole, to first order, is determined by the fact that the field at p^+ is larger compared to the one at p^- by $d(\Delta H_z/\Delta z)$. The resulting force on m = pd is $F_z = p d \Delta H_z/\Delta z = |\mathbf{m}| \Delta H_z/\Delta z$

magnetization induced in diamagnetic or superconducting materials is negative when a magnetic field is applied, arises from the minus sign in (5.3). Actually, paramagnetic materials always have a diamagnetic contribution to the susceptibility but it tends to be weaker compared to the paramagnetic part.

In the following sections we shall discuss three important examples where forces on magnetic moments play the key role.

3.5.1 The Stern–Gerlach Experiment

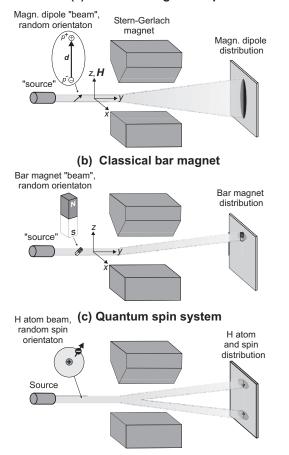
The discovery of the direction quantization of the magnetic moments in 1921 by Stern and Gerlach with an atomic beam of silver *atoms* is one of the important consequences of (3.22), yet it involves going beyond a classical picture. The experiment is probably the most beautiful early demonstration of the concept of quantization and it constitutes one of the foundations of modern magnetism, which is based on the concept of spin and its quantum mechanical behavior. It is for this reason that it is often used as an illustration of the counterintuitive quantum behavior of the spin, e.g., by Sakurai [126].

In the experiment, a beam of silver atoms was directed through an inhomogeneous magnetic field, in a geometry illustrated in Fig. 3.8, with the shown atomic H source replaced by a silver atom source. After the magnet, the beam hits a screen so that the deposited distribution of silver atoms could be directly observed. Ag has 47 electrons and the outer 5s electron is unpaired and gives rise to a spin-only magnetic moment. After inspection of the detector screen, two distinct spatially separated Ag spots were observed. The story of the discovery is nicely described in an article by Friedrich and Herschbach [15] from which the picture of the postcard in Fig. 1.3 is taken.

We shall now discuss the significance of this observation by comparing three hypothetical experiments. In one experiment we assume that the spin is a classical dipole, as pictured in Fig. 3.7. We shall see that the interaction of a classical dipole with the magnetic field cannot explain the observed result, which therefore demonstrates the breakdown of classical concepts. We shall also show how the experiment can be explained by the quantum mechanical description of the spin, which is counterintuitive yet underlies our modern thinking and description of the electron spin.

As illustrated in Fig. 3.8, we imagine that a source produces beams consisting of three kinds of magnetic "objects," either small classical dipoles, small bar magnets, or hydrogen atoms which contain a single electron with an unpaired spin. We have designed our "Gedanken" experiments to bring out the difference in behavior of all three objects as they traverse the Stern–Gerlach (SG) magnet. The beams are directed along the y direction and the magnetic field and its gradient are along the z direction, as in Fig. 3.7.

The case of *classical magnetic dipoles* is shown in Fig. 3.8a. We assume that the dipoles are the idealized objects shown in Fig. 3.7 so that the force exerted by the magnetic field is given by (3.24). Because of the necessity to conserve energy and angular momentum, the idealized dipoles cannot



(a) Fictitious magnetic dipole

Fig. 3.8. Illustration of the quantum behavior of the electron spin. We consider a Stern-Gerlach experimental arrangement consisting of a source, a gradient magnet that produces a force on a magnetic object along z as in Fig. 3.7, and a detector screen where the arriving objects produce a characteristic intensity distribution. In (a) we consider a collimated "beam" of fictitious dipoles (see Fig. 3.7) with random orientation relative to the field direction z. When this beam traverses the gradient magnet, the force on the individual dipoles depends on their orientation according to (3.24), resulting in a beam intensity on the detector screen that resembles a vertical line. In (b) we imagine a beam of bar magnets. These objects behave differently from the classical dipoles in (a) because frictional torque associated with the precession of the magnetization inside the physical body of the bar leads to the rotation of the bar into the field direction so that all bars are deflected into the same direction. In (c) we consider a simple atomic beam of H atoms which are charge neutral but have a single spin per atom which we assume to be randomly oriented. In accordance with the original Stern–Gerlach experiment the quantum behavior of the spin results in two spots on the detector screen corresponding to H atoms with spins parallel and antiparallel to z. Because of the opposite direction of m and s, the antiparallel "down" spins are deflected upward as shown

change their orientation relative to the magnetic field as this corresponds to a change of angular momentum and of energy. The classical force acting on the magnetic dipole, given by (3.24), is directed along the z-axis and varies as $F = |\mathbf{m}| \cos \theta (\partial H_z / \partial z)$ with the angle θ between \mathbf{m} and the z-axis. Thus the intensity distribution on the detector screen lies along a continuous line between the maximum beam deflections determined by the force maxima $F = \pm |\mathbf{m}| (\partial H_z / \partial z).$

In Fig. 3.8b we replace the ideal dipoles by real small bar magnets with a magnetic material with magnetization M connected to their physical barshaped body. Such real magnetic bodies, even if consisting of only few atoms, possess a large number of vibrational and rotational modes. These modes couple to the magnetization and thus can accept energy and angular momentum from a change of the direction of the magnetic moment of the particle. As mentioned in Sect. 3.3 and discussed in more detail in Sect. 3.6, for real magnets like a compass needle, one has to consider the action of two torques in addition to the force (3.24). We know by experience that the compass needle turns into the field direction as shown in Fig. 3.2. Thus if we assume that the little bar magnets quickly turn into the field direction as they enter the Stern–Gerlach magnet, the force $\mathbf{F} = \mathbf{m}(\partial H_z/\partial z)$ will bend the beam upward, resulting in a single spot on the detector screen.

The observed intensity distribution on the detector screen actually depends on the time it takes the bar magnets to turn into the field direction relative to their flight time through the SG magnet. The detailed process will be discussed in Sect. 3.6 below and goes as follows. The precessional torque acting on the magnetization, causes M to precess at a constant angle about the average field direction $H \parallel z$. The change in angular momentum associated with the precession of M relative to the field H is absorbed by the SG magnet as a whole. The precessional motion of M relative to the physical body of the bar induces a frictional or damping torque which causes M to rotate into the field direction $H \parallel z$. This process is accompanied by a change in energy and angular momentum which needs to be dissipated. When it is passed to the lattice of the bar magnet (on a timescale of several hundred picoseconds), the whole body of the bar responds. If the angular momentum and energy cannot be passed on further from the body to the environment, e.g., when the experiment is conducted in vacuum, the torque passed from the magnetization to the magnet body will cause the body to perform complicated motions (nutations). If the body can transfer energy to the environment, e.g., to the surrounding gas, the body will physically align itself with the magnetization.

The difference between the ideal dipole and the bar magnet therefore lies entirely in the frictional torque and the associated damping time of the magnetization (not the body). If the damping time of the magnetization is long compared to the beam transit time through the SG magnet, the bar magnet will *not* turn into the field direction while traversing the SG magnet. The pattern on the detector screen will then be a line as for the ideal dipole in Fig. 3.8a. If the damping time is much shorter than the flight time, which is more typical, we will observe the intensity distribution in Fig. 3.8b. This experiment has actually been done with tiny bar magnets consisting of clusters of 5–1,000 atoms of Ni, Co, and Fe [127, 128], and results are shown in Fig. 3.9. The clusters exhibit ferromagnetic ordering of the spin moments and therefore each cluster has a large magnetic moment depending on the number of atoms, but the orientation of that moment fluctuates on the 10^{-9} s time scale. This is possible in those cases where the moment is only weakly attached to the cluster atomic lattice. Thermal agitation from the cluster vibrational modes causes the moment to explore all possible orientations during the several hundred μ s the cluster spends in the SG-magnet. The average magnetic moment along the magnetic field direction in the SG-magnet is then responsible for the deflection of the cluster according to (3.24). The average moment is related to the total magnetic moment by the Langevin

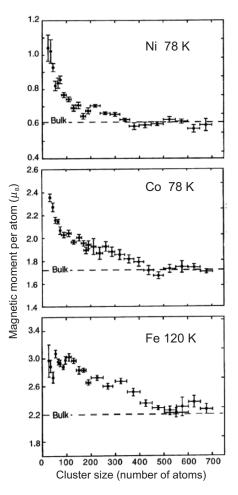


Fig. 3.9. Magnetic moment per atom of small transition metal clusters in a low-temperature molecular beam measured in a Stern–Gerlach apparatus [127]. Small clusters have larger, more atomic like, magnetic moments

function given by (3.18). It can therefore be determined from the observed deflection of the cluster beam.

In the determination of the magnetic moments of the clusters shown in Fig. 3.9 it was assumed that the intensity distribution in Fig. 3.8b is applicable. The derived result is that the smaller the number of atoms in a cluster, the more the magnetic moment per atom approaches the large value of the free atom. Only with clusters containing about 700 atoms, the magnetic moment per atom settles to the reduced value observed in bulk Ni, Co, and Fe, as shown in Fig. 3.9. However, Bennemann and coworkers [129] have shown that this simple picture does not hold under all conditions. The anisotropy field introduced in Sect. 11.2 is attached to the rotating atomic lattice of the cluster. It acts on the cluster magnetization like an oscillating magnetic field. This can induce resonant transitions of the magnetization with respect to the magnetic field direction. The strength of the anisotropy field and the relaxation time are thus important variables that determine the magnetic behavior of the clusters in the SG-experiment. It often lies in between case (a) and case (b).

The effect on the *spin* is illustrated by the simple case of a H atom beam in Fig. 3.8c. The experiment was actually performed by Phipps and Taylor in 1927 [130]. The simplicity is due to the fact that the H atom in vacuum has no degrees of freedom to absorb the energy or angular momentum that is connected with a change of the direction of the magnetic moment. Hence, due to the conservation laws, it has to remain in the state in which it entered the SG-magnet. The positively charged H nucleus renders the atoms charge-neutral, so that the magnetic field acts only on the spin. The H atom distribution on the detector screen consists of only two spots, as for the actual SG experiment with neutral Ag atoms. This result is obviously at odds with classical expectations based on either of the experiments in Fig. 3.8a, b.

The fascinating result requires a new quantum mechanical concept, the Pauli spinor formalism, discussed in more detail in Sect. 8.4.2, that can be stated as follows.⁶

The quantum mechanical superposition principle describes a spin s, oriented at an arbitrary angle relative to a magnetic field H that defines the quantization axis, as a coherent superposition of two partial waves with spin parallel ("spin up" \uparrow) and antiparallel ("spin down" \downarrow) to H. A general spin wavefunction has the form,

$$\chi = u_1 |+\rangle + u_2 |-\rangle = u_1 |\uparrow\rangle + u_2 |\downarrow\rangle , \qquad (3.25)$$

where u_1 and u_2 are complex numbers with $|u_1|^2 + |u_2|^2 = 1$.

 $^{^{6}}$ More generally, the superposition principle states that if two states have the same energy then a general state with that energy can be written as a linear superposition of the two states.

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Thus an electron with arbitrary spin orientation relative to the quantization axis has a probability $u_1u_1^*$ to be in the "spin up" $|+\rangle = |\uparrow\rangle$ state and a probability $u_2u_2^*$ to be in the "spin down" $|-\rangle = |\downarrow\rangle$ state. For the special case that the spin is oriented perpendicular to z we have $|u_1| = |u_2| = 1/\sqrt{2}$ (see Fig. 8.3 below).

Like the magnetic dipoles, the H atoms with magnetic moments \boldsymbol{m} along +z are deflected into the +z direction of increasing field strength by the force $F = +|\boldsymbol{m}|\partial H_z/\partial z$ while the atoms with magnetic moments along -z are deflected toward the weaker field direction -z by the force $F = -|\boldsymbol{m}|\partial H_z/\partial z$. In contrast to the classical magnetic dipole case, however, atoms with magnetic moments perpendicular to z, must be thought of as consisting of two quantum components, parallel and antiparallel to z. They therefore do not go straight through the field without deflection but have a 50% probability of being deflected in either of two directions $\pm z$ by forces $F = \pm 2\mu_{\rm B}s_z(\partial H_z/\partial z)$. On average, they therefore contribute equally to the two discrete intensity spots observed. In general, all atoms with finite angles θ of their spins relative to z contribute to both spots, with the relative contributions $u_1u_1^*$ and $u_2u_2^*$ determined by θ (see Sect. 8.4).

3.5.2 The Mott Detector

Unfortunately, it is not possible to separate the two spin states of a free electron in the same way, as discussed in detail by Kessler [131]. This is due to the fact that electrons unlike the neutral silver atoms carry a charge and therefore experience a Lorentz force, given by (4.10). For typical low-gradient macroscopic magnetic fields the Lorentz force is many orders of magnitude larger then the force on the magnetic moment given by (3.22). Therefore, according to this reasoning, known as Bohr's argument, it is not possible to spatially separate the two spin states of the *free* electron in a macroscopic magnetic field. In Bohr's days some people thought that this excludes the existence of free spin-polarized electrons.

Mott recognized that this means that classical mechanics cannot describe the motion of a free electron. Instead, he suggested to separate the two spin states by scattering the free electron on the Coulomb field of heavy atoms [132]. This is often referred to as spin–orbit coupling in elastic Coulomb scattering. To this day, "Mott scattering" is still mostly used to measure the spin polarization of an electron beam. It is also an instructive example of the effect of the force on the magnetic moment of the free electron and we shall discuss it below.

In the original concept of Mott scattering, one prepares an electron beam of fairly high energy of a few hundred keV. The de Broglie wavelength is then rather small and one can assume classical electron trajectories. As a scattering center, we first consider an atom with a high nuclear charge, in actual practice mostly a gold atom. The scattering electron penetrates deep into the Coulomb field of the atom. In the rest system of the electron, the

atom moves toward the electron. When the electron is inside the atom the atomic charge is dominated by the positive nuclear charge. In the rest frame of the electron, the moving electric field generates a magnetic field as discussed in Sect. 4.2.2 and the magnetic field lines are circular according to Sect. 2.3. The magnetic field is inhomogeneous, it becomes weaker as the distance to the atomic nucleus increases. The large magnetic field gradient exercises a sizeable force on the magnetic moment of the electron. This force is superimposed onto the Coulomb force acting on the charge of the electron.

If the magnetic moment is "up" and if the electron passes on the right side of the atom, magnetic field and magnetic moment are parallel and the force given by (3.22) pushes the electron toward increasing field, that is toward the left, as illustrated in Fig. 3.10. If the electron passes on the left side of the atom, magnetic field and magnetic moment are antiparallel and the force (3.22) pushes the electron toward the weaker field, that is toward the left, as well. Altogether, an electron with magnetic moment "up" with respect to the scattering plane is then preferentially scattered to the left, and an electron with magnetic moment "down" is preferentially scattered to the right. The scattering plane in this elastic scattering is defined by the linear momentum

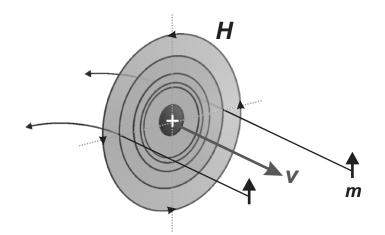


Fig. 3.10. Illustration how spin-orbit coupling in elastic Coulomb scattering can spatially separate the two spin states: The electron with its magnetic moment up is incident on an atom whose projection perpendicular to the incidence direction is shown. In the rest system of the electron, the positive charge of the atomic nucleus moves toward it with a velocity v. This is equivalent to an electric current with circular magnetic field lines as shown. The force F on the magnetic moment of the electron is directed toward increasing field when the moment is parallel to the field (*right*), but toward decreasing field when it is antiparallel (*left*). If m and H are perpendicular the force is zero. In this way, the magnetic moment of the electron experiences a force toward the left when it is aligned upward no matter on which side of the atom it passes. In contrast, electrons with magnetic moment "down" are preferentially scattered to the right in our figure

p of the incident electron and the momentum p' of the electron scattered by the scattering angle θ . The product $p \times p'$ is an axial vector perpendicular to the scattering plane. This is the reason why one can determine the direction of the axial magnetic moment by scattering on a polar electric field as long as the moment has a component perpendicular to the scattering plane.

Figure 3.11 sketches an experimental setup that can be used to determine the degree of spin polarization P_{\perp} of an electron beam perpendicular to the scattering plane. As discussed in Sect. 8.4.3 below, the *degree of spin polarization* is given by

$$P_{\perp} = \frac{n^{\uparrow} - n^{\downarrow}}{n^{\uparrow} + n^{\downarrow}} . \tag{3.26}$$

Here n^{\uparrow} and n^{\downarrow} are the numbers of electrons in the beam with spin up and down, respectively. The beam hits a very thin gold foil so that one mainly has scattering on a single gold atom. Two detectors at exactly the same scattering angle θ to the right and to the left count the number of scattered electrons. If the electron spin (antiparallel to the magnetic moment) has a preferred projection onto the normal of the scattering plane, i.e., points below or above the plane shown in Fig. 3.11, one counter will count more electrons than the other. According to (8.32), the scattering asymmetry is given by

$$A = \frac{I^{\text{right}} - I^{\text{left}}}{I^{\text{right}} + I^{\text{left}}} , \qquad (3.27)$$

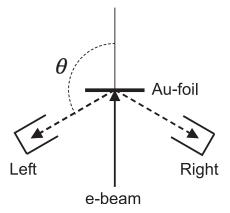


Fig. 3.11. Experimental setup to measure the scattering asymmetry A caused by the spin polarization of an electron beam. The electrons elastically scattered into the scattering angle θ to the right and to the left are measured. If the spins of the electrons in the incident beam are polarized perpendicular to the scattering plane, a scattering asymmetry occurs which is proportional to the degree of spin polarization P_{\perp} .

where I^{right} and I^{left} are the currents of electrons scattered to the right and to the left, respectively. The asymmetry A is proportional to the degree of spin polarization P_{\perp} according to $A = SP_{\perp}$. The Sherman function $S(\theta, E)$ has been calculated in the central field approximation and is as large as 0.4 at E = 150 keV and $\theta \sim 120^{\circ}$ in the case of a gold-atom [133].

Originally it was thought that one needed relativistic electron energies to obtain large asymmetries. This turned out not to be the case. In fact, close to complete spatial separation of the spins is obtained in scattering on gold atoms at $E \simeq 100 \,\text{eV}$. The reason is that at these electron energies, the de Broglie wavelength is of the order of the diameter of the atom and one obtains a diffraction pattern where the scattered intensity can be close to zero at certain scattering angles. The zero intercept occurs at different θ values for the two spin states because the electron penetrates deep enough into the gold atom to become relativistic [134]. Hence close to the destructive interference experienced by one spin state, the other one still has a sizeable scattering probability. An additional advantage occurs due to the fact that at these low energies, the scattered electrons stem mostly from the first atomic layer of the solid gold target, and the scattered intensity is given in good approximation by the superposition of the intensity scattered from single atoms. Hence it is sufficient, for example, to let electrons of $150 \, \text{eV}$ energy impinge normal to the surface of an amorphous gold film and measure the intensity of the elastic diffuse scattering to the right and to the left in order to determine the degree of spin polarization perpendicular to the scattering plane. The characteristic of such low-energy spin-polarized scattering from atoms is the occurrence of rapid changes of the Sherman function S = A/P from positive to negative values close to the scattering angles where the intensity is small (Fig. 3.12). To detect the spin polarization, low-energy scattering is applied in spin-resolved photoemission and in secondary electron microscopy with spin polarization analysis (SEMPA) [68]. In practice, one still uses the more robust high energy Mott scattering in many applications.

However, substantially better detection schemes for the spin polarization are on the horizon based on the ferromagnetic exchange interaction of the electrons in magnetic materials. It will be shown in Chaps. 8 and 12 that these interactions provide excellent spin filters in transmission of polarized electrons [135, 136] and also generate energy gaps in the electronic structure which are responsible for spin-dependent reflection of electrons from a magnetic surface or interface. The spin-dependent reflection is already used in spin polarized low energy electron microscopy (SPLEEM), where spin-polarized electrons from a GaAs-type photocathode are reflected at low kinetic energy from the magnetic surface yielding dynamic information on magnetic processes at surfaces at video frequencies and at ~10 nm spatial resolution [74]. The high speed in conjunction with good spatial resolution achieved in SPLEEM proves that *exchange scattering* used in elastic reflection from a magnetic surface is a more

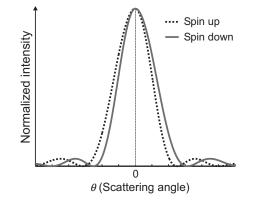


Fig. 3.12. Schematic diffraction pattern as observed in electron scattering from atoms at low electron energies of ~100 eV. The scattered intensity is plotted versus the scattering angle θ . At some θ the interference is destructive and no electrons are scattered but due to spin–orbit coupling, the zeros occur at different θ for the two spin states. In this way, separation of the two spin states can occur with characteristic rapid changes of the sign of the Sherman function $S(\theta, E) = A/P$ as θ varies

efficient way to spatially separate the spin states compared to the *spin-orbit* scattering utilized in Mott detectors. An example for the spin asymmetries in reflection of electrons from an Fe surface is given in Fig. 13.11.

3.5.3 Magnetic Force Microscopy

Another application of (3.22) is magnetic force microscopy (MFM). A very fine tip is prepared from a ferromagnetic metal such as cobalt. For the magnetic moment of the fine tip the approximation of the "macrospin" may be valid, meaning that all the magnetic moments of the electrons in the tip are tightly coupled to form one giant magnetic moment fixed in its direction along the tip axis. This magnetic moment experiences an attractive or repulsive force in an inhomogeneous magnetic field depending on whether it has a component parallel or antiparallel to the field, respectively. Hence the measurement of the force allows one to determine the gradient of H as it depends for instance on location above the surface of a magnetic medium. Since the tip can be made quite fine, of the order of few nanometers, the spatial resolution of magnetic force microscopy is high enough to detect the stray fields above the magnetic bits of 40 nm width, written into the magnetic medium of the hard disks of computers, as shown in Fig. 3.13. The magnetic force that can be detected is amazingly small: It has recently been shown that one must flip only one single electron spin to produce an observable change of the force on a magnetic tip [137].

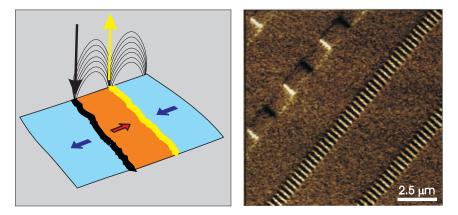


Fig. 3.13. Magnetic recording bits with alternating in-plane magnetization, shown on the *left*, give rise to strong out-of-plane magnetic field gradients near the transition regions, as shown. The field direction depends on the orientation of the magnetization in the adjacent bits. On the *right* is shown a magnetic force microscope image of such a bit pattern. The pattern in the upper left has a transition density of 500 transitions per mm, the pattern on the lower right has a density of 5,000 transitions per mm (the shown track corresponds to an areal density of 3 Gbits inch⁻²) (courtesy of A. Moser, Hitachi Global Storage Technologies)

3.6 The Torque on a Magnetic Moment in a Magnetic Field

If the magnetic field is homogeneous, it has the same magnitude at the location of the poles p^+ and p^- of a magnetic dipole, as shown in Fig. 3.6. Hence it exerts an equal but opposite force $\mathbf{F} = p \mathbf{H}$ on each magnetic pole. The net force is then zero. However, the dipole experiences a torque \mathbf{T} .

The torque on a dipole m in a field H is given by

$$T = m \times H . \tag{3.28}$$

T is an axial vector perpendicular to m and H and has the units [VAs] of energy.

The derivation of the above torque equation for the magnetic moment in a field follows from Fig. 3.6, by use of the definition of the mechanical torque caused by a force F acting on a lever r,

$$\boldsymbol{T} = \boldsymbol{r} \times \boldsymbol{F}.\tag{3.29}$$

The torque causes the vector of the angular momentum L to move according to Newton's classical equation of motion dL/dt = T. By use of (3.28) we obtain

$$\frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t} = \boldsymbol{T} = \boldsymbol{m} \times \boldsymbol{H}. \tag{3.30}$$

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3.6.1 Precession of Moments

Historically the relationship between the magnetic moment \boldsymbol{m} and angular momentum \boldsymbol{L} that appear in (3.30) is written in terms of the gyromagnetic ratio γ , according to $\boldsymbol{m} = \gamma \boldsymbol{L}$, where \boldsymbol{L} is given in units of VAs² and $\gamma = qg\mu_0/2m_{\rm e}$. The sign of γ depends on the charge q of the particle. We have seen before in (3.9) that for an electron \boldsymbol{m} and \boldsymbol{L} have opposite signs and therefore $\gamma = -eg\mu_0/2m_{\rm e}$ is negative in this case. By substituting $\boldsymbol{m} = \gamma \boldsymbol{L}$ in (3.30) we obtain an important equation.

The equation of motion of a magnetic moment \boldsymbol{m} in a field \boldsymbol{H} is given by

$$\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\,\boldsymbol{m} \times \boldsymbol{H} \, \right] = \gamma \,\boldsymbol{T} \,\,. \tag{3.31}$$

 $\gamma = qg\mu_0/2m_e$ is the gyromagnetic ratio which is negative for an electron with charge q = -e. This leads to the Larmor precession of \boldsymbol{m} about the magnetic field \boldsymbol{H} at the angular frequency $\omega = -\gamma H$.

It is not difficult to derive the Larmor precession frequency. According to (3.31), the change $d\boldsymbol{m}$ of the magnetic moment is perpendicular to both \boldsymbol{m} and \boldsymbol{H} . Therefore, \boldsymbol{m} can only precess around \boldsymbol{H} . If m_{\perp} is the component of \boldsymbol{m} perpendicular to \boldsymbol{H} , than $d\boldsymbol{m} = m_{\perp} d\varphi$ where $d\varphi$ is the angle by which \boldsymbol{m} precesses in the time interval dt. This yields $d\boldsymbol{m}/dt = \omega m_{\perp}$. From (3.31), $d\boldsymbol{m}/dt = \gamma m_{\perp} H$ yielding $\omega = \gamma H$. Figure 3.14 shows the precession of the magnetic moment of an electron about the field direction.

The motion of m is in agreement with the conservation of angular momentum. Because of Newton's law *actio* = *reactio*, the torque acting on m acts with the opposite sign on the source of the magnetic field and, in principle, sets it in opposite rotation so that the total angular momentum is conserved.

It is remarkable that the precession frequency ω does not depend on the angle between the magnetic moment and the magnetic field. This means that ω is independent of the component m_{\perp} of the magnetic moment perpendicular to the axis of precession and explains why quantum mechanics delivers the same result for the Larmor frequency as the classical approach. In quantum mechanics, the component of the magnetic moment perpendicular to the axis of quantization remains undetermined, yet whatever its value may be, it precesses with ω .

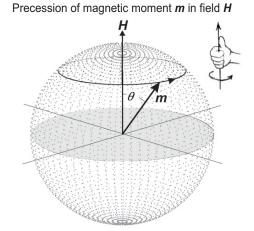


Fig. 3.14. The magnetic moment m of an electron precesses about a field H with the *Larmor frequency* $\omega = -\gamma H$, as derived from the torque (3.31). The gyromagnetic ratio γ is negative for an electron and this determines the precession direction according to the right hand rule as shown. The torque vanishes when m and H are parallel and it is largest when the two vectors are perpendicular. Note that ω is independent of the angle θ enclosed by H and m

It is important to note that the angle θ between H and m does not change in the precession, hence the energy $E = -m \cdot H = -mH \cos \theta$ is constant and not at a minimum. Obviously, this contradicts experience since we know that magnetic moments do turn into the field direction when given sufficient time. Changing θ and thus the energy of the dipole requires an additional torque that precesses at the same rate as the magnetization. We shall see below that this additional torque arises from damping or friction.

The Larmor precession frequency of the spin moments in magnetic fields typically present in ferromagnets sets the time scale for magnetization dynamics. According to Sect. 2.6, the relevant demagnetization fields are of the order of $\mu_0 H \sim M$, that is of the order of 1 T. For an electron we have g = 2 and $\gamma = -e\mu_0/m_{\rm e}$ so that the spin precession frequency is $\omega = -\gamma H = (e/m_{\rm e})B$. It can be shown that the relationship between the angular velocity vector $\boldsymbol{\omega}$ and the field \boldsymbol{B} is a true vector equation [118]. If we move the direction of \boldsymbol{B} the direction of $\boldsymbol{\omega}$ moves with it to keep it parallel to \boldsymbol{B} .

The angular velocity $\boldsymbol{\omega}$ of a precessing spin in a field \boldsymbol{B} is given by $\boldsymbol{\omega} = \frac{e}{2} \boldsymbol{B} \qquad (3.32)$

$$\sigma = \frac{1}{m_{\rm e}} B \ . \tag{3.32}$$

 $\boldsymbol{\omega}$ is an axial vector. We have

$$\frac{\omega}{B} = 1.759 \times 10^{11} \,\mathrm{rad} \,\mathrm{T}^{-1} \mathrm{s}^{-1}. \tag{3.33}$$

In a field of 1 T an electron spin makes one full precession in 36 ps.

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Since in a 1 T field the spin precesses by $1 \operatorname{rad} = 360^{\circ}/2\pi = 57.3^{\circ}$ in 5.7 ps it is convenient to remember that it takes about 10 ps for a 90° spin precession, which is required for initiating a switch of the magnetization into the opposite direction. We see that the magnetization dynamics in ferromagnets caused by typical external fields occurs on the tens of picosecond time scale. With the advent of spectroscopic techniques to measure the magnetization in a time as short as $\sim 10^{-12}$ s, the precession can now be directly imaged in the time domain as discussed in Chap. 15.

3.6.2 Damping of the Precession

Experience tells us that the magnetic moment eventually moves into the field direction. This fact underlies the earliest magnetic device, the compass. We have seen that the precessional torque $T = m \times H$ cannot accomplish this as it is perpendicular to H. As illustrated in Fig. 3.15 an additional torque $T_{\rm D}$ must be introduced which is perpendicular to the precessional torque and perpendicular to m. We shall call $T_{\rm D}$ the damping torque.

From Fig. 3.15 we see that we can write

$$T_{\rm D} = C \left[\boldsymbol{m} \times \frac{\mathrm{d} \boldsymbol{m}}{\mathrm{d} t} \right].$$
 (3.34)

The constant of proportionality C is purely phenomenological, analogous to the friction coefficient for a linear motion. According to Fig. 3.15 $T_{\rm D}$ causes a rotation toward the +z axis for positive C. It describes unspecified dissipative phenomena in a material whose exact nature remains an intriguing topic of magnetism research. As expected for a dissipative phenomenon the torque $T_{\rm D}$ changes sign when time is inverted in contrast to the precessional torque

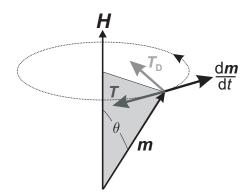


Fig. 3.15. The precessional torque T and the damping torque $T_{\rm D}$ acting on the precessing m. The precessional torque $T = (1/\gamma) \, \mathrm{d}m/\mathrm{d}t$ causes m to precess into the direction $\mathrm{d}m/\mathrm{d}t$ since γ is negative, and the damping torque $T_{\rm D} = (\alpha/m)[m \times \mathrm{d}m/\mathrm{d}t]$ turns m into the direction of H for a positive damping parameter α . The motion is depicted in Fig. 3.16 as calculated from the Landau–Lifshitz–Gilbert equation (3.39) inserting $\alpha = +0.15$.

 $T = m \times H$ which is invariant with time reversal. We have the following important fact.

The damping torque $T_{\rm D}$ causes the motion of m to become irreversible.

A realistic equation of motion for m is the Landau–Lifshitz (LL) equation

$$\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha \gamma}{m} \left[\boldsymbol{m} \times (\boldsymbol{m} \times \boldsymbol{H})\right], \qquad (3.35)$$

where $m = |\mathbf{m}|$. A modified version of the LL equation, the so-called Landau–Lifshitz–Gilbert (LLG) equation, is often used. It reads

$$(1+\alpha^2)\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha\gamma}{m} \left[\boldsymbol{m} \times (\boldsymbol{m} \times \boldsymbol{H})\right], \qquad (3.36)$$

and hence contains another term $(1 + \alpha^2)$ which is negligible for small α . The LLG equation is typically written in a slightly different form that is equivalent to (3.36).⁷

The Landau–Lifshitz–Gilbert (LLG) equation is given by $d\boldsymbol{m} \qquad \boldsymbol{\alpha} \begin{bmatrix} & d\boldsymbol{m} \end{bmatrix}$

$$\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha}{m} \left[\boldsymbol{m} \times \frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t}\right] \,. \tag{3.39}$$

The phenomenological constant α , the so-called *damping parameter*, stands for unspecified dissipative phenomena.

The first term describes the precession of \boldsymbol{m} at a fixed angle θ about the magnetic field direction \boldsymbol{H} , as illustrated in Figs. 3.14 and 3.15 due to the torque $\boldsymbol{T} = \boldsymbol{m} \times \boldsymbol{H}$ into the direction $d\boldsymbol{m}/dt = \gamma \boldsymbol{T}$ (note γ is negative for an electron). The second term describes the change of \boldsymbol{m} due to the damping torque $\boldsymbol{T}_{\rm D}$, causing \boldsymbol{m} to turn toward the direction of \boldsymbol{H} for a positive value of α , as shown in Fig. 3.15. Solving the LL- or the LLG-equation shows how \boldsymbol{m} spirals into the magnetic field direction as depicted in Fig. 3.16.

⁷To prove the equivalence of (3.39) and (3.36) we start from (3.39) and insert for the last term the entire expression for dm/dt to obtain

$$\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha}{m} \left[\boldsymbol{m} \times \left(\gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha}{m} \left[\boldsymbol{m} \times \frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t}\right]\right)\right] .$$
(3.37)

By use of the cross product rules in Appendix A.2 we get

$$\frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \gamma \left[\boldsymbol{m} \times \boldsymbol{H}\right] + \frac{\alpha \gamma}{m} \left[\boldsymbol{m} \times \left(\boldsymbol{m} \times \boldsymbol{H}\right)\right] - \alpha^2 \frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} , \qquad (3.38)$$

which is the same as (3.36).

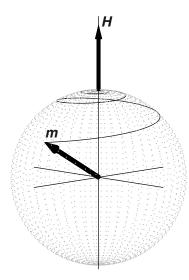


Fig. 3.16. Precessional motion of the magnetic moment \boldsymbol{m} according to (3.39) with a positive damping parameter $\alpha = +0.15$. \boldsymbol{m} spirals into the direction of the field \boldsymbol{H} at which point both the precessional torque and the damping torque vanish

The damping may be thought of as being generated by an effective magnetic field $\mathbf{H}_{\rm eff} \propto \mathrm{d}\mathbf{m}/\mathrm{d}t$. Induction currents indeed create a magnetic field varying with the frequency of the precessing magnetization \mathbf{m} but in nanoscopic materials and thin films they cannot contribute to the damping torque $\mathbf{T}_{\rm D}$ [138]. Therefore different mechanisms than electromagnetic induction must be active in thin films to explain the observed damping. As shown in Fig. 3.16, during the damping process the magnetization spirals into the field direction and this process corresponds to a change in angular momentum. Angular momentum must be transferred to another reservoir. These processes will be discussed in detail in Sect. 15.2.2. We shall see that initially angular momentum may be transferred within the spin system itself by excitation of spin waves (see Sect. 11.1.5), but ultimately the angular momentum is transferred to the lattice.

The LL and LLG equations describe the motion of a magnetic moment \boldsymbol{m} with a constant absolute value $|\boldsymbol{m}|$, so that the endpoint of \boldsymbol{m} moves on a sphere as shown in Fig. 3.16. When the formalism is applied to the description of the magnetization \boldsymbol{M} of a magnetic body one therefore implicitly assumes that the magnetization of the body $\boldsymbol{M} = \boldsymbol{m}/V$, where V is the volume containing \boldsymbol{m} , remains constant in magnitude. This assumption constitutes the "macrospin approximation" as discussed in Sect. 3.3, in which the individual spins in the entire volume of the body, $V_{\rm B}$, are strongly coupled parallel to each other to form the "macrospin" or "macromoment" $\boldsymbol{m}_{\rm ms} = V_{\rm B}\boldsymbol{M}$. We shall later see in Chap. 15 that this assumption may break down in certain cases, e.g., when the individual spins dephase in the course of an excitation, and thus the magnitude $|\boldsymbol{m}_{\rm ms}|$ changes in time. In such cases, the basic assumption of the LLG equation is not fulfilled and it cannot be used. Instead, one

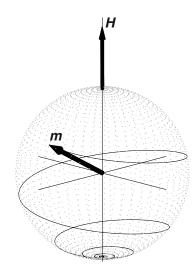


Fig. 3.17. Precessional motion of the magnetic moment \boldsymbol{m} according to (3.39) with a negative damping parameter $\alpha = -0.15$. \boldsymbol{m} spirals away from the direction of the field \boldsymbol{H} into a final position opposite to \boldsymbol{H} thereby gaining energy

might be able to use the phenomenological Bloch-equations discussed briefly in Sect. 3.6.3 below. We therefore need to keep in mind the following fact.

The LL and the LLG equations describe the temporal evolution of a magnetic moment \boldsymbol{m} or magnetization $\boldsymbol{M} = \boldsymbol{m}/V$, assuming that the magnitudes $|\boldsymbol{m}|$ or $|\boldsymbol{M}|$ remain constant in time.

In 1996 John Slonczewski [84] and Luc Berger [85] independently proposed that the damping torque may have a *negative* sign as well, corresponding to a negative sign of α . Under this condition, m moves into a final position antiparallel to H as illustrated in Fig. 3.17.

The seemingly bizarre negative damping is familiar in mechanics with special spinning tops having a low lying center of gravity. Due to the friction on their support, these "tippe" tops flip their angular momentum by π . Figure 3.18 shows that the motion of a "tippe" top fascinated even some of the great minds of physics.

In magnetism, the negative damping phenomenon is highly welcome since it allows one to switch the magnetization. Clearly, energy has to be supplied to achieve the motion of m in which the angle θ between m and H is enlarged. This energy is thought to be provided by injecting spin-polarized electrons from an adjacent ferromagnet, magnetized in the opposite direction compared to the magnetic material under consideration. The injected electrons are then minority spins and therefore at higher energy than the average electron. If their spin polarization is conserved, they will add to the magnetization component antiparallel to H thus effectively enlarging θ .

In fact, a number of experiments have already demonstrated the existence of spin switching as discussed in the later Sects. 14.2 and 15.6.3. It can happen



Fig. 3.18. Wolfgang Pauli (*left*) and Niels Bohr marvel at the motion and eventual upside-down flip of a "tippe" top

only in nanosized contacts supporting high current densities and in magnetic samples that are not thicker than the spin relaxation length, which is typically a few nanometers only. This shows that spin switching is a topic confined to magnetism in nanoscopic samples and therefore naturally supports the technological quest for smaller devices and faster switching.

Pulsed magneto-optics in the visible and X-ray energy range offers the possibility to directly observe the motion of m. X-rays offer the advantage of higher spatial resolution and are able to probe nanoscale phenomena. Once X-ray methods are fully developed, one can expect great progress in the understanding of the damping torque. Studies addressing the motion of m are discussed in detail in Chap. 15.

3.6.3 Magnetic Resonance

Historically, the dynamics associated with the motion of m in an external magnetic field has been thoroughly studied by means of magnetic resonance techniques. The fields and torques underlying a magnetic resonance experiment are illustrated in Fig. 3.19. A strong static field H causes the magnetic moment to precess, and a weaker field H' that rotates in a plane perpendicular to H is used to keep the precession angle θ constant. The field H' therefore

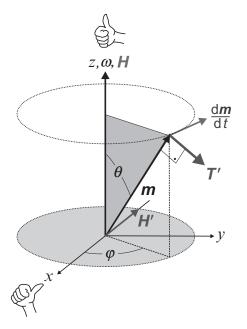


Fig. 3.19. Fields and torques in magnetic resonance for the case of an electron spin. A constant field $H \parallel z \ (\mu_0 H \simeq 1 \text{ T})$ causes the magnetic moment m to precess about z according to the right hand rule (3.31), with dm/dt parallel to the x-y plane. A weaker magnetic field $H' \perp m \ (\mu_0 H \simeq 10^{-4} \text{ T})$ in the x-y plane rotates at the same Larmor frequency as m and generates a torque T' on m according to the right hand rule. The resonance condition consists of balancing the characteristic damping torque and energy of the sample, driving m toward H, by the torque T' and energy, generated by the external field H', which drive m away from H. This balance keeps m at a fixed small angle $\theta \sim 1^\circ$. In practice one changes the static magnetic field strength H until maximum absorption of energy occurs from the microwave field H'

supplies the torque and energy to compensate for the damping or "friction" present in the material under study. By establishing the proper balance (i.e., resonance) between the static (H) and frequency dependent (H') fields and the internal properties of the magnetic sample, one can determine fundamental static and dynamic magnetic parameters. Magnetic resonance techniques involve different frequencies, depending on the type of magnetic moments in the sample. The prominent forms are *electron paramagnetic resonance* (EPR) and *ferromagnetic resonance* (FMR) with frequencies in the 10 GHz range and *nuclear magnetic resonance* (NMR) with frequencies of order 10 MHz.

In order to understand the principle of the magnetic resonance technique, we utilize Fig. 3.19 and first consider the coordinate system that rotates with the Larmor frequency about the magnetic field $H \parallel z$. In this system, the magnetic moment m and magnetic field $H' \perp m$ are at rest. In the rotating

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system, the field \mathbf{H}' will exert a torque \mathbf{T}' on \mathbf{m} according to the right hand rule. The torque causes \mathbf{m} to increase its angle θ with the z-axis. This costs energy according to (3.15) which is taken from the field \mathbf{H}' . At resonance, the energy and torque taken from \mathbf{H}' compensate for the characteristic damping torque and energy of the sample which try to reduce θ to zero. The condition for keeping θ constant is that the field \mathbf{H}' and the magnetic moment \mathbf{m} rotate together around \mathbf{H} at the Larmor frequency.

In the case of the electron spin, appropriate frequencies of the rotating magnetic field are generated by establishing a standing electromagnetic wave with a wavelength λ of a few cm in a cavity. Since $\lambda \nu = c = 3 \times 10^8 \,\mathrm{m\,s^{-1}}$ this corresponds to frequencies in the Gigahertz range. The H' field is oriented in the x-y plane of the coordinate system in Fig. 3.19 and the EM wave can be linearly polarized, because a linear polarized wave is a superposition of a right and a left circularly polarized wave. The sample under study is placed into the antinode of the standing wave and the absorption of energy from the EM field is measured. In practice, one changes the static magnetic field strength H until maximum absorption of energy occurs from the microwave cavity. Then the precession around H and the frequency in the microwave cavity are exactly equal, inducing a steady-state precession with constant angle θ . In this condition, the energy absorbed from the microwave cavity exactly compensates the energy loss from the damping of the precession in the material.

The measurement of the resonance of atomic and nuclear magnetic moments has many applications which are discussed in the specialized literature. Examples are the determination of the gyromagnetic ratio of particles and atoms, the measurement of the magnetic field strength with very high precision, and most importantly, the use of NMR for the structure determination of proteins that cannot be crystallized and for *magnetic resonance imaging* (MRI) of large biological molecules. In MRI, the resonance of the proton spin is used to measure the magnetic field generated by the valence electrons at the site of the proton. This field varies depending on the nature of the chemical bond of the proton in the organic molecule. Magnetic resonance imaging has become a very powerful and entirely nondestructive tool, e.g., for medical diagnostics of carcinogenic tissue.

Magnetic Resonance, Spin-Flip Transitions and Spin De-Phasing

One may also view a magnetic resonance experiment in a frequency domain picture. The absorption reaches a maximum when the externally applied static field \boldsymbol{H} together with the intrinsic fields present in the sample reach the condition of resonance, where the Larmor frequency equals the frequency of the EM standing wave associated with \boldsymbol{H}' . At resonance, a transition from $s_z = \hbar/2$ to $s_z = -\hbar/2$, or vice versa takes place. The energy which is absorbed or emitted in such a "spin-flip" transition is $\Delta E = 2 \,\mu_{\rm B} H$ per electron and corresponds to the absorption or emission of one quantum $\hbar\omega$ from or to the EM field in the cavity, i.e., we have

$$\Delta E = \hbar \omega = 2\,\mu_{\rm B} H. \tag{3.40}$$

Inserting $\mu_{\rm B} = \mu_0 e \hbar/2m_{\rm e}$ yields $\omega = (e/m_{\rm e})B$ which is the Larmor frequency. This argument can be considered as either a proof of energy conservation or as an elegant way to derive the Larmor frequency. Angular momentum is conserved since the absorbed or emitted circularly polarized radiation quantum carries an angular momentum \hbar which is transferred to the electron.

The magnetic resonance process may be described phenomenologically by the so-called *Bloch equations* [139, 140]. Within these equations two types of dissipative processes are specifically specified.⁸ One damping mechanism that affects the magnetic moment component m_z along the static field direction $\boldsymbol{H} \parallel z$ is due to spin-flip transitions. It is characterized by the so-called *longitudinal relaxation time* T_1 . The second damping mechanism arises from the interactions between different moments, in particular, the decay of their phase relationship as they precess about \boldsymbol{H} . This spin de-phasing mechanism affects the components m_x and m_y and is described by a characteristic *transverse relaxation time* T_2 . We shall come back to the processes of spin-flips and spin de-phasing in Sect. 8.6.2 when we consider the fundamental interactions of spin polarized electrons with matter.

Ferromagnetic Resonance

Of special interest to magnetism is ferromagnetic resonance (FMR). Before we discuss the technique in more detail, let us briefly continue the idea of "spin-flips" mentioned above in conjunction with FMR. It turns out that "spin-flips" in FMR are intimately connected with the important concept of *spin waves*, suggested in 1930 by Felix Bloch [141].

Let us assume for simplicity that the constant external magnetic field H is used to align the magnetization along the anisotropy axis. Then the magnetic moments precesses around the combined external and anisotropy fields with

$$\frac{\mathrm{d}m_x}{\mathrm{d}t} = \gamma m_y H - \frac{m_x}{T_2}$$

$$\frac{\mathrm{d}m_y}{\mathrm{d}t} = -\gamma m_x H - \frac{m_y}{T_2}$$

$$\frac{\mathrm{d}m_z}{\mathrm{d}t} = -\frac{m_z - m_0}{T_1},$$
(3.41)

where γ is the gyromagnetic ratio and m_0 the value of the equilibrium magnetic moment. T_1 is the longitudinal and T_2 the transverse relaxation time.

⁸For the geometry shown in Fig. 3.19 the Bloch equations are,

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a typical value $\mu_0 H \simeq 1$ T. This field causes a splitting between the up and down states $\Delta E = 2 \,\mu_{\rm B} H \simeq 40 \,\mu\,{\rm eV}$, corresponding to a radio frequency of 10 GHz. Thus in this case the "spin-flip" energy per electron is quite small, much smaller than the exchange splitting in a ferromagnet, which is of order 1 eV as we shall see in Sect. 11.1 below. Following the ideas of Stoner [30,31], a "spin-flip" in a ferromagnet should cost the energy of the exchange splitting. The discrepancy of the two energies is explained by Bloch's concept of spin waves [141]. Spin waves involve spins on different lattice sites. This concept allows the energy of a spin wave to cover a large energy range from nearly zero when the spin excitation extends over many sites to the Stoner splitting when only one spin is involved. We shall come back to the important concept of spin waves in Sect. 11.15 below.

In bulk metals the rotating magnetic field cannot penetrate due to the induction of eddy currents. Typical penetration depths or "skin depths" of the magnetic field at Gigahertz frequencies are of the order of $0.1-1 \,\mu$ m. On the other hand, nanoscopic metallic samples or thin films are well suited for electron spin resonance if their dimensions are small compared to the skin depth. In FMR one usually asserts that the macrospin approximation is valid so that the magnetization precesses as a whole around the sum of all fields existing in the ferromagnetic sample. This is called the uniform FMR-mode. Such measurements give important information on the magnetic moments and their dynamics which we shall briefly discuss now.

We have seen earlier that the total magnetic moments have a spin and orbital part according to (3.14) or

$$\langle \boldsymbol{m}_{\rm tot} \rangle = \langle \boldsymbol{m}_{\rm s} \rangle + \langle \boldsymbol{m}_{\rm o} \rangle = -\frac{\mu_{\rm B}}{\hbar} \left(g_s \langle \boldsymbol{s}_z \rangle + g_\ell \langle \boldsymbol{\ell}_z \rangle \right) .$$
 (3.42)

and that the g-factors for the spin and orbital atomic moments are $g_s = 2$ and $g_{\ell} = 1$, respectively. With atoms the total magnetic moment is an integer multiple of $\mu_{\rm B}$. This is not the case with the magnetic moment per atom in the 3d transition metals. Experiments show that the magnetic moment/atom at zero temperature is 2.19, 1.57, and 0.62 $\mu_{\rm B}$ for Fe, Co, and Ni, respectively. This will be discussed in detail in Sect. 7.4.1. The magnetic moments also contain a small orbital moment contribution. This contribution can be directly inferred by magnetic resonance measurement. When the magnetic resonance equation (3.31) is written in terms of the dimensionless gyromagnetic factor, the FMR resonance frequency $\omega = -\gamma H$ directly determines γ , which is characteristic of the total magnetic moment of the atoms in the sample. From γ one can then determine a material dependent g-factor according to

$$g = -\frac{2m_{\rm e}\gamma}{e\mu_0} \ . \tag{3.43}$$

One finds that the g-factors of the pure metals g = 2.09 (Fe), g = 2.18 (Co), and g = 2.21 (Ni), deviate from the spin-only value of 2.0 by a small amount. This difference is a direct consequence of the presence of an orbital moment.

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Its ratio to the spin moment may be derived from the measured g-values by use of Kittel's formula [142, 143]

$$\frac{g-2}{2} = \frac{\langle \boldsymbol{m}_o \rangle}{\langle \boldsymbol{m}_s \rangle} \ . \tag{3.44}$$

This shows that the total moments for Fe, Co, and Ni metal are predominantly generated by the spin of the electron (which would give g = 2), with an orbital moment contribution of only about 4–10%. Although small, the orbital moment is nevertheless essential to magnetism. As discussed in Sect. 11.2 it turns out that in crystals both the orbital moment $\langle \boldsymbol{m}_o \rangle$ and the g-factor may be anisotropic relative to the lattice directions. The favored direction of the orbital moment then generates a favored magnetization direction in the crystal, i.e., the easy magnetization axis.

In FMR the *width* of the resonance is a measure of the damping of the precessional motion, as discussed in Sect. 3.6.2. With a single electron in vacuum, the damping of the precessional motion is absent for all practical purposes, and the resonance will be a δ -function. In a solid the spin or magnetization gradually turns into the field direction and, at resonance, energy and angular momentum is taken from the external field H' to compensate for the intrinsic damping. This situation corresponds to a forced harmonic oscillator (see Sect. 9.4.2) where the damping term broadens the δ -function into a characteristic resonance lineshape of finite width. The measured FMR linewidth is therefore proportional to the amount of damping. Damping in a solid occurs by angular momentum transfer to some other reservoir. In ferromagnetic metals this typically involves excitation of spin waves (discussed in Sect. 11.1.5), but finally the angular momentum (and energy) is transferred to the lattice, a mechanism called *spin-lattice relaxation*. From the width of the FMR resonance for nearly perfect transition metal films, one can determine the intrinsic spin-lattice relaxation time to be about 100 ps as discussed in detail in Sect. 15.2.2.

It is interesting that FMR studies have revealed a direct relationship between the deviation of the g-factor from the value 2.0, given by (3.44), and the Gilbert damping parameter α in (3.39), as reviewed by Pelzl [143]. This indicates that orbital magnetism which provides the link between the spin system and the lattice plays the key role in both the static and dynamic spin–lattice coupling.

When nonuniform modes are excited, the width of the resonance curve does not necessarily yield the true intrinsic damping [144]. In fact, the nonuniform precession can be viewed as two coupled resonances that are close in frequency and hence produce a larger apparent width of the total resonance. Generally, the angle θ between m and the magnetic field is very small ($\leq 1^{\circ}$) in FMR, so that the damping derived from the uniform FMR-mode cannot be directly applied to determine the damping in a magnetization reversal process where θ is of course large. This is discussed in more detail in Sect. 15.6. We may summarize important points of this section as follows.

The position of the ferromagnetic resonance line as a function of the size and direction of the applied magnetic field yields the gyromagnetic ratio (g-factor) and the magnetic anisotropies. The width of the resonance line contains information on the spin-lattice relaxation.

3.7 Time–Energy Correlation

The motion of spins in magnetic fields discussed above provides a good opportunity to introduce and discuss an important concept that is extensively used in physics and chemistry to describe the dynamics of a system. It is the correlation between energy and time. There are two good reasons for our discussion. First, as expressed by the title of our book, time-dependent phenomena are of great importance in modern magnetism research and they may be studied either in the frequency (energy) or time domain. For example, FMR measures the magnetization dynamics in the frequency domain and magnetic imaging can directly observe the time evolution. The question of interest then concerns the link between such energy and time domain measurements. A second reason for taking a closer look at the energy–time correlation concept is that there is considerable confusion in the literature about its physical basis and its relationship with the Heisenberg uncertainty principle.

3.7.1 The Heisenberg Uncertainty Principle

Let us start with the Heisenberg principle. In 1927 Werner Heisenberg [145] formulated a general quantum mechanical principle that, in its most common form, states that it is not possible to simultaneously determine the position and momentum of a particle. The better the position r is known, the less well the momentum p is known, and vice versa. The principle is commonly known as the *Heisenberg uncertainty principle*, and can be stated as

$$\Delta r \,\Delta p \ge \frac{\hbar}{2}.\tag{3.45}$$

This inequality is a special case of the uncertainty between arbitrary observables A and B associated with quantum mechanical operators A and B. The general uncertainty relation then states that for any two operators Aand B,

$$\Delta A \,\Delta B \ge \frac{1}{2} |\langle \mathbf{i}[\boldsymbol{A}, \boldsymbol{B}] \rangle| \tag{3.46}$$

where $[\mathbf{A}, \mathbf{B}]$ denotes the commutator. If the operators commute, the uncertainty is zero, if they do not commute as for example \mathbf{r} and \mathbf{p} , the right side in (3.46) is finite.

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Heisenberg's original paper does not attempt to rigorously determine the exact quantity on the right side of the inequality, but rather uses physical arguments to show that the uncertainty is *approximately* given by Planck's constant h. Heisenberg also gave an alternative form involving the uncertainty between energy and time, which he stated as [145]

$$\Delta E \,\Delta t \sim h. \tag{3.47}$$

The more precisely you know the time (uncertainty Δt) when an event occurs, the less you know about the energy involved and vice versa.

In contrast to the position/momentum uncertainty the energy/time uncertainty is not a special case of (3.46) since time in quantum mechanics is not an *operator* but a *parameter* [126]. Thus if we let A = H, the Hamiltonian, and B = t, the time, the right side of (3.46) is zero since all observables commute with complex numbers. Thus the validity of an energy-time uncertainty relation is a nontrivial matter [146]. Although it is guided by a similar expression, the energy-time correlation of interest to us here is *not* based on the uncertainty principle but rather on a quantum mechanical description of the system which satisfies the time dependent Schrödinger equation [126].

The time evolution of a quantum mechanical system is treated extensively in quantum mechanics books [126, 147] and for brevity we restrict ourselves here to the treatment of a specific example, dealing with the important concept of *spin precession* discussed earlier. We shall discuss the spin precession process shown in Fig. 3.20 from a classical point of view and in terms of a time-dependent quantum mechanical treatment.

3.7.2 Classical Spin Precession

We start with a classical treatment. We assume an electron with spin s which is placed at an angle θ with respect to a homogeneous magnetic field H aligned along the z axis of our coordinate system, as shown in Fig. 3.20.

We have earlier used semiclassical arguments to derive the motion and energy associated with the moment in the field. Assuming g = 2 the spin will precess about H with an angular velocity or Larmor frequency ω given by (3.32) or

$$\boldsymbol{\omega} = \frac{e\mu_0}{m_{\rm e}} \boldsymbol{H} \;. \tag{3.48}$$

and the energy of the associated magnetic moment in the field is given by (3.15)

$$E = -\boldsymbol{m} \cdot \boldsymbol{H} = \frac{2\,\mu_{\rm B}}{\hbar}\,s_z\,H \tag{3.49}$$

so that with $s_z = -\hbar/2$ we have $E_1 = -\mu_{\rm B}H$ and for $s_z = +\hbar/2$ we have $E_2 = +\mu_{\rm B}H$. We see from (3.33) that for a field $B = \mu_0 H = 1$ T the spin precesses with an angular velocity $\omega = 0.176 \text{ rad ps}^{-1}$ so that it takes a time of 35.8 ps for a full 360° spin precession.

3.7 Time–Energy Correlation 99

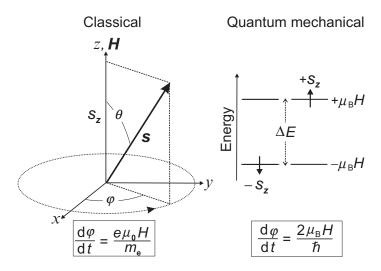


Fig. 3.20. Classical (*left*) and quantum mechanical (*right*) picture of the motion of an electron spin s in an external magnetic field H directed along the z-axis of our coordinate system. In the classical picture a spin that is not aligned with the field precesses about it with the Larmor angular frequency $d\varphi/dt = \omega = e\mu_0 H/m_e$ that is independent of θ . According to (3.31), the precession direction is given by the right hand rule as in Fig. 3.14. In the quantum mechanical picture the spin has finite probabilities in both, the spin-up state $+s_z$ and the spin-down state $-s_z$. Spin precession about H corresponds to a change in the *phases* of the up and down spin components, and the *precession frequency* is given by $d\varphi/dt = \omega = 2\mu_{\rm B}H/\hbar$. Changes in the angle θ correspond to a change in the relative *probabilities* of the up and down states, so that any angular rotation $d\theta/dt$, if present, is determined by the *spin-flip frequency* between the two states. Such a θ rotation into the field direction corresponds to dissipative processes

3.7.3 Quantum Mechanical Spin Precession

The quantum mechanical picture looks quite different. Again we assume that the electron is placed into the magnetic field and that the spin and field are not collinear. To describe the spin motion in the field by quantum theory we start at a time t = 0 and then calculate the time dependence by acting on the initial state of the system at t = 0 by a time evolution operator

$$\mathcal{U}(t,0) = \exp\left(\frac{-\mathrm{i}\,\mathcal{H}\,t}{\hbar}\right) \tag{3.50}$$

that takes the system from a state at time t = 0 to a new state at time t. In our case the time evolution of the moment in the field is entirely determined by the Hamiltonian \mathcal{H}

$$\mathcal{H} = \frac{2\mu_{\rm B}}{\hbar} H s_z, \qquad (3.51)$$

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where s_z is a quantum mechanical operator that acts on the wavefunctions. From (3.25) we know that the spin wavefunction has the general form

$$\chi = u_1 \left| + \right\rangle + \left| u_2 \right| - \right\rangle \,, \tag{3.52}$$

with $|u_1|^2 + |u_2|^2 = 1$. Here $|u_1|^2$ and $|u_2|^2$ are the probabilities of the electron to be in the up (along +z) and down (along -z) states, respectively. We have not yet discussed the origin of the form of the wavefunction (3.52) in detail but will do so in Sect. 8.4.2 below. Borrowing another result from that section, we have for the specific cases that the spin is aligned along the x and y axes of our coordinate system (z being the quantization axis) (see Fig. 8.3 below),

$$\chi_{+x} = \frac{1}{\sqrt{2}} |+\rangle + \frac{1}{\sqrt{2}} |-\rangle$$

$$\chi_{+y} = \frac{1}{\sqrt{2}} |+\rangle + \frac{i}{\sqrt{2}} |-\rangle . \qquad (3.53)$$

This allows us to see how the wavefunction changes as the spin rotates in the x-y plane. The 90° rotation is seen to correspond to a change in the phase of the complex spin down coefficient by $e^{i\pi/2} = i$. We therefore expect to find that, quantum mechanically, the spin precession corresponds to a change in the phases of the coefficients u_1 and u_2 . Let us now discuss how this comes about in general.

We assume that the spin is oriented at an angle θ from the field direction as shown in Fig. 3.20 but we do not specify it specifically.⁹ Instead we assume that at the time t = 0 the spin state $\chi(0)$ is given by the general form (3.52), so that it points into some arbitrary direction. The quantum mechanical time evolution of the state $\chi(0)$ to the state $\chi(t)$ at a later time t is given by

$$\chi(t) = \mathcal{U}(t,0)\,\chi(0) = e^{-i2\mu_{\rm B}Hs_z t/\hbar^2} \left[u_1 \left|+\right\rangle + \left.u_2 \left|-\right\rangle\right] \,. \tag{3.55}$$

This can be evaluated by use of the known operator rules $s_z |+\rangle = \hbar/2 |+\rangle$ and $s_z |-\rangle = -\hbar/2 |-\rangle$ (see Table 6.1 below) as

$$\chi(t) = u_1 \operatorname{e}^{-\mathrm{i}\mu_{\mathrm{B}}Ht/\hbar} |+\rangle + u_2 \operatorname{e}^{+\mathrm{i}\mu_{\mathrm{B}}Ht/\hbar} |-\rangle.$$
(3.56)

We can now replace $\mu_{\rm B}H$ by the difference in the energies E_1 and E_2 for the spin-down and spin-up states, as defined in Fig. 3.20. In particular, we have for the total splitting $\Delta E = E_2 - E_1 = 2\mu_{\rm B}H$ and obtain

$$\chi(t) = u_1 e^{-i\Delta E t/2\hbar} |+\rangle + u_2 e^{+i\Delta E t/2\hbar} |-\rangle.$$
(3.57)

Relative to the original state $\chi(0)$, the time-evolved state $\chi(t)$ therefore corresponds to a phase shift in the spin up and spin down coefficients, expressed

$$\cos\theta = |u_1|^2 - |u_2|^2 . \tag{3.54}$$

 $^{^{9}\}text{According to Sect. 8.4.3}$ the angle θ is related to the spin-up and spin-down probabilities according to

by the exponential factors in (3.57). The total phase shift between the up and down states is seen to be $\varphi = \Delta E t/\hbar$.¹⁰ We can state as follows.

Spin precession about a field H, in quantum mechanics corresponds to a change in the phase between the up and down spin states. The phase change with time is given by

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t} = \omega = \frac{\Delta E}{\hbar} \;, \tag{3.59}$$

where $\Delta E = 2\mu_{\rm B}H$.

In our derivation of (3.59) we have assumed that the spin is at an arbitrary angle θ with respect to the field **H**. Therefore we find that the precession frequency does not depend on θ , as for the classical result.

It is important to distinguish the change in φ which corresponds to a change in phase between the up and down states as the spin precesses, from the change in θ . The latter corresponds to a change in the occupation of the up and down spin states (see footnote 9), and is therefore associated with "spin flips." We shall come back to this process later in Sects. 8.6.2 and 12.6.

Our quantum mechanical result (3.59) is identical to the classical Larmor precession frequency in (3.48), which is easily seen by use of $\mu_{\rm B} = \mu_0 e\hbar/2m_{\rm e}$. The precession frequency ω is determined by the energy $\Delta E = 2\mu_{\rm B}H$ that separates the up and down spin states, that is the two eigenvalues of the Hamiltonian (3.51). The system changes through a complete cycle $\varphi = 2\pi$ in a time $t = h/\Delta E$. We can take this as our (approximate) quantum mechanical time energy relation.

A quantum mechanical two level system separated by two eigenstates with energy separation ΔE changes over a characteristic time $t=2\pi/\omega$ or $\tau=1/\omega$ according to

$$t \simeq \frac{h}{\Delta E} \quad \text{or} \quad \tau \simeq \frac{\hbar}{\Delta E},$$
 (3.60)

where $h = 4.136 \times 10^{-15}$ eV s and $\hbar = 0.6583 \times 10^{-15}$ eV s.

$$\langle S_x \rangle = \frac{\hbar}{2} \cos\left(\frac{\Delta E t}{\hbar}\right)$$
 (3.58)

and therefore this quantity oscillates with an angular frequency $d\varphi/dt = \omega = \Delta E/\hbar$.

¹⁰The oscillatory motion of the system can also be derived by calculating the expectation value of $\langle S_x \rangle = \langle \phi_x(t) | S_x | \phi_x(t) \rangle$. With the operator rules of Table 6.1 it is readily shown that

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This relationship allows the connection between a time-dependent measurement of the orientation of the magnetization and an energy or frequency dependent measurement.¹¹ From a time-dependent measurement we would be able to determine the magnetization motion in real space and could find the cycle time t, corresponding to a 360° spin rotation in the (x-y) plane (see footnote 11). From a frequency dependent measurement, like an inelastic spectroscopic measurements that measures an energy loss, we would find that the system resonantly absorbs energy at a certain cycle frequency $\nu = 1/t = \Delta E/h = 2\mu_{\rm B}H/h$.

Examples of Time–Energy Relations

We may generalize our energy-time relation (3.60) to other two level systems, involving a precession, as illustrated in Fig. 3.21 for three prominent cases. On the left we show again the precession of a magnetic moment of the general form $\boldsymbol{m} = -g_J \,\mu_{\rm B} \boldsymbol{J}/\hbar$ (see Sect. 3.2.2) about a magnetic field, as discussed earlier. The moment may be due to the spin, orbital or a coupled momentum. The characteristic time $\tau = 1/\omega$ of a precession by 1 rad corresponds to the inverse Zeeman energy.

In the middle of Fig. 3.21 we illustrate the case of the precession of an electron in a magnetic field. The cyclotron frequency with which an electron circles around a homogeneous magnetic field $\boldsymbol{B} = \mu_0 \boldsymbol{H}$ is determined from the equilibrium between the centrifugal force and the magnetic part of the Lorentz force (4.10), $m_{\rm e}r\omega^2 = evB$. With $v = \omega r$ one obtains for the cyclotron frequency

$$\omega = \frac{e}{m_{\rm e}} B. \tag{3.61}$$

Note that this is an exact result while for the Larmor frequency the same expression (see (3.48)) holds only if $g \equiv 2.0$.¹² In reality, the cyclotron frequency and the Larmor frequency are different on the order of 10^{-3} due to the anomaly of the *g*-factor. Quantum mechanically the system is again described by a Zeeman Hamiltonian $\mathcal{H} = \mu_{\rm B} H \ell_z / \hbar$ since the precessing electron creates an

¹¹ For "frequency" and "time" we use the notation $\tau = 1/\omega = 1/(2\pi\nu) = t/2\pi$. The angular frequency ω has the dimension [angle/time] and is typically given in units of rad s⁻¹ where 1 rad = $360^{\circ}/2\pi = 57.3^{\circ}$. In contrast, the cycle frequency ν is given in units of [Hz] (s⁻¹). It is common to express the energy in either units of [eV] or [Hz]. The conversion is shown in Fig. 4.5 and is given by $1 \text{ eV} = 2.418 \times 10^{14} h$ Hz.

¹²This difference between the cyclotron frequency and the Larmor precession frequency has in fact been used to determine the anomaly of the *g*-factor with incredible precision. Namely, if one injects a particle into a magnetic field with its spin pointing into the direction of the linear momentum $\boldsymbol{p} = m_{\rm e} \boldsymbol{v}$, both the spin \boldsymbol{s} and the linear momentum \boldsymbol{p} will precess with almost the same frequency. However, after ~1,000 revolutions there will be a difference in the direction of \boldsymbol{p} and \boldsymbol{s} which can be detected in a Mott scattering experiment (see Fig. 3.11) or by the asymmetry of the decay of the μ and τ leptons.

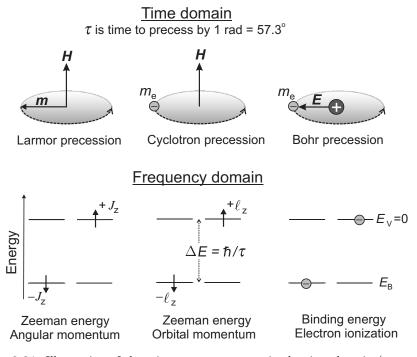


Fig. 3.21. Illustration of three important processes in the time domain (top row) and the frequency domain (bottom row). The processes are the precession of a magnetic moment $\mathbf{m} = -g_J \,\mu_{\rm B} \mathbf{J}/\hbar$ about a perpendicular magnetic field \mathbf{H} (Larmor precession, *left*), the precession of an electron with initial velocity \mathbf{v} about a perpendicular magnetic field \mathbf{H} (cyclotron precession, *middle*), and the precession of an electron about the nucleus (Bohr precession, *right*). We assume that in the time domain the precession has an angular velocity ω corresponding to a characteristic time $\tau = 1/\omega$. In the frequency domain the precession process corresponds to an energy difference $\Delta E = \hbar \omega = \hbar/\tau$

orbital momentum $\boldsymbol{\ell} = m_{\rm e}(\boldsymbol{r} \times \boldsymbol{v}) = m_{\rm e}r^2\boldsymbol{\omega}$ which interacts with the magnetic field.

The third example in Fig. 3.21 is the electron motion about the nucleus. For simplicity we assume a simple H atom. The classical Bohr precession of an electron is quantum mechanically described by the central field Hamiltonian which for the H atom yields a 1s electron binding energy of $E_{\rm B} = 13.6 \,\mathrm{eV}$. This characteristic energy of the atom (corresponding to the energy difference relative to the vacuum level with binding energy $E_{\rm V} = 0$) can then be used to calculate the Bohr precession time τ . For H this gives a time $2\pi\tau = t = 0.3$ fs for a 360° Bohr orbit precession.

4.1 Overview

We have now developed a good understanding of static electric and magnetic fields. Both are produced by charges that are either stationary or moving. Initially the concepts of electric and magnetic fields appear quite distinct and disconnected. However, this is not so and this chapter will take a look at the connectedness of electric and magnetic phenomena. To do this we shall use well established concepts but we shall illustrate them with new applications. The structure of the chapter is as follows.

We shall first review the laws underlying the description of phenomena in different reference frames, touching on the subject of special relativity, and by reviewing the transformation laws of electric and magnetic fields between reference frames that move relative to each other with a constant velocity, so called *inertial* frames. We shall see, for example, that a pure electric field in one frame may appear as a combination of electric and magnetic fields in another, showing the intricate connectedness of electric and magnetic fields. As an example we shall discuss the electric and magnetic fields surrounding a moving point charge.

In the next two chapters we make an important distinction between fields associated with charges that either move at a constant velocity, so called *velocity-fields*, or are accelerated, *acceleration fields*. Velocity fields move with and are attached to the moving charge and the magnetic field strength is proportional to the current. Since a current is defined as the change of charge with time, there are two ways to increase magnetic fields: either increase the charge or decrease the time over which the charge flows. This chapter discusses a fascinating way to create ultraintense and ultrashort magnetic field pulses that will be used in Chap. 15 for the investigation of ultrafast dynamics in magnetic recording media.

Acceleration fields, discussed in the final section, are the familiar electromagnetic waves which separate from the charge and radiate into space.

$\mathbf{4}$

As examples of EM waves we shall discuss synchrotron radiation and the ultrabright radiation produced by free electron lasers.

4.2 Basic Concepts of Relativistic Motion

In order to illustrate the connectedness of electric and magnetic fields let us consider the transformation of the fields between two reference systems that move relative to each other with a constant velocity v. Such systems are called *inertial systems* and their consideration has played a crucial role in the development of physics, leading to Einstein's special theory of relativity [148]. According to the principle of relativity all laws of nature are identical in all inertial systems. We can state as follows.

The equations expressing the laws of nature are invariant with respect to transformations of coordinates and time from one inertial system to another.

Before we discuss the connection between fields, we have to take a quick look at the laws of relativity [148].

4.2.1 Length and Time Transformations Between Inertial Systems

We define the *rest frame* of an object as the coordinate system in which it is at rest. The length measured in the rest frame is called the *proper length*, and the time measured by a clock in the rest frame is called the *proper time*.

We now want to relate the proper length l_0 in the rest frame to the length l in a system moving with a velocity v relative to the rest frame. For convenience we define the following relationships involving the ratio of v and the speed of light c as

$$\beta \equiv v/c \qquad \gamma \equiv \frac{1}{\sqrt{1-\beta^2}} \ . \tag{4.1}$$

We shall see later that for relativistic electrons with energy $E_{\rm e}$ in units of [GeV] we have $\gamma \simeq 2 \times 10^3 E_{\rm e}$ and therefore γ can be of order $10^3 - 10^5$ in modern electron accelerators. If we measure both l_0 and l parallel to the direction of v we then have the following well known Lorentz relationship¹

¹The general equations governing the Lorentz space–time *coordinate* transformations for motion in the z direction, using the definitions $\beta \equiv v/c$ and $\gamma \equiv 1/\sqrt{1-\beta^2}$, are given by [149]

$$t = \gamma \left(t' + \frac{\beta z'}{c} \right) \qquad z = \gamma \left(z' + \beta c t' \right) \qquad x = x' \qquad y = y'. \tag{4.2}$$

Equations (4.3) and (4.4) are derived from these coordinate equations by taking the difference between two coordinates.

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$$l = \frac{l_0}{\gamma}.\tag{4.3}$$

If l_0 and l are measured perpendicular to v we have $v_{\perp} = \beta c = 0$ and $l_0 = l$. This shows that the length is always largest in the rest frame, which is the well known *Lorentz contraction* observed for a moving system. The time behaves exactly opposite. If we measure a time t_0 in the rest frame, the time t in the moving frame is

$$t = t_0 \,\gamma. \tag{4.4}$$

The proper time measured in the rest frame is therefore always shortest, and we observe a time dilation for a moving system.

4.2.2 Electric and Magnetic Field Transformations between Inertial Systems

We are now ready to discuss the electric and magnetic fields in inertial systems that move relative to each other with a constant velocity $|\boldsymbol{v}| < c$. For the following discussion we define two coordinate systems as shown in Fig. 4.1, with the primed system moving at a velocity $+\boldsymbol{v}$ relative to the unprimed system. The transformation equations for the fields can be found in standard textbooks [118, 149] and they are given below.

The transformation of the fields associated with two inertial systems K and K', where the frame K' moves away from the frame K with a velocity $+\boldsymbol{v}$ is given by

$$\begin{aligned}
 E'_{\parallel} &= E_{\parallel} & E_{\parallel} &= E'_{\parallel} \\
 E'_{\perp} &= \gamma \left(E_{\perp} + v \times B \right) & E_{\perp} &= \gamma \left(E'_{\perp} - v \times B' \right)
 \end{aligned}$$
(4.5)

$$\begin{aligned}
\mathbf{B}'_{\parallel} &= \mathbf{B}_{\parallel} & \mathbf{B}_{\parallel} &= \mathbf{B}'_{\parallel} \\
\mathbf{B}'_{\perp} &= \gamma \left(\mathbf{B}_{\perp} - \frac{\mathbf{v} \times \mathbf{E}}{c^2} \right) & \mathbf{B}_{\perp} &= \gamma \left(\mathbf{B}'_{\perp} + \frac{\mathbf{v} \times \mathbf{E}'}{c^2} \right), \end{aligned} \tag{4.6}$$

where the parallel and perpendicular labels are relative to the direction of \boldsymbol{v} and

 γ

$$= \frac{1}{\sqrt{1 - (\frac{v}{c})^2}} = \frac{1}{\sqrt{1 - \beta^2}}.$$
(4.7)

If the fields have a wave vector and time dependence, we have the transformations

$$e^{i\left(\boldsymbol{k}'\cdot\boldsymbol{r}'-\boldsymbol{\omega}'t'\right)} = e^{i\left(\boldsymbol{k}\cdot\boldsymbol{r}-\boldsymbol{\omega}t\right)}.$$
(4.8)

The last expression means that counting the number of times the field goes through zero should give the same answer in both systems of reference. These equations show that a pure electric field E in the unprimed frame looks

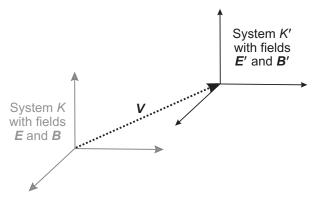


Fig. 4.1. Transformation of electromagnetic fields between coordinate systems with constant relative motion v, so-called *inertial systems*. In our case the frame K' with fields E' and B' moves away from the frame K with fields E and B with a velocity +v

like an electric \boldsymbol{E} plus magnetic \boldsymbol{B} field in the primed frame. In particular, the term $\boldsymbol{v} \times \boldsymbol{B}$ may be interpreted as an additional electric field $\boldsymbol{E}^* = \boldsymbol{v} \times \boldsymbol{B}$. The dimension of \boldsymbol{B} is $[Vs/m^2]$ so that with \boldsymbol{v} in [m/s] we get \boldsymbol{E} in [V/m], as required. Similarly, the term $(\boldsymbol{v} \times \boldsymbol{E})/c^2$ can be interpreted as an additional magnetic field. The latter fact is important when considering the motion of an electronic spin in a pure electric field. The additional magnetic field in the rest frame of the electron may then cause an energy splitting or spin precession (see Sect. 3.7). This is the basis of the *Rashba effect* which exists in two-dimensional semiconductor and metal structures with structural inversion asymmetry [150–153].

Hence we see that, in general, E and B do not exist independently of each other. A mixture of electric and magnetic fields may appear as a pure electric or magnetic field in another inertial system. From the appearance of the factor γ in the field transformation equations we see that the equations include relativistic effects.

The force F acting on a charge q in an electric field E is given by

$$\boldsymbol{F}_E = q \, \boldsymbol{E}.\tag{4.9}$$

This force does not depend on the velocity v of the particle carrying the electric charge. In contrast, the force on a charge moving in the magnetic induction B is the well known *Lorentz force*

$$\boldsymbol{F}_B = q\,\boldsymbol{v} \times \boldsymbol{B} \tag{4.10}$$

and depends on the particle velocity.

If v, B, and E are all perpendicular to each other and the velocity has the special value v = E/B, we have $F_E = -F_B$, and the electron can traverse both fields without experiencing any force. Crossed electric and magnetic fields

can therefore be used as a velocity or energy filter for electrons, known as a *Wien filter*.

4.3 Fields of a Charge in Uniform Motion: Velocity Fields

An important example of the field transformations discussed above are the fields surrounding a charge that moves with a constant velocity. A prominent example of such fields are those surrounding a cluster of charges, or "bunch", in a linear accelerators, as previously shown in Fig. 2.4. The name "accelerator" implies that the charges do not move with a constant velocity. This is indeed so at the beginning of the accelerator. However, as soon as the velocity reaches an energy that is of order 10 times the electron rest mass of 0.5 MeV the electrons already move well within 1% of the speed of light as seen from (4.22). As the energy is further increased, the speed remains almost constant and therefore the acceleration is negligible (only the mass increases according to (4.23)). Since 5 MeV is considered a small energy for most high energy physics accelerators, one may consider the electrons in uniform motion through most of the accelerator.

The electric and magnetic fields for the case of uniform motion are called *velocity fields*, and one calls the fields associated with accelerated charges *acceleration fields*. Other names for velocity fields are *Coulomb fields* and *near fields* because we shall see that they fall off fast with the inverse of the distance squared. Acceleration fields are also called *far fields* but are best known by a familiar name, *electro-magnetic radiation*, as will become clear in Sect. 4.4 later.

4.3.1 Characteristics of Velocity Fields

The fields that we will discuss in this section are for charges moving with *constant velocities* and the field transformations between stationary and moving charges are therefore those between inertial systems and the field transformations are described by (4.5) and (4.6). We would like to compare the strength and angular distribution of fields surrounding a moving charge, for example an electron. In the rest frame of the electron we know that there is a radial electric field that terminates on the negatively charged electron (q = -e) as shown in Fig. 2.1 and there is no magnetic field and $\mathbf{B} = 0$. The situation is shown on the left side of Fig. 4.2.

In order to derive the fields of a moving electron we shall assume that the electron sits at the origin of the frame K' in Fig. 4.1 which moves away with a velocity $+\boldsymbol{v}$ from our observer frame K. We can then transform the fields from the electron rest frame K' back into the observer frame K. We start in the frame K' and denote all quantities in that frame by primes. The fields in

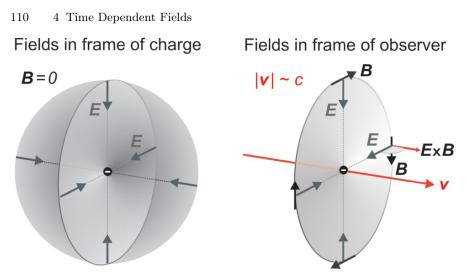


Fig. 4.2. Example of the electric and magnetic fields of a single electron in different reference frames. Left: Electric field in the frame of the electron with charge q = -e, which is the well known radial Coulomb field with the electric field vector pointing toward the negative electron. There is no magnetic field. Right: The same electron is assumed to move with a highly relativistic (constant) velocity $|v| \approx c$ relative to the stationary observer, and the fields are observed from the stationary frame. The electric field is now nearly contained in a plane perpendicular to v since the component $E_{\perp} \perp v$ is enhanced by a factor γ according to (4.15) and the component parallel to the field is reduced by a factor $1/\gamma^2$ according to (4.14) over the field in the rest frame of the electron. The moving charge also gives rise to a field B which lies in the plane perpendicular to v and at any point has the direction and magnitude $B = (v \times E)/c^2$ according to (4.6). Both the electric and magnetic fields move with the electron and hence there is no "radiation"

the primed electron rest frame are expressed in terms of the proper distance r'. If we denote the unit position vectors in the two frames as r_0 and r'_0 , we have

$$E' = \frac{q}{4\pi\epsilon_0 (r')^2} r'_0 \qquad B' = 0.$$
 (4.11)

We can use the transformation properties for the fields given by (4.5) and (4.6) to derive the fields of the moving charge in the observer frame K

$$\boldsymbol{E}_{\parallel} = \boldsymbol{E}'_{\parallel} \qquad \boldsymbol{B}_{\parallel} = \boldsymbol{B}'_{\parallel} = 0. \tag{4.12}$$

and

$$\boldsymbol{E}_{\perp} = \gamma \boldsymbol{E}'_{\perp} \qquad \boldsymbol{B}_{\perp} = \gamma \, \frac{\boldsymbol{v} \times \boldsymbol{E}'}{c^2}.$$
 (4.13)

We now need to express the field E' in (4.11) in terms of coordinates r in the frame K since the distance in the two frames are different due to relativistic effects. According to (4.3) we have the following relationships,

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$$egin{aligned} & m{r_0}, m{r_0'} \parallel m{v}: & m{r'} = \gamma \, m{r} \ & m{r_0}, m{r_0'} \perp m{v}: & m{r'} = m{r}. \end{aligned}$$

We obtain:

$$E_{\parallel} = \frac{q}{4\pi\epsilon_0 \,\gamma^2 \,r^2} = \frac{E'}{\gamma^2} \tag{4.14}$$

$$E_{\perp} = \frac{q\gamma}{4\pi\epsilon_0 r^2} = \gamma E'. \tag{4.15}$$

These are our desired results for the fields of a charge moving with a constant velocity. The above equations directly compare the fields of the moving charge E_{\parallel} and E_{\perp} seen by the observer to the fields E' that the same charge would produce if it was stationary located at the same distance r in the frame of the observer. We see from (4.14) and (4.15) that the field is reduced by a factor $1 - \beta^2 = 1/\gamma^2$ parallel to the propagation direction² and enhanced by a factor $\gamma = 1/\sqrt{1-\beta^2}$ perpendicular to \boldsymbol{v} . Hence to the stationary observer the field lines extending radially out from the charge look squished along the propagation direction. The situation is shown on the right side of Fig. 4.2 for the case of an electron moving with nearly the speed of light.

We can write (4.14) and (4.15) in a single general expression [154, 155]

$$\boldsymbol{E}(\boldsymbol{r}) = \left[\frac{1-\beta^2}{(1-\beta^2\sin^2\theta)^{3/2}}\right] \frac{q}{4\pi\epsilon_0 r^2} \, \boldsymbol{r}_0 = \left[\frac{1-\beta^2}{(1-\beta^2\sin^2\theta)^{3/2}}\right] \, \boldsymbol{E}'(\boldsymbol{r}), \ (4.16)$$

where θ is the angle between E and the direction of motion v.

In addition we see from (4.12) and (4.13) that the moving charge also creates a magnetic field **B** given by

$$\boldsymbol{B}_{\perp} = \gamma \frac{\boldsymbol{v} \times \boldsymbol{E}'}{c^2} \qquad \boldsymbol{B}_{\parallel} = 0.$$
(4.17)

The field is entirely contained in the plane perpendicular to v, as shown in Fig. 4.2 for the case of a single electron.

In the relativistic limit $v \to c$ we have a large magnetic field of magnitude $B = \gamma E'/c = E/c$. At nonrelativistic speeds $v \ll c$ we have $\gamma \to 1$ so that $E \simeq E'$ and we obtain with $c^2 = 1/\epsilon_0 \mu_0$

$$\boldsymbol{B} \simeq \frac{\boldsymbol{\boldsymbol{v}} \times \boldsymbol{\boldsymbol{E}}}{c^2} = \frac{q}{4\pi\epsilon_0 c^2 r^2} \left(\boldsymbol{\boldsymbol{v}} \times \boldsymbol{\boldsymbol{r}}_0 \right) = \mu_0 \frac{q}{4\pi r^2} \left(\boldsymbol{\boldsymbol{v}} \times \boldsymbol{\boldsymbol{r}}_0 \right) \,. \tag{4.18}$$

This is the *Ampère–Biot–Savart* expression for the magnetic field of a moving charge.

²This seems to contradict (4.12), stating that $E_{\parallel} = E'_{\parallel}$, but one needs to realize that this assumes that the field E'_{\parallel} is expressed in terms of coordinates r' in the frame K'. The relativistic correction comes from expressing the field in terms of coordinates r in the frame K.

Note that for a relativistic electron bunch, the charge is relativistically stretched along the beam direction in the rest frame of the electron and the magnetic field in the laboratory frame would look like that around a onedimensional line of electrons or a current, similar to the Biot-Savart field around a straight current carrying wire, given by (2.3). It is derived from (4.18) by superimposing the fields coming from the charge at various positions along a straight path, that is by integration over the length of the wire [149]. The magnetic induction then falls of with 1/R, where R is the distance perpendicular to the wire direction according to

$$B = \frac{\mu_0 I}{2 \pi R}.\tag{4.19}$$

We see that the integration over the path of the electron positions (the current) yields a factor of 2 relative to just substituting qv = Ir and r = R in (4.18). It also changes the general distance dependence from $1/r^2$ to the special 1/R falloff as a function of the perpendicular distance R.

Figure 4.2 illustrates that the fields stay attached to and move with the charge. They do not "radiate" away from, i.e. separate from, the charge. We shall come back later to the difference between velocity fields and electromagnetic radiation. At this point we can make the following summary statement regarding the velocity fields surrounding a charge in uniform motion.

Velocity fields are attached to the charged particle and they extend out radially from the particle to infinity, with the sign of the radial field determined by the sign of the charge. The angular field pattern depends on the speed \boldsymbol{v} of the particle. For a single charge the fields fall off with the distance r from the particle as $1/r^2$. For a line of charged particles the fields fall off with the perpendicular distance R as 1/R.

4.3.2 Creation of Large Currents and Magnetic Fields

High magnetic fields are of great value in many scientific fields such as biosciences, chemistry, geosciences, materials science, and physics and several laboratories have been constructed around the world to achieve ultrahigh magnetic fields. Examples are the National High Magnetic Field Laboratory in the United States [156] or the Grenoble High Magnetic Field Laboratory [157] in Europe. The highest fields are created in pulsed coils and field strength of about 100 T over a period of several milliseconds have been achieved with nondestructive pulsed magnets. The fields from such magnets are limited by the problem of the exceedingly high electromechanical stresses, with the magnet conductor and reinforcement materials experiencing plastic deformation. Destructive pulsed magnets sidestep the materials problem and are designed to explode with every pulse. Since the intense magnetic field exists only as long as it takes a shock-wave to propagate through the magnet, the pulse duration is limited to a few microseconds. The highest magnetic fields are achieved by explosively compressing the magnetic field into the sample. The sample itself is destroyed with each pulse! Field strengths of up to 1,000 T over a period of several microseconds can be produced.

Here we want to discuss another fascinating way to achieve ultrahigh magnetic field strengths and we shall show later in Sect. 4.3.3 that, in addition, the field pulses can be made as short as tens of femtoseconds. We have already seen in conjunction with Fig. 2.4 that large current densities can be produced in linear accelerators and that they allow the generation of large and ultrashort magnetic field pulses. We shall now explore the reason behind this remarkable fact.

Electron beams in accelerators consist of individual electron "bunches" that contain a large number of electrons. For a moving electron bunch, we measure the temporal pulse width τ or the pulse length l in our laboratory reference frame, and we see from (4.3) and (4.4) that strange things happen as $v \to c$. Let us consider realistic cases of v/c. If we denote the energy of the beam in the laboratory system by $E_{\rm e}$, the ratio of $E_{\rm e}$ and the rest energy of the electron $m_{\rm e}c^2 = 0.511$ MeV is given by³

$$\frac{E_{\rm e}}{m_{\rm e}c^2} = \frac{1}{\sqrt{1 - (\frac{v}{c})^2}} = \gamma \ . \tag{4.20}$$

With $E_{\rm e}$ in units of [GeV] this leads to the simple relationship

$$\gamma = 1.96 \times 10^3 E_{\rm e}$$
 (4.21)

The particle velocity v can then be expressed in terms of the parameter γ as

$$v = \frac{\sqrt{\gamma^2 - 1}}{\gamma} c , \qquad (4.22)$$

and we see that the particle travels already at v = 0.992 c at a moderate accelerator energy of 4 MeV. As the particle energy is further increased, the particle velocity remains relatively constant at about the speed of light, with the increase in energy originating from the increasing relativistic mass m_e^* of the particle according to

$$m_{\rm e}^* = \gamma \, m_{\rm e},\tag{4.23}$$

which follows from writing $E_{\rm e} = m_{\rm e}^* c^2$ in (4.20).

For different beam energies we can now relate the proper length and time in the frame of the moving electron to the length and time measured by a stationary observer according to

³Note that the electron mass m_e in S.I. units is given by $m_e = 9.109 \times 10^{-31}$ VAs³ m⁻² = 9.109×10^{-31} kg.

$$\ell = \frac{m_{\rm e}c^2}{E_{\rm e}}\,\ell_0 = \ell_0/\gamma \,\,, \tag{4.24}$$

and

$$\tau = \frac{E_{\rm e}}{m_{\rm e}c^2} \,\tau_0 = \gamma \,\tau_0 \,\,. \tag{4.25}$$

For an electron beam of 50 GeV we have $\gamma = 10^5$ and the electrons essentially move with the speed of light. Hence an electron bunch that appears to be $\ell = 1 \text{ mm}$ long in the laboratory frame, has a proper length $\ell_0 = 100 \text{ m}$ in the rest frame of the electron bunch.⁴ This explains why one can obtain high current densities in relativistic beams, as previously discussed in conjunction with Fig. 2.4. Since the electrons are distributed over a large length in their rest frame their Coulomb repulsion is reduced and one can pack more electrons into a bunch, of the order of 1 nC or about 10^{10} electrons.

In the frame of a stationary observer a bunch length of $\ell = 1$ mm corresponds to a temporal pulse length $\tau = \ell/c \approx 3 \times 10^{-12}$ s, so that typical pulse lengths are a few picoseconds. The peak beam current is given by $I = N_{\rm e} e/\tau$, where $N_{\rm e}$ is the number of electrons in a bunch, and the current density is $j = N_{\rm e} e/(\tau a)$, where a is the lateral cross section (area) of the beam. Using typical numbers of $N_{\rm e} = 10^{10}$, $\tau = 3$ ps and a beam cross section of $a = 5 \,\mu {\rm m}^2$ we obtain a peak current of $I \simeq 500$ A and a current density of $j \simeq 10^{14} \,{\rm A/m}^2$. To date current densities of $10^{16} \,{\rm A/m}^2$ have been reached by tightly focusing the relativistic electron beam [158].

Relativistic beams containing a large charge give rise to large fields. In order to derive a value for the fields, we assume that the electron bunch with $N_{\rm e}$ electrons has a Gaussian bunch profile in all directions, and we shall characterize the beam in the rest frame of the observer by standard deviations in space and time. Note that the standard deviation or "one-sigma" width σ is related to the full width at half maximum Γ according to $\sigma = \Gamma/2.355$ (see Appendix A.10). For simplicity we shall use our previous temporal and physical length labels $\tau = \ell/c$ and associate them with standard deviations. We have $\tau = \sigma_t = \sigma_z/c = \ell/c$ along the beam and $\sigma_r = \sigma_x = \sigma_y$ perpendicular to the beam. At distances larger than the diameter of the bunch⁵ the magnetic field resembles that around the current in a straight wire and is given by

$$B(r,t) = \frac{\mu_0 I(t)}{2\pi r} = B_0(r) \exp\left[-\frac{t^2}{2\tau^2}\right],$$
(4.26)

$$B(r,t) = \frac{\mu_0 N_{\rm e} e}{(2\pi)^{3/2} \tau r} \left(1 - \exp\left[-\frac{r^2}{2\sigma_r^2}\right] \right) \exp\left[-\frac{t^2}{2\tau^2}\right] \,.$$

 $^{^{4}}$ Another interesting way of looking at the relativistic effect is that the 3 km long Stanford linear accelerator appears to be 3 cm long from the moving frame of a 50 GeV electron!

 $^{{}^{5}}$ The general expression for the field, which is also valid inside or close to the bunch is given by

where

$$B_0(r) = \frac{\mu_0 N_e e}{(2\pi)^{3/2} \tau r} \tag{4.27}$$

is the peak intensity of the magnetic field pulse at a distance r from the center of the bunch. In particular we see from (4.27) that the factor $B_0 \tau$ is directly proportional to $N_e e$, the total amount of charge in the bunch. This factor plays an important role in considering the switching of a magnetic sample by such a beam as discussed in detail in Chap. 15.

The magnetic induction has a peak value B_{peak} at $r = 1.58 \sigma_r$, the outside edge of the bunch. With τ in [ps] and σ_r in [µm] the peak value in Tesla $(1T = 1 \text{ Vs/m}^2)$ is obtained from (4.27) as

$$B_{\rm peak} = \frac{5.8 \times 10^{-9} \, N_{\rm e}}{\sigma_r \, \tau} \, . \tag{4.28}$$

For typical beam parameters $\tau = 1$ ps, $\sigma_r = 1 \,\mu\text{m}$, and $N_e = 2.5 \times 10^{10}$ electrons we obtain a remarkable magnetic peak field amplitude of 145 T. The peak electric field in [V/m] is given by

$$E_{\text{peak}} = c B_{\text{peak}} = \frac{1.74 N_{\text{e}}}{\sigma_r \tau} . \qquad (4.29)$$

For the same beam parameters we obtain a peak electric field of 4.4×10^{10} V/m corresponding to an energy of 9 eV over the 0.2 nm size of an atom. The dependence of the **B** field on the distance from the beam center is shown in Fig. 4.3 for some realistic beam parameters.

The absence of relativistic effects limits the achievable peak current densities in low energy electron beams (energies of tens of keV) that are easily generated in one's laboratory. Since $\ell \sim \ell_0$ for such energies, the strong Coulomb repulsion limits the number of electrons per bunch or pulse, thus precluding the generation of ultrashort low-energy electron pulses with reasonable intensities. Such pulses would be of great value for the study of ultrafast dynamics in many systems, e.g., the study of chemical reactions on the femtosecond scale [159].

Another example of the importance of the relativistic effects discussed above is the beam lifetime in today's electron storage rings used for the generation of synchrotron radiation. In high-brightness storage rings the electron bunch is compressed as much as possible and the beam lifetime is often limited by the so-called *Touschek effect*, which is due to electron–electron scattering within a bunch. It is clear from our discussion above that in the rest frame of the bunch the separation between electrons decreases the scattering. This leads to longer beam lifetimes in higher energy rings.

4.3.3 Creation of Ultrashort Electron Pulses and Fields

Besides being useful for the creation of short and large field pulses, relativistic electron bunches can also be used for the production of short, high-intensity

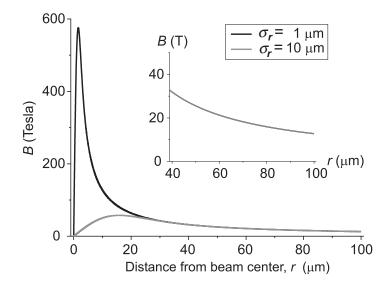


Fig. 4.3. Amplitude of magnetic induction B in units of Tesla as a function from the beam center, measured perpendicular to the propagation direction. We have assumed 1×10^{11} electrons per pulse and a Gaussian bunch profile in all directions, with standard deviations $\sigma_r = \sigma_x = \sigma_y = 1 \,\mu\text{m}$ (black) or $10 \,\mu\text{m}$ (gray) perpendicular to the beam and $\sigma_z = \ell = 330 \,\mu\text{m}$ corresponding to a temporal pulse width of $\tau = 1$ ps. The peak value of the field occurs at $r = 1.58 \,\sigma_r$ from the beam center, effectively at the "edge" of the bunch

synchrotron radiation pulses when bent in a magnetic field, as discussed in more detail later. The shorter the length of the electron bunches in the laboratory frame, the shorter the photon pulses that can be produced with it. In fact both electron and photon pulses have comparable lengths. For the study of ultrafast dynamics by means of high intensity X-rays or with large magnetic field pulses, it is therefore highly desirable to compress the electron bunches, preferably without losing electrons.

This has indeed been accomplished by use of the 3 km long Stanford linear accelerator (linac), which can generate ultrarelativistic electron beams with energies up to 50 GeV. At an energy of 28 GeV a bunch length as short as $24\,\mu\text{m}$ in the laboratory frame has been achieved while maintaining 2×10^{10} electrons in the bunch. Such bunches pass by a point in the laboratory in a time span of 80×10^{-15} s or 80 femtoseconds (fs) and therefore create a peak current of 3×10^4 A. The manipulation of the shape and size of relativistic electron bunches has become a science in itself and so has the accurate measurement of the pulse characteristics.

The bunch compression of nearly a factor of 1,000, from initially 50 ps to 80 fs, actually occurs in three stages. The first compression from 50 ps to 9 ps occurs as the electron bunch travels around a curve and begins its journey down the linac. The second compression occurs at the 1 km point of

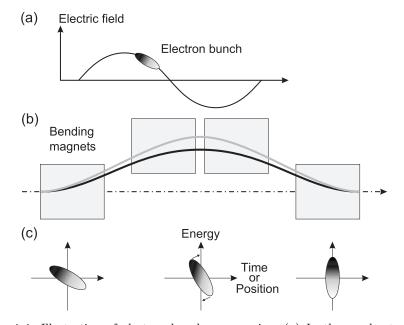


Fig. 4.4. Illustration of electron bunch compression. (a) In the accelerator the relativistic electron bunch can be made to surf on the accelerating RF-wave and acquire an energy/position "chirp", meaning that the electron energy varies with position, being lower in the front and higher in the back of the bunch. Note that at the high energies all electrons in the bunch travel with the same speed, independent of their small energy differences. (b) When passed through a four-bending-magnet chicane the bunch rotates by 90° due to the shorter path of the electrons in the tail. The emerging bunch is compressed in its physical and temporal length but its energy spread is increased as shown in (c)

the linac where the electrons have been accelerated to an energy of 9 GeV. In the acceleration process, the electron bunch is positioned so that it rides slightly ahead of the maximum electric field amplitude of the radio-frequency (RF)-wave as shown in Fig. 4.4a.

By riding the RF-wave the tail of the electron bunch acquires more energy compared to the front. It should be kept in mind that at 9 GeV, all electrons travel very closely with the same speed, the speed of light, irrespective of their energy. The beam then enters a series of four bending magnets, called a "chicane", as illustrated in Fig. 4.4b. The electrons with lower energy, which are located in the front of the bunch, take a longer path through the chicane compared to the electrons with higher energy in the tail end of the bunch. Therefore the tail of the bunch catches up with the front and the bunch is compressed as shown in Fig. 4.4b. The phase space product of pulse length and energy spread is kept constant so that the emerging beam is better defined in time but less so in energy, as shown.

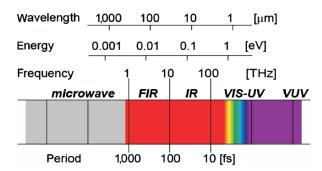


Fig. 4.5. Wavelength, energy, frequency, and oscillation period ranges associated with terahertz radiation. It is seen to fall into the far infrared (FIR) and infrared (IR) parts of the electro-magnetic spectrum

The final compression step occurs at the end of the linac when the beam is compressed from 0.4 ps to 80 fs, corresponding to a bunch length of $12\,\mu$ m. This ultrashort electron bunch can be used to create ultrafast X-ray beams as discussed in Sect. 4.4.2 later.

4.3.4 The Temporal Nature of Velocity Fields

An important characteristic of velocity fields is that both the \boldsymbol{E} and \boldsymbol{B} fields are attached to and move with the charge as illustrated on the right side of Fig. 4.2. The fields do not separate from the charge and hence do not "radiate" away from it [149,160]. For an ultrarelativistic charge the electric and magnetic fields are perpendicular to the direction of charge motion \boldsymbol{v} , so that $\boldsymbol{E} \times \boldsymbol{B} =$ const. \boldsymbol{v} . The two fields are also perpendicular to each other and they obey the same relationship $|\boldsymbol{E}| = c|\boldsymbol{B}|$ just like an electromagnetic wave.⁶ When such an electron beam traverses a sample or passes by it, the velocity fields look to the sample just like an EM wave. The only difference is that the "wave intensity" is not constant along the wavefront but for a line of charges, representative of a relativistic electron bunch, it falls off perpendicular to the beam as the inverse distance from the beam center.

In fact, the picosecond ($\tau = 10^{-12}$ s) field pulses from a linac may be thought of as pseudo-radiation consisting of pseudo-photons with a frequency spectrum extending to about one terahertz (THz), owing to the fact that $1/\tau = 10^{12}$ Hertz = 1 THz. From Table A.1 in the Appendix we find that radiation of 1 THz frequency has a photon energy of $\hbar\omega = 4.14$ meV and a wavelength of 300 µm and corresponds to far-infrared radiation as illustrated in Fig. 4.5.

⁶Strictly, $|\mathbf{E}| = c|\mathbf{B}|$ is only true for photons but for highly relativistic electrons it is a good approximation.

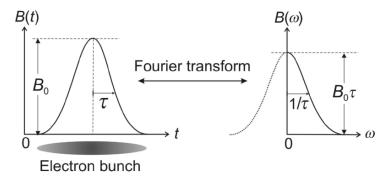


Fig. 4.6. Illustration of a temporal Gaussian magnetic field pulse and its Fourier transform which again is a Gaussian. As the temporal width τ of the pulse decreases the corresponding frequency spectrum of the pulse, given by the Fourier transform contains increasingly higher frequency components

In order to explore this concept in more detail we assume a beam with the Gaussian profile given by (4.26). Its Fourier transform is also a Gaussian as shown in Appendix A.10 and illustrated in Fig. 4.6. It is given by

$$B(r,\omega) = B_0(r) \tau \exp\left[-\frac{\omega^2}{2(1/\tau)^2}\right].$$
 (4.30)

The Fourier transform $B(\omega)$ of the temporal pulse B(t) exhibits a peak at zero frequency (note that only positive frequencies are allowed) whose value $B_0\tau$ is directly proportional to the total integral of the field. The fact that $B(\omega)$ is maximum at zero frequency shows that the field has a major dccomponent. This important fact is discussed in more detail in Appendix A.11, where the properties of a picosecond Gaussian pulse surrounding a relativistic electron bunch are compared to those of terahertz EM waves consisting of only half a cycle or a few cycles. The transform $B(\omega)$ has a bandwidth $1/\tau$ and we see that by making the electron bunch shorter while keeping the number of electrons constant, we add higher frequency components to the Fourier spectrum. We shall see in Chap. 15 that this has important consequences and leads to a limitation of the ultimate speed of precessional switching for magnetic materials.

We have seen above that the fields around a relativistic electron resemble a plane wave moving in the direction of the beam, but with a decaying field strength away from the beam center. This fact can be used in describing the field properties by the *pseudo-photon method* proposed by Fermi [161,162]. In this picture, illustrated in Fig. 4.7, the Fourier spectrum of the temporal pulse profile can be simply thought of as a plot of the number of pseudo-photons as a function of their energy.

When the Fourier intensity is plotted on a logarithmic scale it bears a striking resemblance to the synchrotron radiation intensity emitted by a bending magnet source as a function of photon energy (see Fig. 4.13 later). One may

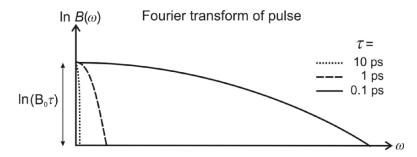


Fig. 4.7. Pseudo-photon spectrum associated with the fields of a relativistic electron bunch in a linac. Shown are the Fourier transforms or the Fourier spectra plotted as a function of frequency for different temporal lengths τ of the electron bunch. As the bunch length gets shorter, the spectrum extends to higher frequency. When the magnitude of the Fourier intensity $B(\omega)$ is converted into the number of pseudophotons according to (4.31), the plot corresponds to the spectrum of pseudo-photons emitted by the bunch. The pseudo-photons propagate in the direction of the bunch and their intensity falls of perpendicular to the bunch as the inverse distance from the center of the bunch

envision that the energy of the electromagnetic field per volume element is stored as $N_{\rm ph}(\omega)$ pseudo-photons per unit energy $\hbar\omega$ in the same volume. This equivalence is expressed by the relation,

$$N_{\rm ph}(\omega) = \frac{B^2(\omega)}{\mu_0 \hbar \omega} = \frac{B_0^2 \tau^2}{\mu_0 \hbar \omega} \exp\left[-\omega^2 \tau^2\right]. \tag{4.31}$$

For example, for an electron bunch of pulse length $\tau = 1$ ps that contains a sufficient number of electrons to create the field $B_0(r) = 1$ T at a point on the sample (which is located at a perpendicular distance r from the center of the beam) we can calculate the number of pseudo photons as a function of frequency or photon energy. We can then calculate the number of $\hbar\omega =$ 1 meV (242 GHz) photons by means of (4.31) and obtain $N_{\rm ph}(\omega) \approx 5 \times 10^{15}$ pseudo-photons. Relativistic electron beams are therefore a powerful source of far-infrared pseudo-photon radiation. For all practical purposes these pseudophotons act on the sample the same way as real photons.

The velocity fields surrounding a relativistic electron beam may be separated from the electron bunch by making the beam traverse a dielectric medium, resulting in so-called *transition radiation*. As the electron bunch approaches the boundary between vacuum and the dielectric medium, it forms an electric dipole with its mirror image in the dielectric. The time-dependent dipole field then causes the emission of EM radiation [163].

4.4 Acceleration Fields: Creation of EM Radiation

The EM fields associated with a moving electron come in two categories as mentioned earlier, velocity fields and acceleration fields. Historically their calculation posed a considerable challenge because of the finite speed of light. The complication arises from the fact that the light that is detected by an observer at a time t at a distance r was actually emitted by the charge at an earlier time t - r/c, called the retarded time. The calculation of the fields radiated by an electron that moves with an arbitrary velocity was first accomplished by Alfred-Marie Liénard (1869–1958) in 1898 [164] and independently by Emil Wiechert (1861–1928) in 1900 [165]. Today, the electric fields and radiation patterns associated with a charge in arbitrary motion can be visualized by the real time radiation simulator written by Shintake, which is available on the web [166].

Before we come to the mathematical description of the fields of a moving charge, the Liénard–Wiechert fields, we shall first discuss the concept of "EM radiation", in particular, how it differs from conventional electric and magnetic fields.

We have learned in Sect. 4.2 that systems that move relative to each other with a constant velocity v, so-called inertial systems, are special in that the laws of nature are invariant in going from one system to another. Whether a charged particle is at rest or in uniform motion, the electric field lines emanating out from the particle to infinity are also at rest or in uniform motion. As illustrated in Fig. 4.2, when the velocity becomes large, the electric field lines in the frame of a stationary observer become squished along the propagation direction, but they are still straight and radial, as shown in Fig. 4.8a. The velocity fields are therefore always intimately attached to the particle.

When a particle is accelerated it moves relative to an inertial system and this causes a distortion of the electric field lines as shown in Fig. 4.8b. Here we have assumed that a particle is accelerated from a time t_0 to the time t_1 with an acceleration **a**. We picture the event in the inertial frame of the particle associated with its uniform motion (v = const.) prior to t_0 . The fact that the particle has accelerated from t_0 to t_1 is known only within a limited area – the event horizon – since the "signal of acceleration" travels away from the particle source at the finite speed of light c. Therefore, field lines outside the shaded radius $c(t_1 - t_0)$ around the position of the particle at time t_0 are the same as before. They still point to the original location of the particle at t_0 . Within the event horizon, the field lines emerging from the particle are bent and join the old straight field lines at the event horizon. The bent field lines within the event horizon have a nonradial component along the direction of acceleration a. It is this field distortion with an E-component parallel to a and traveling away from the particle with the speed of light, that we call radiation.

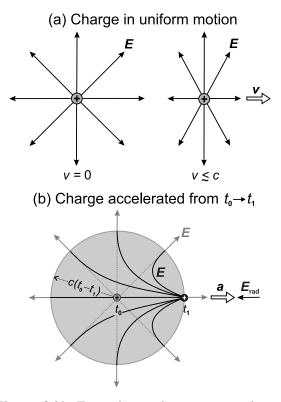


Fig. 4.8. (a) Electric fields E seen by an observer at rest that originate from a charge that is at rest or in uniform motion v = const. (also see Fig. 4.2). In (b) we picture a charge in an inertial reference system (v = const.) that is accelerated from t_0 to t_1 along a direction a. The acceleration causes a distortion of the field lines within an "event horizon" shown in gray shading, given by the distance $c(t_1 - t_0)$ around the charge position at time t_0 . Outside the event horizon the field lines still resemble those at time t_0 . Continuity of the field lines at the event horizon determines the form of the bent field lines inside the horizon (adapted from Wiedemann [160]). The direction of the radiated field E_{rad} is also indicated

Electro-magnetic radiation is the electric field distortion E that is created parallel to the acceleration direction a of a charged particle. It moves away from the particle with the speed of light and the associated fields fall off with the distance r from the particle as 1/r.

In our earlier discussion we have described the field distortion in the inertial frame of the particle which may move with any constant velocity v relative to a stationary observer. In the frame of a stationary observer we also need to account for the effect of the uniform motion v. A simple example is accelerated motion of a particle along a straight line so that both a and

v point in the same direction, as in a linear accelerator. A more important case, however, is if the particle moves around a circle. Then the velocity v is in the tangential direction and the acceleration a points toward the center of the circle. This is the case of synchrotron radiation emitted by an electron storage ring, and we shall come back to it later.

Our conceptual discussion of the difference in velocity and acceleration fields is mathematically founded in the *Liénard–Wiechert field equations*. We shall not derive them here but will simply state the result later. For a detailed discussion the reader is referred to other texts [149, 155, 167]. In particular, the book of Hofmann [155] provides a nice derivation of the field equations and their application to different situations, especially the description of synchrotron radiation. As mentioned earlier, the tricky part in describing the fields mathematically is the treatment of the so-called "retardation effects".

Retardation effects arise from the finite velocity of light. Let us for a moment assume that the velocity of light was infinite. We could then describe all fields in a "snapshot picture" that instantaneously correlates time and position. For example, the E-field measured at a given time could be directly expressed as a function of the position of the charged particle at the same time, as in electro-statics. However, since the speed of light is finite, the snapshot concept does not work in certain cases. For example, for EM radiation there is a time difference between the emission and observation of the light since it takes the light a finite time $\Delta t = R/c$ to travel the distance R. We can then no longer simply write down an expression for the field E(t), measured at an instantaneous time t, in terms of the particle properties (e.g., position, velocity, and acceleration) at that very same time t, since the relevant particle properties that determine E(t) occurred at an earlier time $t^* = t - R/c$.

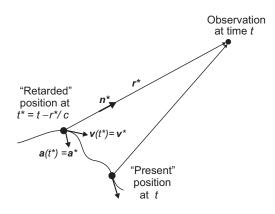


Fig. 4.9. Illustration of the retarded time concept. A charge moves on an arbitrary trajectory. The fields at the observer at a time t are determined by the position r^* , the velocity $v(t^*) = v^*$, and the acceleration $a(t^*) = a^*$ at the retarded time $t^* = t - r^*/c$

This important concept of retardation is illustrated in Fig. 4.9. In order to calculate the field at an observer at time t we must know the position r^* , the velocity $\boldsymbol{v}(t^*) = \boldsymbol{v}^*$, and the acceleration $\boldsymbol{a}(t^*) = \boldsymbol{a}^*$ of the charge q at the retarded time t^* . The relation between t and t^* is given by two general equations [155] but they may have very complicated solutions for certain particle motions!

$$t = t^* + \frac{r^*}{c} , \qquad \mathrm{d}t = \left(1 - \frac{\boldsymbol{n}^* \cdot \boldsymbol{v}^*}{c}\right) \mathrm{d}t^*$$
(4.32)

Liénard and Wiechert succeeded in deriving equations that express the electric and magnetic fields of a point charge in arbitrary motion. Later we give these equations using the notation of Fig. 4.9, where at the time of emission the unit vector $\mathbf{n}^* = \mathbf{r}^*/r^*$ points from the charge to the observer [149, 155, 167].

The Liénard–Wiechert field $\boldsymbol{E}(t)$ of a point charge q detected by an observer at a time t is determined by the distance r^* , the velocity v^* , and acceleration a^* of the charge at the emission or retarded time $t^* = t - r^*/c$. Defining $\boldsymbol{\beta}^* = \boldsymbol{v}^*/c$ we have

$$\boldsymbol{E}(t) = \frac{q}{4\pi\epsilon_0} \underbrace{\frac{1-(\boldsymbol{\beta}^*)^2}{(r^*)^2 (1-\boldsymbol{n}^* \cdot \boldsymbol{\beta}^*)^3} [\boldsymbol{n}^* - \boldsymbol{\beta}^*]}_{\text{velocity field}} + \frac{q}{4\pi\epsilon_0} \underbrace{\frac{1}{c^2 r^* (1-\boldsymbol{n}^* \cdot \boldsymbol{\beta}^*)^3} \{\boldsymbol{n}^* \times ([\boldsymbol{n}^* - \boldsymbol{\beta}^*] \times \boldsymbol{a}^*)\}}_{\text{acceleration field}}.$$
(4.33)

We have indicated all retarded quantities by an asterisk.

Our sign convention is that of Fig. 4.9, where $\mathbf{n}^* \cdot \mathbf{v}^* \geq 0$ is the velocity component of the charge toward the observer. Equation (4.33) is valid for any given motion of the electron with any velocity. However, it holds only if the particle is a point charge. The reason is that only then can the particle's instantaneous motion and position be described in terms of a single retarded time. In (4.33) we have explicitly identified the two contributions to the electric field of the charge.

We readily see that (4.33) yields well known expressions in certain limits. For example, for $v^* = a^* = 0$ we have

$$\boldsymbol{E}(t) = \boldsymbol{E}^{\text{rest}} = \frac{q}{4\pi\epsilon_0 (r^*)^2} \, \boldsymbol{n}^* = \frac{q}{4\pi\epsilon_0 r^2} \, \boldsymbol{n}$$
(4.34)

which is just the Coulomb field of a point charge, and by omission of the asterisk we have indicated that retardation effects are absent. For $a^* = 0$ the

second term in (4.33) vanishes and the first velocity term can be evaluated to yield (4.16) [155]. Note that in our earlier expression (4.16) the distance r is not the distance r^* at the retarded time t^* . Rather, in the actual evaluation of the retarded field expression, r^* has been expressed in terms of the distance r at the observation time t.

We see from (4.33) that the velocity fields decrease with the square of the distance from the charge to the observer while the acceleration fields decrease more gradually with the first power. At large distance the acceleration fields dominate and we see from the second term in (4.33) that the field \boldsymbol{E} is perpendicular to \boldsymbol{n}^* pointing from the charge at the retarded time t^* toward the observer. For both terms in (4.33) the \boldsymbol{E} and \boldsymbol{B} fields are perpendicular and are linked by the following relation (also see Sect. 5.2 later),

$$\boldsymbol{B}(t) = \frac{1}{c} \left[\boldsymbol{n}^* \times \boldsymbol{E}(t) \right] \quad . \tag{4.35}$$

4.4.1 Polarized X-rays: Synchrotron Radiation

Today, one of the most important applications of the Liénard–Wiechert equation (4.33) is the description of synchrotron radiation. It is created by electrons or positrons of constant energy (a few GeV) and velocity that circle around a storage ring. The electrons are propelled forward by a microwave radiofrequency (rf) field that consists of "rf-buckets" that rotate around the ring. Electrons that are filled into a bucket form a so-called "bunch". In the stationary frame of an observer such bunches have a typical length $\ell \simeq 10$ mm, corresponding to a pulse length of about $\tau = \ell/c \simeq 30$ ps, a lateral crosssection of about 100 µm, and one bunch contains of the order of 10^{10} electrons. The charged particles are kept on the desired horizontal orbit by vertical magnetic fields produced at locations around the ring by dipole electro-magnets. Other magnets, such as quadrupoles and sextupoles, help keep the bunches focused to a well defined cross-section. In general, magnetic devices play a prominent role in accelerator technology! Examples of different magnets used in an electron storage ring are shown in Fig. 4.10.

Within a bending magnet, the electron bunch travels on an approximately circular path around the vertical magnetic field lines. The velocity vector \boldsymbol{v} points in the tangential direction and the perpendicular acceleration \boldsymbol{a} points toward the center of the orbit, as illustrated in Fig. 4.11.

The calculation of the emitted acceleration fields, i.e., synchrotron radiation, proceeds via the Liénard–Wiechert equation (4.33) [155]. The calculation of the complete angular and time (or frequency) dependence of the fields is quite complicated and outside the scope of the present book. We shall only touch on some important points and start with the form of the radiation pattern as illustrated in Fig. 4.11.

Magnets in electron storage rings

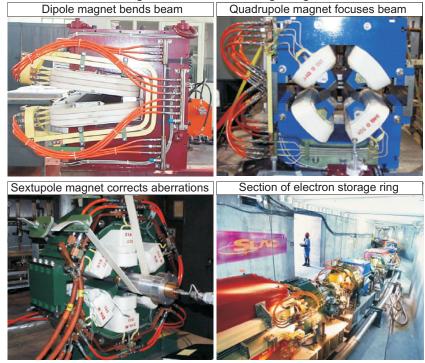


Fig. 4.10. Different kinds of electro-magnets used in charged particle storage rings and, on the bottom right, a complete magnet assembly forming the storage ring SPEAR-3 at SLAC

In the calculation of the angular radiation pattern we can fortunately ignore the time dependence of the fields and therefore do not have to worry about retardation effects. We simply evaluate the fields at the emission (retarded) time and give them at a fixed time later, without their time dependence. Obviously, our approach will not give information on the emitted frequency spectrum of the emitted radiation. We can then drop the asterisk superscripts in (4.33). By evaluating the cross products (see Appendix A.2) we obtain the radiation field \boldsymbol{E} created by an electron (q = -e) as

$$\boldsymbol{E}(t) = -\frac{e}{4\pi\epsilon_0} \frac{[\boldsymbol{n} - \boldsymbol{\beta}](\boldsymbol{n} \cdot \boldsymbol{a}) - \boldsymbol{a}(1 - \boldsymbol{n} \cdot \boldsymbol{\beta})}{c^2 r (1 - \boldsymbol{n} \cdot \boldsymbol{\beta})^3} , \qquad (4.36)$$

where r is the distance between the electron and the observer in the direction n. The E-field is always perpendicular to n.

The radiation pattern is given by the radiated X-ray intensity which is given by the Poynting vector

$$\boldsymbol{S} = \boldsymbol{E} \times \boldsymbol{H} = \frac{1}{\mu_0} \boldsymbol{E} \times \boldsymbol{B}$$
(4.37)

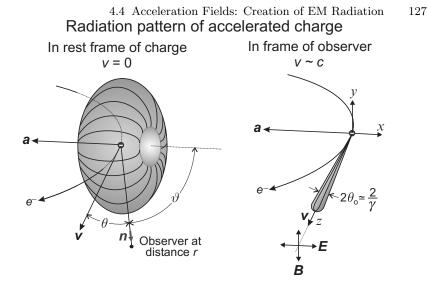


Fig. 4.11. Illustration of the radiation pattern emitted by a charge moving on a circular orbit with a tangential velocity v. The acceleration a points toward the center of the orbit. On the left the radiation pattern is pictured in the rest frame of the charge (v = 0). It has the shape of the donut centered about the axis defined by the acceleration direction a. On the right we show the radiation pattern in the frame of a stationary observer, assuming a relativistic velocity of the charge $v \sim c$. This is the characteristic pattern of synchrotron radiation emitted by electron storage rings. The opening angle containing most of the radiation is about $2/\gamma$ as discussed in the text

and because of (4.35), S can be written in terms of the square of the electric field _____

$$\boldsymbol{S} = \sqrt{\frac{\epsilon_0}{\mu_0}} |\boldsymbol{E}|^2 \boldsymbol{n} = c\epsilon_0 |\boldsymbol{E}|^2 \boldsymbol{n} .$$
(4.38)

By means of (4.36) we obtain for our case of $\boldsymbol{v} \perp \boldsymbol{a}$,

$$S = \frac{ce^2}{16\pi^2\epsilon_0} \frac{a^2(1-n\cdot\beta)^2 - (n\cdot a)^2(1-\beta^2)}{c^4 r^2 (1-n\cdot\beta)^6} .$$
(4.39)

The left case illustrated in Fig. 4.11 corresponds to the radiation pattern observed in the frame of the electron ($\boldsymbol{v} = \boldsymbol{\beta} = 0$). In this case, the pattern given by (4.39) is cylindrically symmetric about the acceleration direction. This is seen by expressing (4.39) in terms of the angle ϑ between \boldsymbol{n} and \boldsymbol{a} , as shown in Fig. 4.11, so that

$$\boldsymbol{S} = \frac{ce^2}{16\pi^2\epsilon_0} \frac{\boldsymbol{a}^2 - (\boldsymbol{n} \cdot \boldsymbol{a})^2}{c^4 r^2} = \frac{ce^2}{16\pi^2\epsilon_0} \frac{a^2 \sin^2 \vartheta}{c^4 r^2} \,. \tag{4.40}$$

The radiation pattern has a node along \boldsymbol{a} ($\vartheta = 0$) and resembles the shape of a donut, as shown on the left in Fig. 4.11. This is the well known *dipole* radiation pattern.

In contrast, the radiation pattern observed by a stationary observer at a large distance from the source is quite different when the electron velocity becomes relativistic, as is the case in a typical electron storage ring operating at an electron energy of several GeV. In this case the pattern is distorted as shown on the right of Fig. 4.11 and most of the intensity is emitted into the forward direction. The distortion is due to relativistic effects, expressed through the terms containing β in (4.39), and it is easily seen by evaluating this equation for different extreme directions of \boldsymbol{n} . While for the (moving) electron rest frame the pattern has a node along the \boldsymbol{a} direction, in the (stationary) observer frame, the nodal direction of the radiation pattern is bent forward in the $\boldsymbol{a} - \boldsymbol{v}$ (or z - x) plane. Defining the angle between the observation direction \boldsymbol{n} and the velocity \boldsymbol{v} as θ (see Fig. 4.11) the node occurs at an angle θ_0 . This angle is readily calculated from (4.39) by finding the condition for zero intensity, i.e.,

$$a^{2}(1-n\cdot\beta)^{2}-(n\cdot a)^{2}(1-\beta^{2})=0$$
. (4.41)

If we take n to lie in the orbit plane of the electron defined by a and v we find the emission angle θ_0 where the intensity has dropped to zero as

$$\cos \theta_0 = \beta \ . \tag{4.42}$$

Rewriting we find $\sin^2 \theta_0 = 1 - \beta^2 = 1/\gamma^2$ and for large γ we obtain

$$\theta_0 = \frac{1}{\gamma} \ . \tag{4.43}$$

The total emission angle in the electron orbit plane, between the two intensity nodes, is therefore $2\theta_0 = 2/\gamma$, as shown on the right side of Fig. 4.11.

Synchrotron radiation is emitted into a narrow cone of opening angle $2/\gamma$.

Originally considered a "waste product" and nuisance in high energy physics because the radiated energy had to be replaced by electric rf-power, over the last thirty years the utilization of synchrotron radiation has had great impact on many areas of science.

In our previous discussion we have neglected the time and frequency dependence of the radiation emitted by the accelerated charge. The full time dependent treatment of the Liénard–Wiechert fields is quite complicated [155] and we shall therefore take a shortcut. Our goal is to understand the physical processes that determine the spectral distribution, intensity vs. frequency, of the emitted radiation.

Just as the pulsed nature of the electron beam determined the pseudophoton spectrum discussed in Sect. 4.3.4, the pulsed nature of the radiation determines the frequency spectrum or band width of the associated fields. We Determination of synchrotron radiation pulse length

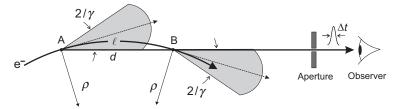


Fig. 4.12. Illustration of the pulse formation of synchrotron radiation. The X-ray pulse seen by an observer through a small aperture has a temporal width Δt that determines the bandwidth $\Delta \omega$ of the synchrotron radiation spectrum as discussed in the text. The length of the arc from A to B is ℓ , that of the straight line is d, and ρ is the bending radius

assume that an observer is located at the end of a "beam line" which is built out in a tangential direction of the storage ring. As the electron bunch travels around the ring it will only radiate down the beam line into the direction of the observer when its radiation cone of full width $2\theta_0 = 2/\gamma$ sweeps by. We shall furthermore assume that the direction of the radiation to the observer is well defined by an aperture as shown schematically in Fig. 4.12.

The duration of the X-ray pulse Δt can be calculated from the time difference between the arrival time of the first photons from point A and the last photons from point B in Fig. 4.12. This is not simply the time it takes the electron to travel along the arc of length ℓ from point A to point B, but rather the difference of the time $t_e = \ell/v$ it takes the electron to move across the arc of length ℓ minus the time it takes the light to cover the straight line of length d from point A to point B. Thus we have

$$\Delta t = \frac{\ell}{v} - \frac{d}{c} = \frac{2\rho}{v\gamma} - \frac{2\rho\sin\left(\frac{1}{\gamma}\right)}{c} .$$
(4.44)

This expression specifically identifies the electron arc length $\ell = 2\rho/\gamma$ as the source of the radiation. It is convenient for our later discussion to express the bending radius ρ experienced by an electron of velocity v in a magnetic field B in terms of the *cyclotron frequency* of a *nonrelativistic electron* given by (3.61) or

$$\omega_0 = \frac{e}{m_{\rm e}} B \qquad (4.45)$$

For a relativistic electron, the mass in the laboratory frame is enhanced by a factor of γ according to (4.23), and accounting for this enhancement we obtain the electron bending radius as

$$\rho = \frac{\gamma \, m_{\rm e} \, v}{e \, B} = \frac{v \, \gamma}{\omega_0}.\tag{4.46}$$

We can now evaluate (4.44) for small angles $1/\gamma$ by using the expansion $\sin(1/\gamma) = 1/\gamma - 1/6\gamma^3$ and for $v \simeq c$ we obtain an expression for a typical width of the emitted radiation spectrum, i.e., the band width,

$$\omega = \frac{1}{\Delta t} = 3 \gamma^2 \frac{e}{m_{\rm e}} B = 3 \gamma^2 \omega_0 \qquad (4.47)$$

It turns out that half this frequency, the quantity $\omega_{\rm C} = 3\gamma^2 \omega_0/2$, actually has a well defined meaning. It corresponds to the so-called *critical energy* $E_{\rm C} = \hbar \omega_{\rm C}$ which divides the total emitted energy, the number of emitted photons times the photon energy, into two equal parts. Because most of the emitted energy is at higher frequencies, $\omega_{\rm C}$ also corresponds to the energy where the number of emitted photons starts to decrease and it is therefore often used as an estimate of the high-frequency "cut-off" of the spectrum. When the emitted intensity is plotted as a function of energy normalized to the critical energy, one obtains a universal synchrotron radiation spectrum [155, 160], which is shown in Fig. 4.13 on linear and logarithmic scales.

The synchrotron radiation spectrum from a bending magnet is determined by the finite pulse length of the radiation seen by a stationary observer, originating from motion of the electron across a small arc of length ℓ .

We have found in (4.47) that the frequency spectrum is related to the angular frequency or cyclotron frequency ω_0 of the moving charge about the

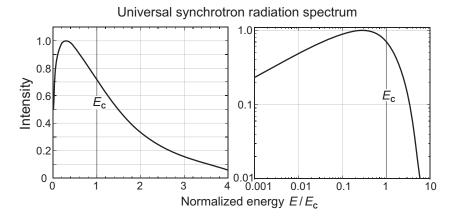


Fig. 4.13. Universal synchrotron radiation spectrum emitted from a bending magnet in an electron storage ring. We have normalized the energy axis to the critical energy E_c and normalized the peak intensity to 1. On the left, the spectrum is plotted on linear scales, on the right on log–log scales. The critical energy divides the total spectrum into two parts of equal area under the curve

perpendicular bending magnet field. One may understand this correlation in another way, namely, that the emitted frequency is determined by the fundamental cyclotron frequency, corrected by reference frame effects for the electron and the emitted radiation. This can be derived in a two step picture. First we place ourselves into the rest frame of the electron (v = 0) just like in Fig. 4.8 and calculate the frequency of the acceleration (radiation) fields created in that frame. We then transform the radiation frequency from the frame of the electron to the frame of the observer by accounting for the Doppler shift.

The idea behind this calculation is that an electron is accelerated in a perpendicular magnetic field due to the Lorentz force $\mathbf{F} = m_{\rm e} \mathbf{a} = -e(\mathbf{v} \times \mathbf{B})$, given by (4.10). This acceleration causes the emission of radiation whose frequency is simply the cyclotron frequency (3.61) $\omega = eB/m_{\rm e}$, where the field is that experienced by the electron in its rest frame. For the electron the bending magnet field B moves toward it with relativistic speed \mathbf{v} and this requires a correction of the field amplitude according to (4.6), leading to an enhancement by a factor of γ so that in the electron rest frame we have

$$\omega_{\rm el} = \gamma \frac{e}{m_{\rm e}} B \ . \tag{4.48}$$

Due to the experienced Lorentz force acceleration, the electron radiates an EM wave with the frequency $\omega_{\rm el}$ in its rest frame, as illustrated in Fig. 4.8. When observed by a stationary observer, the emitted radiation is subject to a Doppler shift. When the radiating electron moves toward an observer in the laboratory with speed $v = c\beta$, the frequency in the laboratory frame $\boldsymbol{\omega}$ is enhanced according to the relativistic Doppler formula [109]

$$\omega = \omega_{\rm el} \, \gamma \, (1+\beta). \tag{4.49}$$

For a relativistic electron we have $\beta \simeq 1$, and the observer sees an EM wave with frequency

$$\omega = 2\gamma^2 \frac{e}{m_{\rm e}} B = 2\gamma^2 \omega_0 \qquad (4.50)$$

This frequency is of the same order of magnitude as the spectral band width given by (4.47). We can therefore make the following statement.

The emitted frequency of synchrotron radiation is determined by the electron cyclotron frequency in the bending magnet field, enhanced by a factor γ due to the relativistic electron motion, and by another factor γ arising from the Doppler shift of the emitted radiation.

The two ways of looking at the origin of the spectrum have the common link that in both pictures the radiation is determined by electron motion across a short arc of length $\ell \simeq 2\rho/\gamma$, illustrated in Fig. 4.12. In one picture

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we consider the time associated with emission of radiation from this arc, in the other we calculate the electron precession frequency or cyclotron frequency associated with electron motion across this arc.

Finally, we briefly address the origin of the polarization of the emitted radiation. While the intensity is governed by the conservation of energy between the electron and photon systems, the polarization is due to the conservation of angular momentum. This is illustrated for a bending magnet source in Fig. 4.14.

As illustrated in Fig. 3.5, the angular momentum of a circulating electron is defined according to the right hand rule. When the fingers of the right hand point in the direction of electron motion, the thumb defines the direction of angular momentum L. For the electron motion shown in Fig. 4.14, L therefore points in the down direction. In the radiation process, energy and angular momentum from the circulating electron are transferred to the x-rays. If radiation in the plane of the electron orbit is selected by a suitable aperture, as illustrated in the middle of the figure, the x-ray propagation direction z is perpendicular to L and the angular momentum component L_z is zero. The emitted radiation is *linearly polarized*.

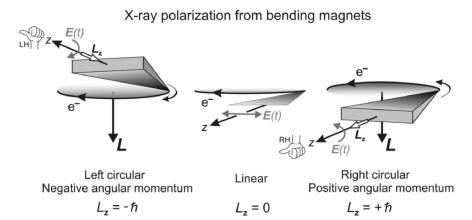


Fig. 4.14. Origin of polarized synchrotron radiation from a bending magnet source. According to Fig. 3.5, electrons moving on a circular orbit have an angular momentum \boldsymbol{L} , which for the electron motion shown here points in the down direction. When the accelerated electron radiates, it transfers both energy and angular momentum to the emitted photons. For radiation emitted in the plane of the electron orbit, as shown in the middle, the x-ray propagation direction z is perpendicular to \boldsymbol{L} . The emitted x-rays have $L_z = 0$ and are *linearly polarized*. In contrast, \boldsymbol{L} has a finite projection L_z along x-ray emission directions below or above the electron orbit plane. For radiation *above* the orbit plane, as shown on the left, the projection of \boldsymbol{L} is along -z and the x-rays have an angular momentum $L_z = -\hbar$. In this case, the \boldsymbol{E} -vector rotates *in time* about the propagation direction (direction of the thumb) according to the left hand rule and the wave is *left circularly polarized*. For radiation *below* the orbit plane, \boldsymbol{L} has a projection along +z, and the x-ray angular momentum has the value $L_z = +\hbar$. Now the right hand rule applies and the wave is *right circularly polarized*.

In contrast, radiation emitted at a finite angle above or below the orbit plane will have a finite angular momentum, since now \boldsymbol{L} has a finite projection L_z along the x-ray propagation direction z. As illustrated in Fig. 4.14, above the orbit plane, the projection L_z is along -z and the circularly polarized wave is called *left handed* and has an angular momentum $L_z = -\hbar$. As discussed in more detail in Sect. 5.4.4 below (see especially Figs. 5.2 and 5.3), we define the "handedness" of the wave as the rotation sense of the \boldsymbol{E} -vector in time relative to the x-ray propagation direction. This is illustrated for x-ray emission above and below the electron orbit plane on the left and right sides of Fig. 4.14, respectively.

It is important to distinguish between the intrinsic angular momentum of a photon L from that along a quantization axis L_z . Since photons are Bosons they possess an even angular momentum L = 1 (in units of \hbar). This leads to the well known optical selection rules $\Delta L = \pm 1$ when the photon angular momentum is transferred in an electronic transition. In contrast, the projection along the quantization direction, L_z , depends on the photon polarization. We need to remember this difference which can be summarized as follows.

Photons are Bosons and possess an even integer angular momentum of magnitude L = 1 (in units of \hbar).

The angular momentum projection along the propagation direction, L_z , depends on the photon polarization. It is $L_z = \pm \hbar$ for circular and $L_z = 0$ for linear polarized photons.

4.4.2 Brighter and Shorter X-ray Pulses: From Undulators to Free Electron Lasers

Starting in the early 1970s, the benefit of synchrotron radiation from bending magnets was recognized and the first experiments were performed. Typically the radiation was used in a parasitic mode, where the control of the accelerator was in the hands of high energy physicists and the synchrotron users were allowed to use the "waste product".⁷ We now call this the first generation of synchrotron radiation research. The success and impact of the early studies led to the construction of dedicated storage rings, the second generation, in the early 1980s.

It soon became clear that tricks could be used to produce radiation with improved properties by manipulating the electron beam by so-called *insertion devices*. These devices that can be inserted in the vacant straight sections of the ring are typically built from permanent magnets. The magnetic fields are configured to make the electron beam oscillate about its propagation direction many times. Devices with strong fields and large oscillation amplitudes are

⁷A notable exception was a small storage ring in Madison, Wisconsin, called Tantalus, which was dedicated to synchrotron radiation production.

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called *wigglers*. In contrast, *undulators* are devices where the beam is only weakly modulated back and forth, either in a plane or on a helical trajectory about the propagation direction. Storage rings designed in the 1990s with optimum space for insertion devices constituted the third generation.

With the beginning of the new millennium, we are embarking on the construction of the fourth generation of synchrotron radiation sources [168]. One may actually argue with this definition because the X-ray free electron lasers now under construction are not mere synchrotron radiation sources. The emitted radiation is no longer simply due to acceleration fields, but is enhanced by a self amplified spontaneous emission (SASE) process that originates from the interaction of synchrotron radiation with the very electron bunch that creates it.

We shall now give a brief discussion of the characteristics of the radiation emitted by insertion devices and free electron lasers. We shall concentrate on concepts rather than details, drawing from the principles underlying synchrotron radiation discussed earlier.

Let us start with wigglers. One may view such devices as many bending magnets lined up with alternating field directions. Therefore the spectrum emitted by wigglers looks similar to that of a bending magnet. It differs in three ways. First, the emitted intensity is enhanced by the number of bends, second, the spectrum has a higher energy cut-off because one uses higher fields (4.47), and finally, the radiation is not circularly polarized but naturally polarized above and below the plane because each bend contributes oppositely. Wigglers are used for experiments that need high photon flux over a wide energy range and have no special polarization requirements.

The undulator spectrum looks quite different. Let us assume that the undulator consists of N oscillation periods of length λ_u (in practice $\sim 5 \text{ cm}$) for a total undulator length of $L = N\lambda_u$. We also assume that the magnetic field deflection of the electron beam is smaller than the natural opening angle $1/\gamma$. Similar to the bending magnet case, we can then calculate the length of the radiation pulse seen by an observer. Because of the weak deflection of the electron beam we can assume that both electrons and photons travel straight as shown in Fig. 4.15.

The radiation delay emitted from two points A and B separated by λ_u is

$$\Delta t = \frac{\lambda_{\rm u}}{v} - \frac{\lambda_{\rm u}}{c} = \frac{\lambda_{\rm u}}{c} \left(\frac{1-\beta}{\beta}\right) \approx \frac{\lambda_{\rm u}}{c} \left(\frac{1}{2\gamma^2}\right). \tag{4.51}$$

Each oscillation period causes the same delay so that the total pulse length seen by the observer is N times longer. This means that the effective bandwidth corresponding to the periodic motion $\Delta \omega = 2\pi/\Delta t$ is reduced by a factor N, the number of undulator periods. The longer effective pulse length therefore leads to more monochromatic radiation with a higher peak intensity. Another way to see this effect is to picture the increased intensity as a constructive interference effect arising from the superposition of the fields Photon emission from an undulator

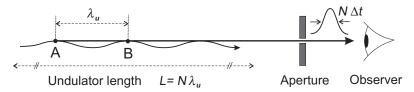


Fig. 4.15. Illustration of radiation from a weak-field undulator with period λ_u , where the deflection angle associated with the electron beam trajectory is smaller than the natural opening angle $1/\gamma$. For each period a delay Δt builds up between the faster photons and the electrons which causes a total delay or pulse length $N\Delta t$ at the position of the observer. This causes a frequency bandwidth reduction by a factor N or an enhancement of the intensity emitted per unit bandwidth. Another way to visualize the enhanced peak intensity is by interference of the fields emitted from the N undulator periods

emitted during the different periods. The wave emitted from point A can constructively interfere with that emitted from point B if the two differ by one wavelength or multiples n thereof, i.e.,

$$n\lambda = c\Delta t = \frac{\lambda_{\rm u}}{2\gamma^2} . \tag{4.52}$$

Thus at such wavelengths we will have an N-fold enhancement of the intensity. The undulator spectrum therefore exhibits a structure of peaked harmonics $n = 1, 2, \ldots$, resulting from interference of the fields emitted during the N radiation periods. For example, a 3 GeV storage ring has a $\gamma \simeq 6 \times 10^3$ and an undulator of period length 5 cm would therefore produce radiation of $\lambda \simeq 0.7$ nm or $\hbar\omega \simeq 1.8$ keV.

The form of (4.52) suggests a simple interpretation of the measured wavelength, similar to what we found for the case of a bending magnet. In the frame of the electron the undulator period is shortened to λ_u/γ due to the relativistic contraction. In fact, the undulator fields look to the electron as an oncoming EM wave of wavelength λ_u/γ . This wave jiggles the electrons which in turn re-emit radiation of the same wavelength. When transformed into the laboratory frame of the observer the radiation is Doppler shifted to an even shorter wavelength by a factor $1/2\gamma$ (see (4.49)).

In practice, undulators in storage rings seldomly have more than about 100 periods, so that the photon flux enhancement is limited to this number. The revolutionary thing associated with undulator radiation, however, is not the photon flux but its brightness (often called "brilliance" in Europe) which exceeds that of bending magnet and wiggler radiation by orders of magnitude. Brightness is the photon flux emitted per unit source area per unit radiation opening angle, where the product (source area \times opening angle) is called the emittance of the source. Undulators are bright because of a dual

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effect, the peak intensity is enhanced at harmonic wavelengths up to a factor N and the emission cone θ_0 associated with these harmonics is reduced as $\theta_0 \propto 1/N$. In practice, θ_0 is of the order of a few microradians, corresponding to a beam diameter of less than 1 mm if one observes it 100 m away from the undulator source. Relative to bending magnet radiation the brightness may thus be enhanced by up to a factor of $N^2 \simeq 10^4$.

Undulators also offer the possibility of complete polarization control. This is accomplished through the creation of the magnetic fields, typically by use of permanent magnets, to induce different periodic electron trajectories through the undulator. When the oscillation is confined to a plane the radiation will be linearly polarized in that plane, with a polarization enhancement relative to a bending magnet due to the many periods. If the path is helical the radiation will be purely circularly polarized with a handedness determined by that of the helix. Today it is possible to construct permanent magnet devices that allow complete polarization control. We can summarize as follows.

The radiation spectrum of an undulator consists of peaks due to the interference of the EM fields emitted from the N undulator periods. The spectral brightness is improved over bending magnets by a factor of up to N^2 , arising from an intensity enhancement by a factor N and another factor N due to the reduction of the emission angle. Undulators allow complete polarization control of the emitted radiation.

We shall not discuss the form of the general undulator spectrum which is complicated for larger fields (up to about 1 Tesla) by the non-negligible oscillation amplitude and the proper treatment of the relativistic Doppler effect for finite emission angles as discussed by Wiedemann [160] and Hofmann [155].

As an example and as the introduction of our next topic, X-ray free electron lasers (X-FEL) [169], we show in Fig. 4.16 the spectrum of a very long undulator (120 m), operated in a strong field mode. In this case the characteristic harmonic structure is still visible but superimposed on a relatively strong continuous background of "wiggler-like" radiation.

The spectrum in Fig. 4.16b was calculated with the parameters of the linac coherent light source, LCLS, the first X-FEL, scheduled to start operation in 2009, with and without the self amplified spontaneous emission or SASE process. An X-FEL consists of a linear accelerator followed by a long undulator (of order 10–100 m) but the X-FEL spectrum is remarkably enhanced by a lasing effect relative to that of an undulator. The operation of a free electron laser was first accomplished in the late 1970s at Stanford [170,171]. Today we distinguish two kinds. When the lasing process is started by interaction of a conventional laser beam with the electron beam (typically an undulator), the system is called a high gain free-electron laser amplifier. If the lasing starts entirely from noise by interaction of electrons in an undulator bunch with

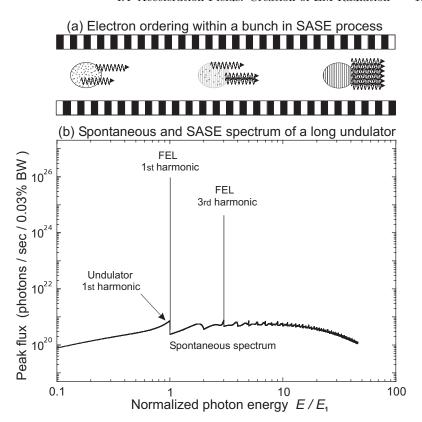


Fig. 4.16. (a) Schematic of the electron ordering within the electron bunch produced by the self amplified spontaneous emission (SASE) process as discussed in the text. (b) Calculated spectrum for the linac coherent light source (LCLS). The photon energy is plotted on a universal scale, normalized to the photon energy of the first harmonic. It falls at 920 eV for a linac beam energy of 4.8 GeV and at 8.3 keV for a beam energy of 14.35 GeV. The spontaneous spectrum of the 120 m undulator shows small peaks indicating the undulator harmonics. At the position of the first and third harmonics, strong and narrow peaks are observed with an intensity increase of four to five orders of magnitude. These peaks arise from gain through SASE associated with lasing. Spectrum courtesy of Roman Tachyn, SSRL

the synchrotron radiation emitted by electrons at the back of the bunch, it is called self amplified spontaneous emission or SASE [172–174].

For the conventional case of an electron bunch moving through an undulator, the total X-ray radiation field generated is the sum of the fields generated by all electrons. When the electrons in a storage ring go through the undulator, there is no correlation between their positions on the scale of the radiation wavelength. As a result, the fields they generate superimpose at random and the radiation is therefore called "spontaneous radiation". Its intensity is proportional to the number of electrons, $N_{\rm e}$, in the bunch. The probability of

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photon emission per electron passing through the undulator is rather low, of order 1%.

In a free electron laser one uses a linac instead of a storage ring, because it offers better spatial and temporal control over the electron beam, and it also readily allows an undulator as long as 100 m to be installed at the end. If the beam is of low quality the emitted spectrum will be that of a long undulator. If the electron bunch has the proper brightness it is possible to arrange the electrons within the bunch in sheets perpendicular to the propagation direction and separated by the X-ray wavelength. The intensity is then proportional to the number of electrons squared, giving an enhancement over the spontaneous undulator spectrum which, in principle, is of order $N_e \simeq 10^{10}$. In the SASE process the periodic electron order is conveniently accomplished by self-organization of the electrons, known as the free-electron laser collective instability. In the process the electron bunch with a random electron position distribution changes into a distribution with electrons regularly spaced at about the X-ray wavelength, as illustrated in Fig. 4.16.

One may describe this remarkable phenomenon by three steps [175]:

- Electrons, propagating through the undulator, interact with the X-ray electromagnetic field generated by other electrons. The interaction changes their energy, and the change is modulated at the X-ray wavelength.
- In the undulator magnetic field the trajectory of electrons with larger (smaller) energy is bent less (more). The resulting length changes of the electron trajectories lead to a periodic grouping of the electrons in planes perpendicular to the propagation direction, separated by the wavelength.
- The electromagnetic fields emitted by the planes of electrons superimpose in phase, and the total field amplitude increases. Thus the electron energy change becomes larger, and the bunching mechanism becomes stronger.

The result is that the amplitude of the electromagnetic field grows exponentially. The rate at which it grows is called the gain length, which depends on the properties of the electron bunch prepared in the accelerator and on the quality of the periodic magnetic fields of the undulator. The exponential growth saturates when all the electrons are well ordered, and emit radiation in phase. The conditions for lasing are harder to achieve at shorter wavelengths and construction of an X-FEL had to await the availability of beams of suitable quality. To reach saturation at an X-ray wavelength of 1 Å with an SASE-FEL operating at 15 GeV electron energy one needs about 1,000 undulator periods. In this case about 0.1% of the electron beam kinetic energy is transformed into photons and one can reach a gain of 10^5 over the spontaneous radiation case as shown in Fig. 4.16b.

Besides orders of magnitude increases in brightness, the emitted X-FEL radiation can also be produced as ultrashort pulses. This is possible because a given electron bunch is simply thrown away after it has done its duty and produced radiation. In contrast to the bunch length in storage rings which is limited by the storage ring equilibrium condition, the electron bunches delivered by linacs can be conveniently compressed by the methods shown in Fig. 4.4. The width of the emitted radiation is then simply determined by the electron bunch length which, under preservation of other important beam parameters to allow lasing, can be compressed to about 100 femtoseconds $(1 \text{ fs} = 10^{-15} \text{ s})$. Improved schemes promise pulses down to the attosecond (1 as $= 10^{-18} \text{ s})$ regime [176].

The remarkable properties of X-FELs are best illustrated by a simple example of an X-ray scattering experiment. With third generation synchrotron radiation sources one obtains a photon flux $(10^{12} - 10^{13} \text{ photons/s})$ on the sample that allows one to record a diffraction pattern in 1 s. With an X-FEL one obtains the same number of photons on the sample in a single ultrashort pulse of order 100 fs. This will offer the opportunity to take snapshots of ultrafast motions with atomic resolution.

We close this chapter with a summary of the characteristics of X-FELs.

A SASE-based X-ray free electron laser consists of a high quality electron beam and a long undulator. The SASE process leads to electron ordering within the electron bunch and exponential growth of the emitted X-ray intensity. The electrons become located in sheets perpendicular to the beam direction, which are spaced by the wavelength of the emitted radiation. The X-ray pulse length is comparable to that of the generating electron bunch.

At the end of the last chapter we were led to the concept of EM radiation. This is indeed an important concept and topic and we shall discuss EM waves now. In the context of this book, EM radiation is important for several reasons. First, EM waves are a key results of Maxwell's theory, showing the connection of electric and magnetic phenomena. Second, modern research in magnetism increasingly utilizes electromagnetic waves in the form of optical and X-ray radiation to explore new materials and phenomena. Third, *polarized* EM waves exhibit important fundamental symmetry properties in addition to the different symmetries of the E and H fields discussed in Sect. 2.7. In particular, we shall discuss the symmetry properties of circularly polarized EM waves in space and time and illustrate them through their interactions with chiral and magnetic materials. The polarization properties of EM fields will constitute an important part of this chapter.

The structure of the chapter is as follows. We start with Maxwell's equations and a look at their symmetries under parity and time reversal. From Maxwell's equations we derive the electromagnetic wave equation. The following section reviews the definition of important quantities like intensity, flux, energy, and momentum of electromagnetic radiation. We then discuss the often confusing definition of the polarization of EM radiation. In particular, we discuss the description of polarized EM radiation in terms of their fundamental linear or circular basis states. We also give the complete description of the general case of elliptical polarization in terms of these basis states.

In the final section we elucidate the important difference between the properties of EM waves in space and time, contained in the terms chirality and angular momentum, by two historically important experiments performed by Faraday around 1845 and Pasteur in 1848 with linearly polarized light. Faraday's experiment, today referred as the *magneto-optical Faraday effect*, revealed the rotation of the polarization vector upon transmission through a magnetically aligned material. Pasteur discovered that a solution of chiral molecules that contains only one type of chirality, i.e., is homo-

$\mathbf{5}$

chiral [177], also rotates the polarization. This effect is today referred to as *optical activity*.

5.1 Maxwell's Equations and their Symmetries

The properties of electric and magnetic fields are summarized in the four Maxwell equations.

Maxwell's equations in the S.I. system are:	
$ abla \cdot \boldsymbol{D} = \rho,$	(5.1)
$\nabla \cdot \boldsymbol{B} = 0,$	(5.2)
$ abla imes oldsymbol{E} = - \dot{oldsymbol{B}},$	(5.3)
$ abla imes oldsymbol{H} = oldsymbol{j} + \dot{oldsymbol{D}}.$	(5.4)
Here ρ is the charge density and j the current density.	

Equations (5.1) and (5.2) determine the static electric and magnetic fields, respectively. In (5.3) we recognize Faraday's induction law mentioned earlier. Ampère's law (2.5) is contained in (5.4) but we see now that it is valid only for stationary electric currents where the dielectric field D does not change with time. The general equation (5.4) includes the curl generated by a varying dielectric field $\dot{D} = dD/dt$.

In vacuum, Maxwell's equations are invariant under the parity transformation. For example, let us look at $\nabla \times \boldsymbol{E} = -\dot{\boldsymbol{B}}$. On the left side both vectors ∇ and **E** are polar vectors and change sign in a parity transformation, so that the vector product is an axial vector, just like \dot{B} on the right side. On the other hand $\nabla \times \boldsymbol{H} = \epsilon_0 \boldsymbol{\dot{E}}$ has a polar vector on both sides of the equation. The scalar product of two like vectors is a true scalar, e.g., $\nabla \cdot \boldsymbol{E} = \rho$. The scalar product of a polar and an axial vector is a "pseudo"-scalar that changes sign upon inversion. A pseudo-scalar must be zero if parity is conserved, and indeed, $\nabla \cdot \boldsymbol{B} = 0$, according to one of Maxwell's equations. This is confirmed by our observations since free magnetic poles have not been found in nature. We see that Maxwell's equations in vacuum are invariant to the parity transformation since polar vectors are always connected with polar vectors and axial vectors with axial ones. This confirms the postulate that parity must be conserved. Hence in vacuum, the equations exhibit the basic symmetries familiar from other great physical theories such as Newton's mechanics. However, they go beyond Newton's mechanics as they are also invariant against the Lorentz transformation in which the length in the direction of the velocity of a coordinate system is contracted while the time is dilated as the velocity approaches the speed of light.

In vacuum, Maxwell's theory is also invariant with respect to time reversal. A light wave travels in opposite directions if time is inverted. Hence time reversal invariance leads to the familiar theorem of geometrical optics that the optical path may be inverted. To prove time reversal invariance in the vacuum, we look at the four Maxwell equations, in turn. Starting with (5.1). time reversal is trivial since neither D nor the electric charge density ρ depend explicitly on time (in the sense illustrated in Fig. 2.11). Equation (5.2) states that the magnetic induction \boldsymbol{B} is free of sources, or in other words it expresses the experimental finding that isolated magnetic poles or "monopoles" do not exist, at least as far as we know today. If magnetic charges existed, time reversal symmetry would be broken since B changes sign with time reversal (see Fig. 2.11), but a stationary magnetic charge would not. In (5.3) $d\mathbf{B}/dt$ contains the time twice hence is independent of the sign of time just like $\nabla \times \boldsymbol{E}$. Finally, in (5.4) all vectors change sign with time reversal. Hence Maxwell's theory is indeed invariant with respect to time reversal. By knowledge of D, \dot{D} , B, and \dot{B} at one particular point in time, all future and past states of the system are determined through the equations. However, this is valid in vacuum, only.

In vacuum, Maxwell's equations are time and parity invariant.

While Maxwell's equations are time and parity invariant in vacuum, this invariance can break down in materials. The two main effects responsible for the breakdown are *transfer of energy and angular momentum*. A prominent example of an irreversible process is electric conduction. In Ohm's law $\mathbf{j} = \sigma \mathbf{E}$, where σ is the electrical conductivity, \mathbf{E} is invariant when time is inverted while \mathbf{j} is not. Hence Ohms law describes an irreversible process. The reason is that the electric current generated by the electric field generates heat, and the heat may never be completely transformed back into electromagnetic energy according to the second law of thermodynamics. The presence of magnetic matter additionally introduces the phenomenon of hysteresis, that is losses through the motion of magnetic domains, which destroys invariance of \mathbf{j} to time reversal, as well.

The damping of spin precession, discussed in Sect. 3.6.2, is another example of an irreversible process. It describes the rotation of the magnetization into the direction of a magnetic field which is indeed one of the fundamental yet ill understood processes governing magnetization dynamics.

5.2 The Electromagnetic Wave Equation

The most important feature of Maxwell's theory was and is the fact that it predicts electromagnetic (EM) waves traveling at the speed of light c. It turns out that $c^2 = 1/\mu_0 \epsilon_0$, hence the speed of light in vacuum, c, can be determined from experiments that measure the force between condenser plates or current

carrying wires, experiments that do not seem to be connected to light at all. The equation that describes EM waves is derived from (5.4). In vacuum, we have $\mathbf{j} = 0$ since there are no particles, and with $\mathbf{D} = \epsilon_0 \mathbf{E}$ and $\mathbf{B} = \mu_0 \mathbf{H}$ we obtain

$$\epsilon_0 \mu_0 \dot{\boldsymbol{E}} - \boldsymbol{\nabla} \times \boldsymbol{B} = 0 \ . \tag{5.5}$$

Differentiating with respect to time t yields $\epsilon_0 \mu_0 \ddot{\boldsymbol{E}} - \nabla \times \dot{\boldsymbol{B}} = 0$ and with (5.3) we obtain

$$\epsilon_0 \mu_0 \ddot{\boldsymbol{E}} + \boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{E}) = 0 .$$
 (5.6)

This is already the wave equation. We are left with only one field, namely \boldsymbol{E} , and the second derivative with respect to time is connected to the derivative with respect to location. By means of the identity $\nabla \times (\nabla \times \boldsymbol{E}) = \nabla (\nabla \cdot \boldsymbol{E}) - \nabla^2 \boldsymbol{E}$ of Appendix A.2 and since $\nabla \cdot \boldsymbol{E} = 0$ in vacuum we obtain the wave equation for the electric field vector of an EM wave travelling at the speed $c = 1/\sqrt{\mu_0 \epsilon_0}$, in its familiar form.

In vacuum, and to a good approximation in air, the wave equation for the electric field is given by

$$\frac{1}{c^2} \, \ddot{\boldsymbol{E}} - \nabla^2 \boldsymbol{E} = 0 \, . \tag{5.7}$$

Any electric field $E(\mathbf{r}, t)$ that satisfies (5.7) is called an electromagnetic (EM)-wave. The equation shows that the *temporal variation* of \mathbf{E} is directly linked with the *spatial variation*. The equation is invariant to time reversal as expected and consequently, the optical path can be inverted as long as there is no damping of the wave.

One solution of (5.7) is $E(\mathbf{r},t) = \text{const.} e^{\pm i(\mathbf{k}\mathbf{r}-\omega t)}$. It describes a wave propagating in the direction of the wave vector \mathbf{k} and has positive phase velocity. Another solution describing a wave that propagates in the opposite direction $-\mathbf{k}$ is $E(\mathbf{r},t) = \text{const.} e^{\pm i(\mathbf{k}\mathbf{r}+\omega t)}$. It has a negative phase velocity. Within this book we shall make a choice of phase which follows that of Jackson [149] and is also commonly used in the X-ray literature [109, 178].

We describe the *electric and magnetic fields of an EM wave* traveling in the direction of the wavevector $\mathbf{k} = (\omega/c)\mathbf{k}_0$ as

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{\epsilon}_{\mathrm{p}} E_0 \,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \,, \qquad (5.8)$$

and

$$\boldsymbol{B}(\boldsymbol{r},t) = \frac{1}{c} (\boldsymbol{k}_0 \times \boldsymbol{\epsilon}_{\mathrm{p}}) E_0 \,\mathrm{e}^{\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} \;. \tag{5.9}$$

Here $\epsilon_{\rm p}$ is a unit polarization vector, which is real for linear polarized waves and complex for circularly polarized waves as discussed later.

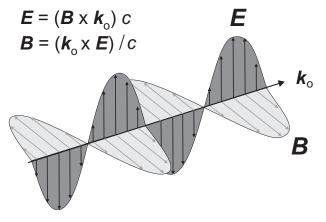


Fig. 5.1. Amplitude and phase of a linearly polarized electromagnetic wave. The electric field vector E characterizes the polarization direction. It is in phase with the magnetic field vector B and they are both perpendicular to the X-ray propagation, labelled by the unit wave vector k_0

The wave equation can also be written in terms of the magnetic field by simply substituting $E \to B$ in (5.7). The related nature of the electric and magnetic fields is also evident from Fig. 5.1, where we show the relationship between the E and B fields in a linearly polarized EM wave.

It is remarkable that the wave equation describes EM waves with wave lengths $\lambda = 2\pi/k$ that span the enormous range from km to the dimensions of the atomic nucleus.

5.3 Intensity, Flux, Energy, and Momentum of EM Waves

The magnitude and direction of energy flow of an EM wave is given by the Poynting vector

$$\boldsymbol{S} = \boldsymbol{E}(\boldsymbol{r}, t) \times \boldsymbol{H}(\boldsymbol{r}, t) \tag{5.10}$$

whose units $[VAm^{-2}]$ show that it represents the radiated power per unit area or the energy per unit time per unit area. With (5.8) and (5.9) and using the relations $\boldsymbol{B} = \mu_0 \boldsymbol{H}$ and $c = 1/\sqrt{\epsilon_0 \mu_0}$ we obtain

$$\boldsymbol{S} = \sqrt{\frac{\epsilon_0}{\mu_0}} |\boldsymbol{E}|^2 \boldsymbol{k}_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} |\boldsymbol{H}|^2 \boldsymbol{k}_0 , \qquad (5.11)$$

and can now determine the size of the electric and magnetic fields from the incident power density.

The electric field $|\boldsymbol{E}|$ in $[V m^{-1}]$ and magnetic field $|\boldsymbol{H}|$ in $[A m^{-1}]$ are obtained from the incident power density $|\boldsymbol{S}|$ in $[W m^{-2}] = [V A m^{-2}]$ as $|\boldsymbol{E}| = 19.41 \sqrt{|\boldsymbol{S}|}, \qquad (5.12)$

$$H| = 0.0515 \sqrt{|S|}$$
 (5.13)

Some important quantities associated with an EM wave include the *total* energy which is [149]

$$E = \frac{1}{2} \int_{V} \left(\epsilon_0 |\boldsymbol{E}|^2 + \frac{1}{\mu_0} |\boldsymbol{B}|^2 \right) \, \mathrm{d}V = \epsilon_0 \int_{V} |\boldsymbol{E}|^2 \, \mathrm{d}V, \tag{5.14}$$

where we have used (5.11) to obtain the last expression. By confining the EM fields to a box of volume V we obtain [149]

Energy:
$$E = \frac{V}{2} \left(\epsilon_0 |\mathbf{E}|^2 + \frac{1}{\mu_0} |\mathbf{B}|^2 \right) = \epsilon_0 V |\mathbf{E}|^2$$
. (5.15)

When the EM field is quantized the energy given by (5.14) simply becomes the photon energy $\hbar\omega$. Using the same box normalization, the classical expression of the *momentum* of an EM wave is [149]

Momentum :
$$\boldsymbol{P} = \frac{V}{c^2} \boldsymbol{S} = \frac{\epsilon_0 V}{c} |\boldsymbol{E}|^2$$
, (5.16)

where \boldsymbol{S} is the Poynting vector with magnitude $|\boldsymbol{S}| = \epsilon_0 c |\boldsymbol{E}|^2$. The momentum has the dimension (energy \times time/length).

Other important properties of an EM wave are the incident *intensity*, I_0 , and the *photon flux*, Φ_0 , which will be needed for the quantitative description of X-ray scattering and absorption, below. Classically, the X-ray *intensity* is given by the Poynting vector

Intensity:
$$I_0 = |\mathbf{S}| = \epsilon_0 c |\mathbf{E}|^2$$
, (5.17)

and it has units of [power/unit area] or [energy/(time \times unit area)]. The *photon flux* is defined as the number of photons per second per unit area, and is given by the magnitude of the Poynting vector, divided by the photon energy

Flux :
$$\Phi_0 = \frac{|\mathbf{S}|}{\hbar\omega} = \frac{\epsilon_0 c |\mathbf{E}|^2}{\hbar\omega}$$
. (5.18)

As an example let us calculate the size of the electric and magnetic fields in a typical X-ray beam available at third generation light sources. X-ray scientists think in term of the photon flux Φ_0 defined by (5.18), that is the number of photons per second per unit area. From the photon flux we readily obtain the magnitude of the Poynting vector by multiplication with the photon energy in eV and the conversion factor $1 \text{ eV} = 1.602 \times 10^{-19} \text{ Ws}$. Assuming a photon energy of 1,000 eV and a photon flux $\Phi_0 = 10^{12}$ photons per (s mm²) we obtain a power density $|\mathbf{S}| = 1.602 \times 10^2 \text{ Wm}^{-2}$. This gives $|\mathbf{E}| = 246 \text{ Vm}^{-1}$ and $|\mathbf{H}| = 0.65 \text{ Am}^{-1} = 8 \times 10^{-3} \text{ Oe}$. These are weak fields corresponding to an electric field on the atomic scale of $2.5 \times 10^{-8} \text{ V Å}^{-1}$ and a magnetic field that is about 1,000 times weaker than the earth's magnetic field.

The situation changes dramatically for an X-ray free electron laser (X-FEL) source. In contrast to a storage ring which can be considered a continuous wave (CW) source a XFEL is a pulsed source and the relevant quantities are the peak fields. At a photon energy of 1,000 eV an XFEL delivers about $\sim 10^{13}$ photons in an ultrashort flash of 200 fs, yielding a peak power of about 1×10^{10} W. This power is contained in the unfocused beam of $100 \times 100 \,\mu\text{m}^2$ cross section emerging from the laser source. In order to look at the extreme power density limit for such a beam, let us assume that we can focus the beam to a spot size of $1 \,\mu\text{m}^2$ with a loss of a factor 2 through the optical system. This would yield a peak power density $|\mathbf{S}| = 5 \times 10^{21} \,\text{W m}^{-2}$. The fields are enormous in this case. We obtain $|\mathbf{E}| = 1.5 \times 10^{12} \,\text{V m}^{-1}$ or on the scale of an atom $150 \,\text{V} \,\text{\AA}^{-1}$. The magnetic field is $|\mathbf{H}| = 3 \times 10^9 \,\text{A m}^{-1} = 3.8 \times 10^7 \,\text{Oe}$ which, as we shall see in Sect. 11.1.1, rivals the molecular or exchange field in a ferromagnet.

5.4 The Basis States of Polarized EM Waves

5.4.1 Photon Angular Momentum

The concept of angular momentum is well defined in classical mechanics, yet it cannot easily be transferred to the case of an EM wave which has no mass. In a classical picture one would expect a wave that exhibits a rotation in time to have an angular momentum. Indeed, we shall see that this intuition is correct. A beautiful experiment by Beth in 1936 [179] proved this picture. Using a high precision torsion pendulum he measured the transfer of angular momentum from a circularly polarized wave to an absorbing sample.

The angular momentum of circularly polarized EM waves is described most elegantly through quantum theory where observables are always defined as expectation values of operators. Photons are Bosons with angular momentum quantum number L = 1 (in units of \hbar). It is customary to define the photon angular momentum by the quantum number L_z , i.e., by the expectation value of the angular momentum operator along the propagation direction z, $\langle L_z \rangle$.

When a photon is absorbed by an atomic electron, the *dipole selection rule* places a restriction on the change in angular momentum quantum number. The excited electron has an angular momentum l that can only differ from that before the excitation by the quantum number of the photon L = 1,

hence $\Delta l = \pm 1$. For example, a *p* electron with l = 1 becomes either an *s* electron with l = 0 or a *d* electron with l = 2, satisfying a change in angular momentum quantum number by one unit of \hbar . This change in *l* is independent of photon polarization. In contrast, the expectation value $\langle L_z \rangle$ defines a specific projection along the photon propagation direction $\mathbf{k} \parallel z$ that depends on the polarization state of the photon. We can upfront state as follows.

The magnitude of the photon angular momentum is L = 1 (in units of h), independent of the state of polarization.

The polarization-dependent photon angular momentum is the expectation value $\langle \mathbf{L}_z \rangle = L_z = 0, \pm 1$ (in units of \hbar) along the photon propagation direction $\mathbf{k} \parallel z$.

Before we can discuss how this comes about, we need to discuss the formalism used to describe the polarization of an EM wave. It turns out that a general polarization state can be written as a linear combination of two orthogonal "pure" states or basis states, either two linearly polarized states or two circularly polarized states. Examples are elliptically polarized light, typically encountered in conjunction with synchrotron radiation, and "unpolarized" or naturally polarized light emitted by conventional discharge lamps or X-ray tubes. Let us therefore look at the definition of linearly and circularly states.

As mentioned above, we conveniently choose the X-ray propagation direction k along +z, so that the electric field vector lies somewhere in the x, yplane of our coordinate system.

5.4.2 Linearly Polarized Basis States

We start with the time and space dependent fields of a linearly polarized electromagnetic wave with frequency ω and wavelength $\lambda = 2\pi/|\mathbf{k}|$, traveling in the direction of the wavevector $\mathbf{k} = (\omega/c)\mathbf{k}_0$, given by (5.8) and (5.9) and pictured in Fig. 5.1. It is customary to define the unit photon polarization vector $\boldsymbol{\epsilon}_{\rm p}$ to point in the direction of the electric field \boldsymbol{E} . For linearly polarized light the polarization $\boldsymbol{\epsilon}_{\rm p}$ is real. By choosing $\boldsymbol{\epsilon}_{\rm p}$ to lie along the x and y directions we have the following two basis states for the electric field $\boldsymbol{E}(\boldsymbol{r},t)$.

Two *linearly polarized basis states* are given by

 $\boldsymbol{E}_{x}(z,t) = \boldsymbol{\epsilon}_{x} \, E_{0x} \, \mathrm{e}^{\mathrm{i}(kz-\omega t) + \mathrm{i}\phi_{0x}} \, . \tag{5.19}$

$$\boldsymbol{E}_{y}(z,t) = \boldsymbol{\epsilon}_{y} \, E_{0y} \, \mathrm{e}^{\mathrm{i}(kz - \omega t) + \mathrm{i}\phi_{0y}} \, . \tag{5.20}$$

The unit vectors $\boldsymbol{\epsilon}_x$ and $\boldsymbol{\epsilon}_y$ are real. The phases ϕ_{0x} and ϕ_{0y} define the phase factors for t = z = 0.

5.4.3 Circularly Polarized Basis States

The unit polarization vectors for a linearly polarized wave are real and the electric field vector oscillates along an axis in space, perpendicular to k. For circularly polarized light, E rotates in space and time and the endpoints of E move on a circle, so that the x and y components have equal magnitudes but are phase shifted relative to each other by $\pi/2$. The constant phase relationship of the two linear components therefore creates a *coherent superposition*.

A circularly polarized wave is a coherent superposition of two orthogonal linearly polarized waves with equal amplitude but a relative phase shift of $\pi/2$.

The 90° phase rotation of the two linear components is mathematically expressed by constructing new complex unit polarization vectors for circularly polarized waves of the form,

$$\boldsymbol{\epsilon}_x \pm \mathrm{i}\boldsymbol{\epsilon}_y = \boldsymbol{\epsilon}_x + \mathrm{e}^{\pm \mathrm{i}\pi/2}\boldsymbol{\epsilon}_y. \tag{5.21}$$

The two different linear combinations are commonly referred to as "left" and "right" circular polarization. The two complex circular states are also orthogonal and can be used as alternative basis states for the description of polarization.

We define the rotation sense of the circularly polarized waves, described by (5.21), by the following picture. When the thumb points in the direction of $z \parallel \mathbf{k}$ we determine the rotation sense of the \mathbf{E} -vector in time according to the right or left hand rules, as shown in Fig. 5.2. When the right hand rule applies, we call the wave right circular. Similarly, we call a wave that follows the left hand rule *left circular*. We shall identify the two waves by the labels \mathcal{L} for "left" and \mathcal{R} for "right" and use the abbreviations LCP and RCP.

At this point a short note on the definition of "handeness" is necessary. Close inspection of Fig. 5.2 reveals that the rotation sense of a given circularly polarized wave about its propagation direction is opposite in space and time. We have applied the right and left hand rules to the *temporal* motion of \boldsymbol{E} about the propagation direction \boldsymbol{k} (taken to be the direction of the thumb). This is the convention typically used in high energy physics [118]. In the optics community, it is customary to use the opposite definition, which corresponds to either pointing the thumb toward the source of the wave, i.e. in the direction $-\boldsymbol{k}$, or applying the right and left hand rules to the motion of the \boldsymbol{E} -vector in space with the thumb along \boldsymbol{k} [180].

Mathematically, our definition corresponds to the following circular polarization basis states. A RCP wave is described by

$$\boldsymbol{E}_{\mathcal{R}}(z,t) = -\frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_x + \mathrm{i}\boldsymbol{\epsilon}_y \right) E_0 \,\mathrm{e}^{\mathrm{i}(kz - \omega t) + \mathrm{i}\phi_0} \,. \tag{5.22}$$

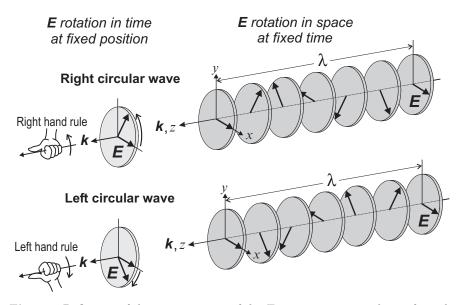


Fig. 5.2. Definition of the rotation sense of the E-vector in space and time for right and left circularly polarized waves. When the thumb of the right hand points in the direction of the wave vector k, the E-vector rotates in time according to the right hand rule for a right circular wave. Similarly, the rotation sense in time for a left circular wave is determined by the left hand rule

where the overall minus sign is chosen to conveniently agree with the sign convention used for spherical harmonics or spherical tensors as used later in Chap. 10. A LCP wave has the form

$$\boldsymbol{E}_{\mathcal{L}}(z,t) = \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_x - \mathrm{i}\boldsymbol{\epsilon}_y) E_0 \,\mathrm{e}^{\mathrm{i}(kz - \omega t) + \mathrm{i}\phi_0} \,. \tag{5.23}$$

The real phase factor ϕ_0 , which we are free to choose, defines the phase of the waves at $kz = \omega t = 0$. It does not affect the relative phase shift of $\pm 90^{\circ}$ between the two linear components.

In magneto-optics, of interest in conjunction with our book, we are concerned with the spin or angular momentum L of an electromagnetic wave and hence one would like to know which way the angular momenta of our LCP and RCP waves point. Let us therefore use a quantum mechanical approach to calculate the angular momentum of the two waves in (5.23) and (5.22).

The angular momentum of an EM wave is defined as the projection of the angular momentum vector \boldsymbol{L} along the photon propagation direction \boldsymbol{k} , taken to be the z-axis, and is calculated according to

$$\langle L_z \rangle = \frac{\int E^*(z,t) L_z E(z,t) d\Omega}{\int E^*(z,t) E(z,t) d\Omega} , \qquad (5.24)$$

To evaluate this expression we describe the motion of the E vector in the x, y plane in terms of the well-known spherical harmonics $Y_{\ell,m}$ for $\ell = 1, m = \pm 1$ [181, 182],

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{4\pi}} \frac{1}{\sqrt{2}} \frac{x \pm iy}{r} , \qquad (5.25)$$

with $r = \sqrt{x^2 + y^2}$. We recognize the similarity between the form of $Y_{1,\pm 1}$ and the vectors $\mp(\epsilon_x \pm i\epsilon_y)/\sqrt{2}$ in (5.23) and (5.22). We can write the vector equations for $E_{\mathcal{R}}(z,t)$ and $E_{\mathcal{L}}(z,t)$ in *scalar* forms by using

$$\mp \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_x \pm \mathrm{i} \boldsymbol{\epsilon}_y \right) \cdot \frac{\boldsymbol{r}}{r} = \mp \frac{1}{\sqrt{2}} \frac{x \pm \mathrm{i} y}{r} = \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}.$$
(5.26)

By choosing $\phi_0 = 0$ in (5.23) and (5.22), which we are free to do, we can write

$$E_{\mathcal{R}}(z,t) = -\frac{1}{\sqrt{2}} \frac{x+iy}{r} E_0 e^{i(kz-\omega t)} = \sqrt{\frac{4\pi}{3}} Y_{1,+1} E_0 e^{i(kz-\omega t)} , \qquad (5.27)$$

and

$$E_{\mathcal{L}}(z,t) = \frac{1}{\sqrt{2}} \frac{x - iy}{r} E_0 e^{i(kz - \omega t)} = \sqrt{\frac{4\pi}{3}} Y_{1,-1} E_0 e^{i(kz - \omega t)} .$$
(5.28)

By use of the well-known normalization properties of the spherical harmonics $\int Y_{\ell,m}^* Y_{\ell,m} \, d\Omega = 1$ and the property $\int Y_{\ell,m}^* L_z Y_{\ell,m} \, d\Omega = \hbar m$ we can now calculate the angular momentum expectation value $\langle \mathbf{L}_z \rangle$ of the EM waves (5.27) and (5.28) according to (5.24) and obtain $\langle \mathbf{L}_z \rangle = +\hbar$ for the wave $\mathbf{E}_{\mathcal{R}}(z,t)$ and $\langle \mathbf{L}_z \rangle = -\hbar$ for $\mathbf{E}_{\mathcal{L}}(z,t)$. Another way of establishing this identity is discussed in Sect. 8.7.

This leads to the following mathematical definitions of pure circularly polarized EM waves or basis states.

A right circular photon basis state has angular momentum or photon spin $+\hbar$ and is described by

$$\boldsymbol{E}_{\mathcal{R}}(z,t) = \boldsymbol{E}_{+}(z,t) = -\frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_{x} + i\boldsymbol{\epsilon}_{y} \right) E_{0} e^{i(kz-\omega t)+i\phi_{0}} .$$
 (5.29)

A left circular photon basis state has angular momentum or photon spin $-\hbar$ and is given by

$$\boldsymbol{E}_{\mathcal{L}}(z,t) = \boldsymbol{E}_{-}(z,t) = \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_{x} - i\boldsymbol{\epsilon}_{y}) E_{0} e^{i(kz-\omega t)+i\phi_{0}} .$$
(5.30)

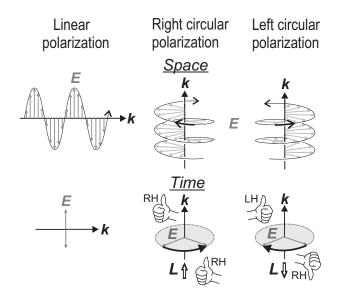


Fig. 5.3. Illustration of linearly and circularly polarized light, showing the motion of the polarization vector E in space and time. For RCP the angular momentum L points into the direction of k and has the value $+\hbar$, and for LCP L points into the direction -k and has the value $-\hbar$. Comparison with Fig. 2.11 shows that that L is an axial vector

The particular sign conventions in (5.29) and (5.30) correspond to the following complex unit polarization vectors

$$\boldsymbol{\epsilon}^{+} = \boldsymbol{\epsilon}^{\mathcal{R}} = -\frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_{x} + \mathrm{i}\boldsymbol{\epsilon}_{y}) , \qquad (5.31)$$

and

$$\boldsymbol{\epsilon}^{-} = \boldsymbol{\epsilon}^{\mathcal{L}} = \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_{x} - \mathrm{i}\boldsymbol{\epsilon}_{y}) . \qquad (5.32)$$

Note that the signs of ϵ^{\pm} agree with those of unit spherical tensors [181, 182], which we shall encounter in the calculation of the X-ray magnetic circular dichroism effect in Chap. 10.

The properties of the waves are summarized and illustrated in Fig. 5.3. In contrast to the rotation sense of E which changes from left to right handed for the two circular waves, the direction of the angular momentum vector L is always determined by the right hand rule relative to rotation direction of E in time. This shows that L is an axial vector.

5.4.4 Chirality and Angular Momentum of Circular EM Waves

From a modern physics point of view it is important to distinguish what aspect of a circularly polarized EM wave one uses in an experiment. There are two important properties of an EM wave: its *angular momentum* and its handedness or *chirality*. Let us take a look at these important concepts and their difference.

In an X-ray experiment of a magnetic sample, the angular momentum of the EM wave couples to the atomic magnetic moments or angular momenta. There is a difference in this coupling whether the angular momenta of the wave and the sample are parallel or antiparallel. This gives rise to the now well known X-ray magnetic circular dichroism (XMCD) effect. The important point is that only the motion of the \boldsymbol{E} vector in time, that is its angular momentum, is important. Indeed, XMCD is calculated by assuming that the forward rotation of the \boldsymbol{E} vector in space can be neglected because the atom is so small – the famous dipole approximation.

In contrast, X-ray studies of nonmagnetic samples consisting of chiral molecules depend on the spatial rotation of the E vector in space, that is the chirality of the EM wave. Now a difference in interaction is observed when the chirality of the EM wave and the chirality of the sample (left or right) are the same or opposite. This gives rise to the well known *natural circular dichroism* (NCD) effect. The importance of the spatial property of the EM wave is reflected by the fact that the NCD effect is zero when the dipole approximation is assumed. In order to account for it one must go beyond the dipole approximation and take into account the spatial forward rotation of the E vector over the absorbing volume.

It is therefore important to understand the difference between the concepts of "angular momentum" and "chirality."

Chirality is defined by a "static" handedness in three-dimensional space. Rotations in space do not change chirality. The chirality is parity-odd (right-handed) and time-even.

Angular momentum is characterized by a handed temporal motion, that is, by a handedness in *time*. A 180° rotation in space changes the sign of the angular momentum. The angular momentum is time-odd $(+\hbar \leftrightarrow -\hbar)$ and parity-even.

Our definitions above clearly show the difference of the two concepts in terms of their symmetry properties. It is interesting and very important that the chirality is preserved if the handed structure is rotated in threedimensional space. Rotations do not change parity and handedness. Only

reflections do.¹ This has important consequences. For example, in order to determine the preferential handedness of biological molecules one does not have to orient the individual molecules but can measure them in the liquid state. This allowed Louis Pasteur to discover the existence of handedness in nature, about 150 years ago, by measuring the *optical activity* of organic molecules in solution. We shall come back to the concepts of temporal (angular momentum) and spatial (chirality) handedness in Sect. 5.6, where we will illustrate the difference by two famous experiments.

At the end of this section we briefly mention that modern optics allows one to create photon states with unusual polarizations [184] and wave topographies. A particularly interesting state is an *optical vortex* which exhibits both chirality and angular momentum [185]. It may be created in the X-ray regime by sending a coherent linearly polarized beam through a suitable transmission phase mask [186]. Such beams are characterized by a helical or corkscrewlike trajectory of the Poynting vector around the propagation direction \mathbf{k} and exhibit zero field amplitude at the beam center. The creation of such beams has led to a distinction in the literature between the "angular momentum" of such light beams from the "spin" of conventional circularly polarized beams [187,188]. We shall not follow this distinction here but throughout this book we shall use the following terms for the polarization properties of light.

In conjunction with *magnetism* we shall label circular polarization by the synonymous terms "photon angular momentum" \equiv "photon spin."

5.4.5 Summary of Unit Polarization Vectors

The above section on pure linear and circular polarization states can be summarized as follows. We can express the polarization of any EM wave travelling in the z direction in terms of either linear or circular unit polarization vectors.

The real unit polarization vectors of *linear polarized EM waves* are:

$$\boldsymbol{\epsilon}_{x} = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}^{-} - \boldsymbol{\epsilon}^{+} \right) = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}^{\mathcal{L}} - \boldsymbol{\epsilon}^{\mathcal{R}} \right) , \qquad (5.33)$$

$$\boldsymbol{\epsilon}_{y} = \frac{\mathrm{i}}{\sqrt{2}} \left(\boldsymbol{\epsilon}^{-} + \boldsymbol{\epsilon}^{+} \right) = \frac{\mathrm{i}}{\sqrt{2}} \left(\boldsymbol{\epsilon}^{\mathcal{L}} + \boldsymbol{\epsilon}^{\mathcal{R}} \right) , \qquad (5.34)$$

¹Rotations followed by reflections perpendicular to the rotation axis are called *improper rotations* [183]. The parity operation corresponds to a rotation of 180° about an axis followed by a reflection through a plane perpendicular to the rotation axis. A mirror reflection corresponds to a 360° rotation followed by a reflection through a plane perpendicular to the rotation axis.

The complex unit polarization vectors of *circular polarized EM waves* are: $\boldsymbol{\epsilon}^{+} = \boldsymbol{\epsilon}^{\mathcal{R}} = -\frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_{x} + i\boldsymbol{\epsilon}_{y} \right) , \qquad (5.35)$ $\boldsymbol{\epsilon}^{-} = \boldsymbol{\epsilon}^{\mathcal{L}} = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_{x} - i\boldsymbol{\epsilon}_{y} \right) . \qquad (5.36)$

5.5 Natural and Elliptical Polarization

We can construct an EM wave with arbitrary polarization from two linearly or two circularly polarized basis states. In describing different experiments the specific choice of basis states often simplifies the mathematical description. There are two important general polarization states, natural polarization and elliptical polarization and we shall discuss them below.

5.5.1 Natural Polarization

Let us first consider *natural light* or "unpolarized" light. The term "unpolarized" light is a bit of a misnomer since the E vector still lies in a well-defined plane perpendicular to the propagation direction because of the transverse nature of EM waves. This leads to polarization effects, e.g., in X-ray absorption spectroscopy, even for natural light. Hence we prefer the name natural polarization. Natural light is composed of a rapidly varying succession of different polarization states, i.e., an *incoherent* superposition of two linear or circular basis states. At a given time the electric field vector of well-defined magnitude E_0 may lie at any orientation in the x, y plane. Mathematically it can be expressed as a linear combination of two basis states ϵ_1 and ϵ_2 that have an arbitrary phase relationship $\phi_1 - \phi_2 \neq \text{const.}$

Natural light has the form

$$\boldsymbol{E}_{\text{nat}}(z,t) = \frac{E_0}{\sqrt{2}} \left(\boldsymbol{\epsilon}_1 \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_1} + \boldsymbol{\epsilon}_2 \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_2} \right) \,, \tag{5.37}$$

where ϕ_1 and ϕ_2 are uncorrelated.

Experiments with natural light can be interpreted as the sum of two intensities ($\sim E^2$), measured independently with two orthogonal linear light orientations or with right and left circular light.

5.5.2 Elliptical Polarization

The most general form of polarized light is said to be *elliptically polarized* and can be written as follows.

An elliptically polarized EM wave has the form $\boldsymbol{E}_{ell}(z,t) = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_x \, E_{0x} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_x} + \boldsymbol{\epsilon}_y \, E_{0y} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_y} \right) \,, \qquad (5.38)$ or $\boldsymbol{E}_{ell}(z,t) = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}^{\mathcal{L}} \, E_{0L} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_L} + \boldsymbol{\epsilon}^{\mathcal{R}} \, E_{0R} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_R} \right) \,. \qquad (5.39)$

The wave is described by three independent parameters, the magnitudes E_{0a} and E_{0b} (a = x, L; b = y, R) and the phase difference $\phi = \phi_a - \phi_b$. The unit linear polarization vectors $\boldsymbol{\epsilon}_x$ and $\boldsymbol{\epsilon}_y$ are real, while the circular unit vectors $\boldsymbol{\epsilon}^{\mathcal{L}}$ and $\boldsymbol{\epsilon}^{\mathcal{R}}$ are complex. The phase factors ϕ_a and ϕ_b define the phase for t = z = 0.

Therefore elliptically polarized light can be characterized of how well it is "linearly" or "circularly" polarized. This is expressed by polarization factors as discussed in Sect. 5.5.3. The amplitudes of the linear basis states E_{0x} and E_{0y} in (5.38) are linear combinations of those of the circular basis states E_{0L} and E_{0R} in (5.39) and vice versa, with the combinatory signs determined by the phase factors ϕ_i (i = x, y, L, R).

In order to illustrate the motion of the E vector of an elliptical wave we choose one of the phase factors for t = z = 0, so that the wave is a function of only the phase difference $\phi = \phi_y - \phi_x$ in (5.38). For convenience we set $\phi_x = 0$ and $\phi_y = \phi_0$ and obtain

$$\boldsymbol{E}_{\text{ell}}(z,t) = \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_x \, E_{0x} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)} + \boldsymbol{\epsilon}_y \, E_{0y} \, \mathrm{e}^{\mathrm{i}(kz-\omega t)+\mathrm{i}\phi_0} \right) \,. \tag{5.40}$$

If we rewrite (5.40) in terms of its real and imaginary parts,

$$\boldsymbol{E}_{\text{ell}}(z,t) = \frac{1}{\sqrt{2}} \left[\boldsymbol{\epsilon}_x \, E_{0x} \, \cos(kz - \omega t) + \boldsymbol{\epsilon}_y \, E_{0y} \, \cos(kz - \omega t + \phi_0) \right] \\ + \frac{\mathrm{i}}{\sqrt{2}} \left[\boldsymbol{\epsilon}_x \, E_{0x} \, \sin(kz - \omega t) + \boldsymbol{\epsilon}_y \, E_{0y} \, \sin(kz - \omega t + \phi_0) \right], \quad (5.41)$$

the real part can be used to visualize the motion of the endpoint of the E-vector in real space.

It can be written in the form of an ellipse, plotted in Fig. 5.4, and given by [180],

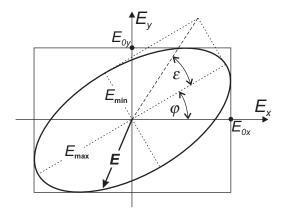


Fig. 5.4. Illustration of the electric field vector rotation for elliptically polarized electromagnetic waves, according to (5.42). The endpoint of the *E*-vector makes a complete rotation as the wave advances by one period and the magnitude changes from a maximum to a minimum over a quarter period. The rotation angle φ of the major axis of the ellipse from the *x*-axis is given by (5.43) and the angle ε is the ellipticity given by (5.54)

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 = 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right)\cos\phi_0 + \sin^2\phi_0 .$$
(5.42)

We see that its principal axes are rotated relative to our coordinate system by an angle φ given by

$$\tan 2\varphi = \frac{2E_{0x}E_{0y}\cos\phi_0}{E_{0x}^2 - E_{0y}^2} .$$
(5.43)

For $\phi_0 = \pm \pi/2$ we have $\varphi = 0$ and we obtain the more familiar principal axis form of the ellipse

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 = 1 .$$
(5.44)

If linearly polarized photons with E along x are incident on a magnetic sample, and the transmitted beam has an elliptical polarization as shown in Fig. 5.4, we call the angle φ the *Faraday rotation* and the angle ε the *ellipticity* (see (5.54)). This will be discussed in more detail in Sect. 8.7.

5.5.3 The Degree of Photon Polarization

In practice it is often important to know the purity of X-ray polarization, usually called the *degree of polarization*, a quantity that varies between 0 and 1. We have seen that linearly and circularly polarized light can be considered to

be special cases of elliptically polarized light. In general, elliptically polarized light can be constructed from either two orthogonal linear states or from the orthogonal right (or $q = +\hbar$) and left (or $q = -\hbar$) circularly polarized states. We can then express the polarization properties of elliptically polarized light in term of its linear or circular components. This is quantitatively accounted for by the *degree of linear polarization* and the *degree of circular polarization*. We shall define them now.

The various expressions for the *degree of polarization* are defined in terms of intensities given by the Poynting vector according to

$$I_{\alpha} = |\mathbf{S}| = \epsilon_0 c \, |\mathbf{E}_{\alpha}|^2 \tag{5.45}$$

where α stands for $\mathcal{L}, \mathcal{R}, x$, or y. For an *elliptically polarized* EM wave we define the degree of polarization as follows. The *degree of linear polarization* is given by²

$$P_{\rm lin} = \frac{|I_x - I_y|}{I_x + I_y} \ . \tag{5.49}$$

An equivalent expression also describes the degree of circular polarization. The *degree of circularly polarized radiation* is given by

$$P_{\rm circ} = \frac{|I_{\mathcal{R}} - I_{\mathcal{L}}|}{I_{\mathcal{R}} + I_{\mathcal{L}}} \ . \tag{5.50}$$

It can be shown that [190],

$$P_{\rm lin} = \frac{|E_{0x}^2 - E_{0y}^2|}{E_{0x}^2 + E_{0y}^2} = \frac{2|E_{0R}E_{0L}|}{E_{0R}^2 + E_{0L}^2}, \qquad (5.51)$$

and we can also rewrite (5.50),

 2 Often the degree of linear polarization is defined differently as [189]

$$P = P_{\parallel} = \frac{I_{\max}}{I_{\max} + I_{\min}} .$$
(5.46)

where I_{max} and I_{min} are the maximum and minimum intensities, corresponding to E lying along the long and short axes of the ellipse in Fig. 5.4. If we define

$$P_{\perp} = \frac{I_{\min}}{I_{\max} + I_{\min}} , \qquad (5.47)$$

we have $P_{\parallel} + P_{\perp} = 1$ and

$$P_{\rm lin} = |P_{\parallel} - P_{\perp}| \tag{5.48}$$

so that P_{lin} defined by (5.49) is smaller than $P = P_{\parallel}$. For example, for synchrotron radiation from a typical bending magnet or wiggler we have $P = P_{\parallel} = 0.85$, $P_{\perp} = 0.15$ and $P_{\text{lin}} = 0.70$. In general $0.5 \le P \le 1$ where P = 1 is pure linear polarization and P = 0.5 is circular polarization with elliptical polarization lying in between.

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$$P_{\rm circ} = \frac{|E_{0R}^2 - E_{0L}^2|}{E_{0R}^2 + E_{0L}^2} = \frac{2|E_{0x}E_{0y}|}{E_{0x}^2 + E_{0y}^2} \,, \tag{5.52}$$

The degree of circular polarization is related to the degree of linear polarization by

$$P_{\rm circ}^2 = 1 - P_{\rm lin}^2 , \qquad (5.53)$$

reflecting the intuitive picture that the more the wave is in one polarization state the less it is in the other.

Another quantity of interest is the *ellipticity* ε of the light, determined by the ratio of the minor to major E vector components along orthogonal directions. With reference to Fig. 5.4 we have the following relation.

The *ellipticity* ε is given by $\tan \varepsilon = \frac{|\boldsymbol{E}_{\min}|}{|\boldsymbol{E}_{\max}|} = \frac{|E_{0R} - E_{0L}|}{|E_{0R} + E_{0L}|} .$ (5.54)

The degrees of polarization can be expressed in terms of the ellipticity,

$$P_{\rm lin} = \frac{\tan^2 \varepsilon - 1}{\tan^2 \varepsilon + 1} , \qquad (5.55)$$

and

$$P_{\rm circ} = \frac{2\tan\varepsilon}{\tan^2\varepsilon + 1} \ . \tag{5.56}$$

5.6 Transmission of EM Waves through Chiral and Magnetic Media

Let us take a look at some famous experiments that illustrate the concepts of parity and time reversal symmetries in practice. Using symmetry concepts one can often predict the outcome of experiments without consideration of the detailed physical mechanisms. The physical origins based on the interaction of the electric and magnetic fields with matter will be discussed in Chap. 9.

Our first example deals with the phenomenon of *optical activity* used by Pasteur to discover the chiral structure of certain molecules. In general, optical activity refers to the ability of a substance to rotate the plane of light polarization (defined by the E-vector and the propagation direction) upon transmission. Surprisingly, a solution of chiral molecules is optically active, despite the fact that the molecules are randomly oriented. This interesting effect is due to the fact that chirality or handedness is conserved upon rotation in space, e.g., a right handed helix remains right handed upon turning it upside down, as illustrated in Fig. 5.5.



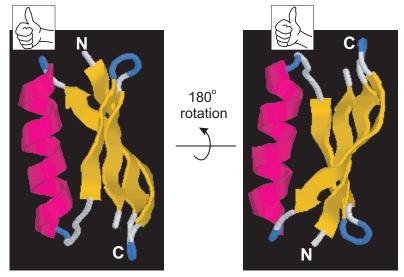


Fig. 5.5. Cartoon of the structure of Protein G, viewed in two orientations that are rotated relative to each other by a 180° rotation about a horizontal axis [191]. The right handed α -helix is shown in pink and the β -strands are broad yellow arrows, pointing from the N to the C terminus. Note that the right handedness of the α -helix is preserved upon rotation

Because of its historical significance and its importance for our further discussion of chiral and magnetic effects later in this section, let us describe a particularly beautiful experiment to demonstrate the chiral nature of molecules. As our example, we use the ubiquitous sugar molecule which naturally occurs in two modifications or enantiomers, defining either a right handed or a left handed atomic structure. For our discussion we refer to Fig. 5.6. We assume that right-handed sugar molecules are dissolved in water. Their thermal motion results in a random molecular orientation in the shown glass tube. Since a molecular rotation in space does not change the chirality the whole solution still has a handedness of the individual molecules, despite the random molecular orientation. While the theory of transmission of polarized EM waves through matter will be discussed later in Chaps. 8 and 9, we here simply use the fact that the optically active sugar solution causes a rotation of the polarization (E) vector about the propagation direction as the wave moves forward. For simplicity we assume that we have chosen a wavelength of light where the rotation sense of the molecules and the rotation sense of the E vector are the same.³

When the glass tube is viewed from the side a handed bright spiral appears which originates from scattered light. The sugar molecules are excited by

³In general, the chirality of the sugar molecule is not necessarily the same as that of the observed helical bright band in Fig. 5.6, since the optical activity is frequency dependent.

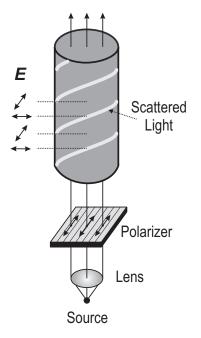


Fig. 5.6. Illustration of light transmission through a solution of a handed molecule. The light source and lens produce a parallel beam of visible light that is linearly polarized by a polarizer and then traverses a glass tube filled with a saturated solution of *right-handed* sugar. As the light traverses the optically active sugar solution the light polarization (E) axis rotates clockwise about the light propagation axis, as shown on the *left*. An outside observes sees scattered light from those locations of the solution where the E vector is oriented perpendicular to the observation direction. The bright locations form a right-handed helical band as shown. The helix therefore reflects the chiral nature of the sugar molecule. It is important that the molecules in the solution are not aligned in any way. The rotation sense of the scattered pattern therefore does not change if the light direction is inverted or if the glass tube is rotated upside down

the incident light and oscillate with the frequency and in the direction of the electric field of the incident radiation, which rotates as the wave moves forward as shown on the left side of Fig. 5.6. The re-emitted or scattered radiation at each position in the solution has the same polarization as the incident radiation. Since the light propagation direction of an EM wave is always orthogonal to the \boldsymbol{E} vector, an outside observer sees the re-emitted or scattered light only from those locations of the solution where the \boldsymbol{E} vector is oriented perpendicular to the observation direction. The other locations remain dark. Since the molecules are randomly oriented, the rotation sense of the bright band would remain the same if the glass tube is rotated upside down or if the polarized light was traversing the solution from top to bottom. If we use a mirror to reflect the light back through the glass tube the light beam and its polarization would simply retrace the original path so that, upon exiting the glass tube the beam could traverse the polarizer and return to the light source.

We now wish to compare the transmission of EM waves through magnetic and chiral samples. This is accomplished in the most direct way if we do not use a chiral sample consisting of randomly oriented molecules, as discussed above, but by use of a single crystal built from chiral molecules. In this way we can directly characterize our chiral sample by an *oriented* right-handed or left-handed helix and our magnetic sample by its magnetization M. This is illustrated in Fig. 5.7.

The case of the chiral sample, chosen to be a right-handed helix H_r , is straight-forward. The helix looks the same, namely right handed, to the light

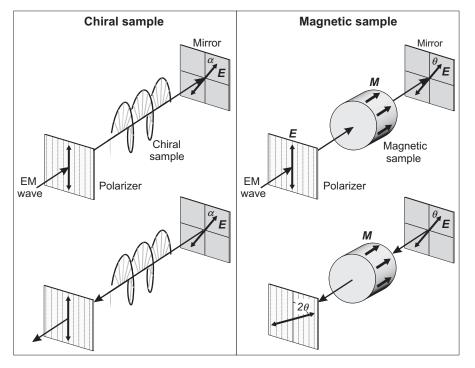


Fig. 5.7. Comparison of transmission of a linearly polarized electromagnetic wave through a chiral and magnetic sample (top row) and its return through the same sample after reflection (bottom row). In both cases the linearly polarized wave experiences a rotation of its polarization upon transmission through the sample. The rotation angles α and θ are shown at the position of the mirror, which reflects the waves and sends them back through the respective samples. The right-handed chiral sample always rotates the polarization clockwise when looking into the propagation direction so that the polarizer the reflected wave will be transmitted. The magnetic sample also rotates the polarization clockwise on its first pass through the sample when the propagation direction points into the direction of M. After reflection the propagation direction is antiparallel to M and the polarization vector rotates anti-clockwise. When the thickness of the magnetic sample is chosen to give a rotation angle $\theta = 45^{\circ}$ the total rotation becomes 90° and the EM wave can no longer pass the polarizer.

on its first pass and second pass. Hence the \boldsymbol{E} vector rotation will follow the helicity and the rotation sense relative to the propagation direction of the EM wave will be the same. Since the light propagation direction reverses on the first and second pass the \boldsymbol{E} vector will retrace its first path on the second pass through the sample. When the reflected wave arrives at the polarizer it is back in its original orientation and can pass the polarizer.

The magnetic sample looks different to the EM wave on its first and second pass. The magnetization M is a vector and it matters whether this vector points into or against the propagation direction of the EM wave. If the polarization vector rotates clockwise by θ on the first path it will rotate anticlockwise by θ on the second path. The two E vector rotations by the sample add up and the final rotation angle will be 2θ . If the thickness of the magnetic sample is chosen to give a rotation angle $\theta = 45^{\circ}$, the polarization of the reflected light will be rotated by 90° and it cannot traverse the polarizer again. This is known as *Rayleigh's light trap*, in which the light can go in but cannot come back out.⁴ In practice, visible light is heavily absorbed by ferromagnetic metals, so that the experimental demonstration is best done by use of microwave radiation (~1 cm wavelength) and an insulating magnetic material such as a ferrite which is nearly transparent. The principle is used in practice to decouple the radio-wave generator from the radiating antenna.

The different behavior of the chiral and magnetic samples in Fig. 5.7 is a direct consequence of the opposite symmetry properties of the two samples, and follows from our discussions in Sects. 2.7 and 5.4.4. Since the *chiral sample* is defined by the electrostatic charge distribution it is *time even* and *parity odd*. The *magnetic sample*, on the other hand is defined by a handed motion of charge and it is *time odd* and *parity even*. The symmetry of the EM wave transmission pictured in Fig. 5.7 is entirely determined by the sample since the linearly polarized EM wave has neither a time nor space handedness and is therefore *time even* and *parity odd* (just like the \mathbf{E} -vector).⁵ If we picture the two passes of the EM wave through the samples as a time reversal process, the time-even chiral sample leaves the time-even polarization unchanged whereas the time-odd magnetic sample causes a change.

Another way of understanding the result is to decompose the linearly polarized wave into a left and right circularly polarized wave and consider the preferential absorption of the two circular components by the chiral and magnetic samples. Since the handedness of the circularly polarized components change upon reflection (right becomes left and vice versa), the chiral sample preferentially absorbs one component in the first pass and the other component in the second pass, leaving the wave with a smaller amplitude but the same linear polarization. The magnetic sample absorbs the same component twice, enhancing the imbalance and leading to a polarization rotation.

The polarization rotation by magnetic materials, called *Faraday rotation* has many useful applications. It is one of the major tools to detect the direction of the magnetization in magnetic materials since the rotation angle of the transmitted light changes sign when the magnetization changes direction. Such

⁴One can also devise a nonmagnetic light trap by replacing the magnetic sample in Fig. 5.7 by an all-optical quarter wave plate whose retardation axis is oriented at 45° relative to the polarizer axis.

⁵Note that the linearly polarized wave keeps its spatial alignment along a specific axis upon reflection, merely changing its phase by 180° (*E*-vector changes sign).

measurements can be done much faster than classical measurements of the magnetization direction by means of electromagnetic induction, the force by which the specimen is attracted in an inhomogeneous magnetic field or torque magnetometry. In addition, the magnetization direction can be imaged by use of polarized light [54] or polarized X-rays (see Chap. 10). Faraday rotation may also be observed in reflection. It then bears the name magneto-optic Kerr effect or MOKE [55, 192]. In this variant the rotation of the plane of polarization is used to image the magnetization direction near the surface of the magnetic material. The sampling depth is determined by the optical absorption depth which is $\sim 10-20$ nm for the strongly light-absorbing ferromagnetic metals. Note that polarization dependent reflection measurements are unsuited to detect the chirality of a crystal structure or a molecule. Another important application of the above ideas is the Sagnac interferometer used in navigation and in fighter planes. It can be used to completely eliminate all polarization changes caused by the optical activity of optical elements in the beam path (such as lenses and windows) and measure the pure magnetic effects with high sensitivity [193].

Exchange, Spin–Orbit, and Zeeman Interactions

6.1 Overview

This chapter reviews how our present quantum theoretical understanding of magnetic interactions came about and thus provides a historical perspective. The quantum theory of magnetism first revealed itself in atomic and molecular spectroscopy. This is not a topic that modern practitioners of magnetism are typically concerned with, yet it is the study of the simplest two-electron systems such as the He atom and the H₂ molecule that forms the basis for the present-day theory of magnetism. The more practically oriented reader may skip the present chapter but it is recommended for students of magnetism. The present chapter is hoped to provide an appreciation for how difficult a problem it is to this day to treat the interactions between more than a few electrons. Only in the simplest of systems can the interactions between electrons be treated without severe approximations. The chapter describes the origin of the main theoretical technique used today, density functional theory, which is based on an ab initio Hamiltonian. It clearly distinguishes ab initio techniques from those built on a toy-Hamiltonian such as the Heisenberg and Hubbard models. It is important to realize that the latter were artificially constructed to map on to the ab initio results for simple systems, such as the H₂ molecule, and then generalized to larger systems to overcome the problems encountered with ab initio methods. While they have proven extremely valuable for a conceptual or qualitative understanding of magnetic phenomena they cannot be used alone to quantitatively explain experimental observations.

Our modern understanding of electronic structure is based on the concepts of charge and spin. Historically, the concept of the spin emerged and was developed over a short important period from 1925 to 1928, involving people like Uhlenbeck, Goudsmit, Heisenberg, Pauli, and Dirac. The key to this development was the understanding of atomic spectra by means of quantum theory. In the process two of the most important concepts in modern physics and chemistry emerged. These fundamental concepts of exchange and spin– orbit coupling form the main topic of the present chapter. In addition we shall

6

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revisit the classical interaction of a magnetic moment with an external magnetic field discussed in Sect. 3.4, this time from a spectroscopy and quantum theory point of view. We shall see that the spectroscopic discovery by Pieter Zeeman in 1896, the *Zeeman effect*, finds its natural explanation in quantum theory.

The interplay between the exchange, the spin–orbit, and the Zeeman interactions is the essence of magnetism research. We can state upfront as follows.

- The *exchange interaction* is the largest magnetic interaction and is the origin of the alignment of the spin system.
- \bullet The *spin-orbit interaction* creates orbital magnetism, couples the spin
- system to the lattice, and gives rise to the magnetocrystalline anisotropy.
- The Zeeman interaction allows the macroscopic alignment of spin and orbital magnetic moments, and therefore allows the creation of useful magnetic devices.

The importance of the exchange and spin-orbit interactions can readily be demonstrated. They underlie our understanding of the electronic structure of atoms and the existence of the periodic table. They explain the bonding and properties of molecules by dictating the filling and occupation of orbitals. They play a key role in all of condensed matter physics which is based on the concepts of charges, spins and orbital moments and their interactions. Without the exchange interaction there would be no spontaneous magnetization and the spin-orbit interaction allows the charges and spins to talk to each other.

The exchange interaction defines the spin system in a magnetic material and it is responsible for the existence of parallel, i.e., ferromagnetic, and antiparallel, i.e., antiferromagnetic, spin alignment. The spin-orbit interaction creates orbital magnetism and couples the spin system to the lattice, allowing energy and angular momentum exchange. It is the very origin of magnetic anisotropy since the exchange interaction itself is isotropic and only the coupling of the spin to the lattice can "lock in" a macroscopic magnetization. The Zeeman interaction of a magnetic moment with an external magnetic field is of great practical importance because it is used to align magnetic materials. In particular, if one wants to align a magnetic material in the hard direction the Zeeman interaction has to overcome the spin–orbit interaction which determines the magnetocrystalline anisotropy. Finally, one needs to distinguish the effect of an external magnetic field and of the exchange field on a magnetic moment. While an external magnetic fields acts on both spin and the motion of charge reflected by linear and angular momenta, the exchange interaction acts on electron spin alone.¹ We shall see below that this may invert the electronic level splitting which is important in spectroscopy.

We shall place particular emphasis on the *exchange interaction* because it is the largest magnetic interaction and the most difficult one to treat theoreti-

¹Note that the exchange interaction does not act on the nuclear spin.

cally. While its treatment is rather satisfactory in small systems such as atoms and small molecules, challenges remain to this day in treating it properly in extended systems like solids. It is for this reason that we shall follow the historical development, starting with the two electron atomic Hamiltonian, then treating the two electron diatomic molecule, and then generalizing the concepts to larger systems like magnetic materials. In general, the treatment of the interaction between the electrons, called "correlation," remains one of the most difficult tasks in all of solid state physics and for a more extensive discussion of correlation effects we refer the reader to the book by Fulde [194].

We shall now discuss the concepts of the three magnetic interactions in more detail. At the fundamental level the origins of these interactions are truly remarkable and we believe that modern scientists should have a clear understanding of how these concepts have evolved.

6.2 The Spin Dependent Atomic Hamiltonian or Pauli Equation

In order to properly treat the electronic and spin structure of atoms one cannot use the conventional Schrödinger equation, since it does not include spin. In principle, one needs to use the relativistic Dirac equation but we shall take a shortcut, instead. Historically the concept of electron spin with half integer angular momentum, $\hbar/2$, was first proposed in 1925 by Uhlenbeck and Goudsmit [18, 19] and was incorporated into wave mechanics by Heisenberg and Jordan [195] in 1926 and Pauli [196] in 1927. Dirac's treatment of an electron in an external electromagnetic field, without explicitly assuming the existence of the electron spin, appeared a year later in 1928 [23, 24]. He found that the spin properties are automatically contained in his equations, and that Pauli's treatment, with a few subtleties, is recovered in the limit of small velocities. Our starting point will therefore be the time-independent **Pauli equation**² [197]. It is the nonrelativistic Schrödinger equation with a term added for the spin, and can be written as

$$[\mathcal{H}_{\rm e} + \mathcal{H}_{\rm s}] \ \psi(\mathbf{r}, t) = E \ \psi(\mathbf{r}, t) \ . \tag{6.3}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = -\nabla \boldsymbol{\Phi}(\boldsymbol{r},t) - \frac{\partial \boldsymbol{A}(\boldsymbol{r},t)}{\partial t}$$
(6.1)

and

$$\boldsymbol{B}(\boldsymbol{r},t) = \nabla \times \boldsymbol{A}(\boldsymbol{r},t) . \tag{6.2}$$

²As discussed by Strange [197] the time-dependent Pauli equation, in its general form, also includes terms due to an external EM field if the usual momentum term p is replaced by p + eA. This produces the correct motion of a charged particle with momentum p in the presence of a time-dependent vector potential A and scalar potential Φ which are linked to the E and B fields by

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The first term on the left, \mathcal{H}_{e} , is the electronic Hamiltonian for an atom at the origin R = 0 with nuclear charge $q_{n} = Ze$ and electrons with charge $q_{e} = -e$ (see footnote³)

$$\mathcal{H}_{\rm e} = \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i^2}{2m_{\rm e}} - \frac{Ze^2}{4\pi\epsilon_0 |\boldsymbol{r}_i|} \right) + \sum_{i< j} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_j - \boldsymbol{r}_i|} . \tag{6.6}$$

It consists of the kinetic energy, the Coulomb interaction between the electrons and the nucleus and the Coulomb interactions between the electrons. We shall see later that the last term in (6.6) gives rise to the *exchange interaction*.

The second term in the Pauli equation (6.3), \mathcal{H}_s , represents the non-relativistic expression for the spin energy [197] and it is of crucial importance for magnetism. It can be written in the familiar form

$$\mathcal{H}_{\rm s} = \frac{e\hbar}{m_{\rm e}} \, \boldsymbol{S} \cdot \boldsymbol{B}^*, \tag{6.7}$$

where S is the atomic spin, and the origin of the magnetic induction B^* will be discussed later. The term naturally arises when the relativistic Dirac equation is evaluated up to order $(v/c)^2$ in the nonrelativistic limit. We shall see below that it will give rise to the *spin-orbit interaction*.

In electronic structure calculations it is important to understand the size of energies associated with different terms in the Hamiltonian, since significant simplifications in the mathematics result if certain terms can be treated by perturbation theory. Also, since the theory is to guide experimental observations it is of great importance for our understanding which terms in the Hamiltonian give rise to large and small level splittings in the atomic spectra. We shall therefore take a look at the relative size of the terms in the Pauli Hamiltonian.

6.2.1 Independent Electrons in a Central Field

The first two terms in round brackets in the electronic Hamiltonian \mathcal{H}_{e} (6.6) are sums of single electron operators, while the last term is a sum of twoelectron operators. The Coulomb interaction between a given electron and

$$\sum_{i < j} = \sum_{\substack{1 \le i \le N-1 \\ i < j \le N}} = \frac{1}{2} \sum_{i \ne j}.$$
(6.4)

For a sum over a single index i, which must differ from a second index j we write

$$\sum_{i(i\neq j)}.$$
(6.5)

³Assuming that we sum over quantities that are symmetric in indices i and j, we use the following double sum notation,

the nucleus, expressed by the second term in (6.6) and that with another electron given by the third term in (6.6) can be of comparable size. Therefore the Pauli (or Schrödinger) equation cannot be separated into those of the individual electrons. We would like to simplify the Hamiltonian in two ways. First, we would like to write it in terms of a spherically symmetric central field problem that only contains single electron operators. Second, we would like to separate out a "smaller" term that represents two-electron operators, so that we can treat it in perturbation theory. The central field part would give us something that corresponds to Bohr's atomic shell (quantum number n) and subshell (quantum number l) model, each subshell i being characterized by quantum numbers $n_i l_i$. The two-electron part would correspond to some finer level splitting of the electronic subshells through interactions of electrons in different subshells $n_1 l_1$ and $n_2 l_2$. This can indeed be done as shown below.

In (6.6) the electron-nuclear Coulomb term is negative while the electronelectron Coulomb term is positive. So we can try to construct a central field felt by a given electron that does not just come from the nuclear field but has some screening contribution from an averaged electron-electron "field." This is typically done by rewriting (6.6) as

$$\mathcal{H}_{\rm e} = \sum_{i} \mathcal{H}^0(r_i) + \mathcal{H}^1, \tag{6.8}$$

where the first "large" term is the spherically symmetric *central field Hamil*tonian

$$\mathcal{H}^{0}(r_{i}) = \frac{\boldsymbol{p}_{i}^{2}}{2m_{\rm e}} - \frac{Ze^{2}}{4\pi\epsilon_{0}|\boldsymbol{r}_{i}|} + \frac{e^{2}}{4\pi\epsilon_{0}} \sum_{j \ (j\neq i)} \frac{1}{|\boldsymbol{r}_{j} - \boldsymbol{r}_{i}|}$$
(6.9)

consisting of a sum of one-electron terms. The second term \mathcal{H}^1 constitutes a difference between two large terms and is "small" relative to $\mathcal{H}^0(r_i)$. It is given by a sum of two electron terms minus an averaged term

$$\mathcal{H}^{1} = \frac{e^{2}}{4\pi\epsilon_{0}} \left(\sum_{i < j} \frac{1}{|\boldsymbol{r}_{j} - \boldsymbol{r}_{i}|} - \overline{\sum_{i,j \ (j \neq i)} \frac{1}{|\boldsymbol{r}_{j} - \boldsymbol{r}_{i}|}} \right) .$$
(6.10)

The central field Hamiltonian effectively decouples the motion of the individual electrons from each other, and so the position of each electron is not correlated with the position of any other electron. By solving the threedimensional Schrödinger equation for $\mathcal{H}^0(r_i)$ we obtain one-electron eigenfunctions. They correspond to atomic orbitals (we will include spin later) which are products of a radial part and spherical harmonics according to

$$\psi_{n,l,m}(\boldsymbol{r}) = R_{n,l}(r) Y_{l,m}(\theta,\phi) . \qquad (6.11)$$

Since the potential is spherically symmetric the electron energy is independent of the quantum number m. The total eigenfunction of $\sum_i \mathcal{H}^0(r_i)$ is a *product* of the individual one-electron orbitals (6.11). However, it needs to be properly

antisymmetrized as discussed later and in practice is a N-dimensional Slater determinant. The corresponding energy is the *sum* of the individual electron orbital energies.

In practice, the solution of the central field Hamiltonian is nontrivial and is calculated self consistently by starting with an approximate parameterized solution which is optimized according to some appropriate criterion. The various methods are discussed by Bethe and Salpeter [198] for two electron systems,⁴ and more generally by Cowan [182]. In our discussion of the exchange interaction below it will become clear that the wavefunctions (6.11) are determined by both the kinetic energy term $p_i^2/2m_e$ and potential energy terms in the central field Hamiltonian (6.9). For example, the kinetic energy term will contribute a (positive) centrifugal term $l(l+1)\hbar^2/2m_er^2$ to the radial Schrödinger equation (see (7.4)), indicating that the kinetic energy is increased for shorter distances r.

It is clear that the one-electron functions (6.11) are incomplete since they do not include spin. The complete spin-orbitals we are looking for are required to be eigenfunctions of the central field Hamiltonian (6.9) and we want to use them as our zero-order function for the perturbation solution of the complete Pauli equation. Since the central field Schrödinger equation does not explicitly contain the spin, it does not dependent on the orientation of the spin relative to the orbital angular momentum. We can therefore specify the direction of the spin relative to the z-axis of our coordinate system, and it is completely described by the simple one-electron spin functions $\alpha \equiv (s_z = +\frac{1}{2})$ and $\beta \equiv (s_z = -\frac{1}{2})$. We write the spin dependence as $\chi(s_z)$ (which is either α or β) and the one-electron *spin orbitals* are given by

$$\psi(\boldsymbol{a}) = \psi(\boldsymbol{r}, \boldsymbol{s}) = R_{n,l}(r) Y_{l,m}(\theta, \phi) \chi(s_z)$$
(6.12)

We have now established the form of a complete single electron wavefunction in an atom and can attack the interaction between two or more electrons.

6.2.2 Interactions between two Particles – Symmetrization Postulate and Exclusion Principle

In the wavefunction (6.12) we have explicitly indicated that the "coordinate" variable \boldsymbol{a} contains the position $\boldsymbol{r} = (r, \theta, \phi)$ as well as the spin orientation s_z of the spin \boldsymbol{s} . The total eigenfunction of the central field Hamiltonian consists of the product of the individual electron orbitals. For a two-electron system we have

$$\Psi(a, b) = \Psi(r_1 s_1; r_2 s_2) = \psi_1(a) \psi_2(b) .$$
(6.13)

Because the two electrons are indistinguishable, this function must be equivalent to

⁴Bethe and Salpeter's book is a wonderful account of the development of the atomic theory for one- and two-electron atoms and its reading is highly recommended.

Equivalent two-electron configurations

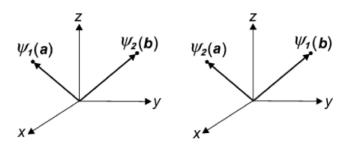


Fig. 6.1. Description of a two-electron atom. The two electrons are labeled by subscripts 1 and 2 and their spatial and spin coordinates are denoted by the vectors a and b. Because the electrons are indistinguishable the configuration described by one-electron wavefunctions $\psi_1(a)$ and $\psi_2(b)$ must be identical to that described by $\psi_2(a)$ and $\psi_1(b)$, where the two electrons are exchanged

$$\Psi(\boldsymbol{a}, \boldsymbol{b}) = \psi_2(\boldsymbol{a}) \,\psi_1(\boldsymbol{b}) \;, \tag{6.14}$$

where the electrons, labeled by subscripts 1 and 2, originally at positions a and b have been exchanged. This is illustrated in Fig. 6.1.

A solution must therefore be of the form

$$\Psi(\boldsymbol{a},\boldsymbol{b}) = \frac{1}{\sqrt{2}} \left[\psi_1(\boldsymbol{a}) \,\psi_2(\boldsymbol{b}) \pm \psi_2(\boldsymbol{a}) \,\psi_1(\boldsymbol{b}) \right] \,. \tag{6.15}$$

The plus sign represents a *symmetric* total wavefunction and the minus sign an *antisymmetric* total wavefunction. Upon exchange of electrons *symmetric* functions remain unchanged

$$\Psi_{\rm sym}(\boldsymbol{a}, \boldsymbol{b}) = \Psi_{\rm sym}(\boldsymbol{b}, \boldsymbol{a}) \tag{6.16}$$

while antisymmetric functions change sign

$$\Psi_{\rm as}(\boldsymbol{a}, \boldsymbol{b}) = -\Psi_{\rm as}(\boldsymbol{b}, \boldsymbol{a}) \ . \tag{6.17}$$

We have the following symmetrization postulates,

The Symmetrization Postulates.

If the system is totally *symmetrical* under the exchange of any particle pair, the particles are called *bosons* and obey *Bose–Einstein* statistics. Bosons have *integer* spins.

If the system is totally *antisymmetrical* under the exchange of any particle pair, the particles are called *fermions* and obey *Fermi–Dirac* statistics. Fermions have *half-integer* spins.

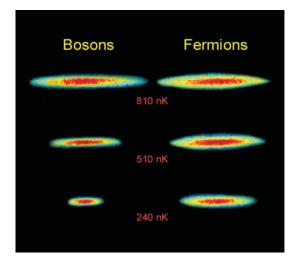


Fig. 6.2. False-color images of ultracold lithium-atom clouds [199]. Lithium has two stable isotopes, one of which is a boson (lithium-7), the other a fermion (lithium-6). The alkali atoms are magnetically confined by an inhomogeneous magnetic field, taking advantage of their magnetic moment and are then cooled with lasers. As the temperature drops, the bosons bunch together, while the fermions remain more apart

As far as we know today all N-particle systems in nature are distinguished by their fundamental symmetry under exchange of any pair of particles. No exceptions are known. Our two-electron system discussed above is but a special case of such general systems. Particles can be composites and, for example, different isotopes may behave differently. Examples are ³He which is a fermion and ⁴He which is a boson. Figure 6.2 shows a beautiful example of the different behavior of clouds of lithium-7 bosons and lithium-6 fermions at low temperature [199].

We are interested in the interactions between electrons which are fermions. The total wavefunction is therefore *antisymmetric*. This can be achieved in two ways. Either the spatial part is symmetric and the spin part antisymmetric or vice versa. We have either

$$\Psi_{\rm as}(\boldsymbol{a}, \boldsymbol{b}) = \Psi_{\rm sym}(\boldsymbol{r}_1, \boldsymbol{r}_2) \,\chi_{\rm as}(\boldsymbol{s}_1, \boldsymbol{s}_2) \;. \tag{6.18}$$

where the antisymmetric two-electron spin function is the *singlet state* with total spin quantum number $S = 0, M_S = 0$,

$$\chi_{\rm as}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \frac{1}{\sqrt{2}} \left[\alpha \beta - \beta \alpha \right] . \tag{6.19}$$

$$\Psi_{\rm as}(\boldsymbol{a}, \boldsymbol{b}) = \Psi_{as}(\boldsymbol{r}_1, \boldsymbol{r}_2) \,\chi_{\rm sym}(\boldsymbol{s}_1, \boldsymbol{s}_2) \;. \tag{6.20}$$

and the symmetric two-electron spin function is the *triplet state* with total spin quantum number $S = 1, M_S = 1, 0, -1$,

$$\chi_{\rm sym}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \begin{cases} \alpha \alpha \\ \frac{1}{\sqrt{2}} \left[\alpha \beta + \beta \alpha \right] \\ \beta \beta \end{cases} \quad . \tag{6.21}$$

The above equations, of course, express the famous *Pauli exclusion principle*, stating that two electrons cannot be in identical states, i.e., have identical quantum numbers. For example, if the electrons have a symmetric spatial part as in (6.18) they tend to have similar quantum numbers nlm, so that the spin quantum number s_z has to differ. This is accomplished by the antisymmetric form given by (6.19).

The Pauli exclusion principle is a manifestation of the antisymmetrization postulate for Fermions. It states that two electrons cannot be in identical states, i.e., have identical quantum numbers.

6.3 The Exchange Interaction

6.3.1 Electron Exchange in Atoms

The concept of "exchange" was originally derived from the interpretation of emission spectra of atoms with two unpaired electrons such as neutral helium, called He I. One of the classic works on the interpretation of the He spectrum was written by Heisenberg in 1926 [200]. For its historical importance and pedagogical value we shall now take a closer look at the He spectrum. It will give us valuable insight and it forms the basis for the Heisenberg spin Hamiltonian, discussed later.

Helium contains two electrons which move in the central field of two protons. The energy level diagram deduced from the analysis of the emission lines is shown in Fig. 6.3, for reference. The diagram is plotted, similar to a Grotrian diagram [181,182,201], to conveniently give the experimental transition energies. They simply correspond to the difference of the energies between two levels. Of particular interest are the transition energies from excited states to the ground state. In the ground state both electrons occupy the 1s orbital, and this two-electron state is therefore denoted 1s1s. It takes 24.59 eV, the ionization energy of He I, to remove one of the 1s electrons. It takes another 54.42 eV, the ionization energy of He II, to remove the second 1s electron.

The emission spectrum of He was measured by exciting one of the electrons in the 1s orbital into a higher orbital nl by an electrical discharge and then

or

Neutral He (He I) energy levels Singlets Triplets Two-One-0 electron electron 1 Binding energy (eV) 2 3 3.37 2p 4 1s2s 2s 21.22 eV 24 1s1s 1s 25

Fig. 6.3. Energy levels for neutral He (He I) [198,202]. We give the binding energies of the energy levels, denoted by multiplet term labels, $n'^{2S+1}L_J$, as well as two-electron (nl, n'l') and one-electron (n'l') (of the second electron) labels. Here S is the total spin, L the total angular momentum and $0 \le J \le L+S$ the coupled angular momentum. Originally all triplet states ${}^{3}L_J$ were associated with "orthohelium" the singlet states ${}^{1}L_J$ with "parahelium." Experimentally observed transitions occur within the singlet and triplet manifolds (cross transition are forbidden) and their energies are simply the differences of the level energies. As an example, the prominent He I line of 21.22 eV, often used for ultraviolet photoemission studies, corresponds to the ${}^{1}P_{1} \rightarrow {}^{1}S_{0}$ transition, as shown by a downward arrow. Levels with binding energies above $3 \, \text{eV}$ are omitted. Particularly important are the absence of the 1s1s triplet state $(1^{3}S_{1})$ and the singlet-triplet splitting of the 1s2s and 1s2p levels as discussed in the text

measuring the emitted photons when the 1snl state decays into the ground state. When a level diagram was made, similar to that shown in Fig. 6.3, from careful inspection of the measured He spectra it appeared that there were two different series of transitions. For lack of better knowledge the two series were originally associated with two forms of helium, "parahelium" (corresponding to singlet states) and "orthohelium" (triplets). The distinction between the two series, which correspond to transitions within the singlet and triplet manifolds, could be made because the dipole selection rule $\Delta S = 0$, governing optical transitions does not allow transitions which involve a change of spin, i.e., cross transitions between singlet and triplet states.⁵ Note that because of the electric discharge excitation method, however, both singlet and triplet states can be populated from the singlet ground state due to the fact that spin exchange may occur between the atomic and the exciting electron in the

⁵In addition, as discussed later, the observed spin–orbit splitting and the Zeeman effect are different between singlet and triplet states.

electron impact process. The fact that excitations to both the lowest excited states $2^{3}S_{1}$ and $2^{1}S_{0}$ are allowed by electron impact yet their decay to the $1^{1}S_{0}$ ground state is dipole forbidden (only $\Delta S = 0, \Delta L = \pm 1$ are allowed) is of great importance for lasers since it leads to long lifetimes ($\gg 10^{-8}$ s) of the excited states, which are called *metastable* [201].

When the energies of the singlet and triplet manifolds were compared, one observed a relative shift between corresponding levels, as illustrated in Fig. 6.3 for the 1s2s and 1s2p states, indicated by wavy brackets. This splitting and the absence of a 1s1s triplet level in the diagram in Fig. 6.3 hold the key to magnetism. The origin of the splitting which is due to the exchange interaction between the two electrons will be discussed below. The absence of the 1s1striplet state $(1^{3}S_{1})$ combined with the knowledge that He has two electrons immediately makes it clear that two electrons cannot exist in quantum states that agree in all quantum numbers. This led Pauli to formulate his famous principle. We can make the following important statement.

The He spectrum holds the key for the quantum mechanical understanding of magnetism. The absence of a 1s1s triplet state $(1^{3}S_{1})$ was the starting point for the Pauli principle. The singlet-triplet splitting of the excited states led to the concept of electron exchange.

We now want to explain the splitting of the energy levels of the twoelectron He atom shown in Fig. 6.3. The Schrödinger equation for helium is represented by the following Hamiltonian (for Z = 2)⁶

$$\mathcal{H}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) = \underbrace{\frac{\boldsymbol{p}_{1}^{2}}{2m_{\rm e}} + \frac{\boldsymbol{p}_{2}^{2}}{2m_{\rm e}} - \frac{2e^{2}}{4\pi\epsilon_{0}|\boldsymbol{r}_{1}|} - \frac{2e^{2}}{4\pi\epsilon_{0}|\boldsymbol{r}_{2}|}}_{\mathcal{H}^{0}(\boldsymbol{r}_{1},\boldsymbol{r}_{2})} + \underbrace{\frac{e^{2}}{4\pi\epsilon_{0}|\boldsymbol{r}_{2} - \boldsymbol{r}_{1}|}}_{\mathcal{H}_{\rm e-e}(\boldsymbol{r}_{1},\boldsymbol{r}_{2})} \quad (6.24)$$

$$\mathcal{H}'(\boldsymbol{r}_1, \boldsymbol{r}_2) = \mathcal{H}^0(r_1, r_2) + \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_2|}.$$
(6.22)

and the perturbation Hamiltonian as

$$\mathcal{H}''(\boldsymbol{r}_1, \boldsymbol{r}_2) = \mathcal{H}_{e-e} - \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_2|}.$$
(6.23)

This gives a better zero-order wavefunction and a more accurate result. Our method used here is chosen for its simplicity.

⁶We note that in (6.24) $\mathcal{H}_{e-e}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is actually not small compared to $\mathcal{H}^0(r_1, r_2)$ and our results are therefore not very accurate. A better choice more in line with Sect. 6.2.1 would be to factor the Hamiltonian (6.24) into a large and a small part. For example, using the notation of (6.24), Heisenberg [200] chose the zero-order Hamiltonian as

We have indicated by wavy brackets our choice for the central field part $\mathcal{H}^0(r_1, r_2)$ and for the two-electron part $\mathcal{H}_{e-e}(r_1, r_2)$. We could have also chosen a different grouping of terms, more in line with (6.9) and (6.10). In fact, many different approaches have been used historically as reviewed by Bethe and Salpeter [198]. Since we are not interested in finding the most accurate method but to illustrate the concept of exchange, we follow the simple approach of Sakurai [126].

We know that the solution of $\mathcal{H}^0(r_1, r_2)$ is of the form (6.17). We start with the ground state of helium where both electrons occupy the 1s orbital. In this case the spatial part of the total wavefunction is symmetric because both electrons are in the same orbital and have the quantum numbers nlm = 100. The spin part therefore has to be antisymmetric, i.e., the electrons have different spin functions α and β . We can write for the ground state wavefunction

$$\Psi_{\rm gs}(\boldsymbol{a}, \boldsymbol{b}) = \Psi_{\rm sym}(\boldsymbol{r}_1, \boldsymbol{r}_2) \,\chi_{\rm as}(\boldsymbol{s}_1, \boldsymbol{s}_2) \\ = \frac{1}{2} \left[\psi_{100}(\boldsymbol{r}_1) \psi_{100}(\boldsymbol{r}_2) + \psi_{100}(\boldsymbol{r}_1) \psi_{100}(\boldsymbol{r}_2) \right] \left[\alpha \,\beta - \beta \,\alpha \right].$$
(6.25)

The solution to the central field equation

$$\mathcal{H}^{0}(r_{1}, r_{2}) \Psi_{\rm gs}(\boldsymbol{a}, \boldsymbol{b}) = E_{0} \Psi_{\rm gs}(\boldsymbol{a}, \boldsymbol{b}) \tag{6.26}$$

gives us the ground state energy E_0 in zeroth order. This energy needs to be corrected by the $\mathcal{H}_{e-e}(\mathbf{r}_1, \mathbf{r}_2)$ contribution in (6.24), which is calculated by perturbation theory (see footnote 6)

$$E_1 = \langle \Psi_{\rm gs}(\boldsymbol{a}, \boldsymbol{b}) | \mathcal{H}_{\rm e-e}(\boldsymbol{r}_1, \boldsymbol{r}_2) | \Psi_{\rm gs}(\boldsymbol{a}, \boldsymbol{b}) \rangle.$$
(6.27)

We shall not carry out the actual calculation of E_0 and E_1 here, which is given by Sakurai [126]. We simply state the results $E_0 = -4e^2/(4\pi\epsilon_0 a_0)$ and $E_1 = +5e^2/4(4\pi\epsilon_0 a_0)$, where a_0 is the Bohr radius. We see that the energy E_1 is sizeable relative to E_0 and both terms need to be considered in obtaining a value close to the experimental value of 79.01 eV, which is the sum of the He I and He II ionization energies of 24.59 and 54.42 eV, respectively.

The He ground state calculation can actually be done without consideration of the spin. Both Hamiltonians $\mathcal{H}^0(r_1, r_2)$ and $\mathcal{H}_{e-e}(r_1, r_2)$ do not explicitly contain the spin and we could have done the calculation by simply using the spatial part $\Psi_{gs}(r_1, r_2)$ of the two electron function in (6.25). In our consideration the spin entered only through the requirement that the total wavefunction be antisymmetric.

The true importance of the requirement of an antisymmetric total wavefunction, however, enters in the calculation of the *excited states* of helium. The excited states were the subject of Heisenberg's important paper in 1926 [200]. As shown in Fig. 6.3, the excited states correspond to the two electrons occupying different orbitals, and there is an energy splitting. This splitting, which is 0.79 eV for the 1s2s and 0.25 eV for the 1s2p states, arises from the very concept of electron exchange in Fig. 6.1 and the symmetrization postulate. Let us take a look at the origin of the very important concept of *exchange*.

We assume one electron in the 1s orbital, denoted nlm = 100 and an another electron in an excited orbital denoted by a general label nlm. The central field wavefunction will have two possible forms, given by (6.18) and (6.20). If the space part is symmetric, the spin state is antisymmetric and given by (6.19). This gives the *singlet* excited state

$$\Psi_{\rm es}^{\rm S}(\boldsymbol{a}, \boldsymbol{b}) = \frac{1}{\sqrt{2}} \left[\psi_{100}(\boldsymbol{r}_1) \, \psi_{nlm}(\boldsymbol{r}_2) + \psi_{100}(\boldsymbol{r}_2) \, \psi_{nlm}(\boldsymbol{r}_1) \right] \chi_{\rm as}(\boldsymbol{s}_1, \boldsymbol{s}_2) \, . \quad (6.28)$$

For an antisymmetric space part we have the *triplet* excited state

$$\Psi_{\rm es}^{\rm T}(\boldsymbol{a}, \boldsymbol{b}) = \frac{1}{\sqrt{2}} \left[\psi_{100}(\boldsymbol{r}_1) \, \psi_{nlm}(\boldsymbol{r}_2) - \psi_{100}(\boldsymbol{r}_2) \, \psi_{nlm}(\boldsymbol{r}_1) \right] \chi_{\rm sym}(\boldsymbol{s}_1, \boldsymbol{s}_2) \, . \quad (6.29)$$

with $\chi_{\text{sym}}(\boldsymbol{s}_1, \boldsymbol{s}_2)$ given by (6.21). If we evaluate the Schrödinger equation for the central potential $\mathcal{H}^0(r_1, r_2)$, we obtain the same energy with either function (6.28) or (6.29). This energy is given by $E_{\text{es}} = E_{100} + E_{nlm}$.

We now consider the effect of the electron–electron interaction \mathcal{H}_{e-e} $(\mathbf{r}_1, \mathbf{r}_2) = e^2/(4\pi\epsilon_0 r_{12})$, where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$, and calculate it by perturbation theory. We obtain a correction E_{e-e} to E_{es} , given by

$$E_{\rm e-e}^{\rm S} = \langle \Psi_{\rm es}^{\rm S}(\boldsymbol{a}, \boldsymbol{b}) | \mathcal{H}^{1}(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}) | \Psi_{\rm es}^{\rm S}(\boldsymbol{a}, \boldsymbol{b}) \rangle = I + J$$
(6.30)

for the singlet spin state (antiparallel spin alignment), and

$$E_{\rm e-e}^{\rm T} = \langle \Psi_{\rm es}^{\rm T}(\boldsymbol{a}, \boldsymbol{b}) | \mathcal{H}^{\rm 1}(\boldsymbol{r}_1, \boldsymbol{r}_2) | \Psi_{\rm es}^{\rm T}(\boldsymbol{a}, \boldsymbol{b}) \rangle = I - J$$
(6.31)

for the triplet state (parallel spin alignment). We therefore have

$$E_{\rm e-e}^{\rm S} - E_{\rm e-e}^{\rm T} = 2 J$$
 (6.32)

The energies I and J are evaluated using the orthogonality of the radial, angular and spin wavefunctions. Because the electron–electron Hamiltonian $\mathcal{H}_{e-e}(\mathbf{r}_1, \mathbf{r}_2)$ does not depend on spin, the matrix elements of the singlet and triplet spin parts of the wavefunctions are simply determined by the orthonormality of α and β . With $\langle \pm \frac{1}{2} | \pm \frac{1}{2} \rangle = 1$ and $\langle \pm \frac{1}{2} | \mp \frac{1}{2} \rangle = 0$ the matrix elements simply give unity and zero when the spins are parallel or antiparallel. We obtain

$$I = \int \int |\psi_{100}(\boldsymbol{r}_1)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\psi_{nlm}(\boldsymbol{r}_2)|^2 \,\mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2, \qquad (6.33)$$

$$J = \int \int \psi_{100}(\mathbf{r}_1) \psi_{nlm}(\mathbf{r}_2) \, \frac{e^2}{4\pi\epsilon_0 \, r_{12}} \, \psi_{100}^*(\mathbf{r}_2) \psi_{nlm}^*(\mathbf{r}_1) \, \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2.$$
(6.34)

The energies I and J have a simple physical meaning. The *Coulomb integral* I represents the electrostatic Coulomb repulsion between the electron densities

 $|\psi_{100}(\mathbf{r}_1)|^2$ and $|\psi_{nlm}(\mathbf{r}_2)|^2$ and it has a *positive* sign, opposite to the negative sign of the electron-nuclear Coulomb attraction. The other quantity J is called the *exchange integral* because it reflects the energy associated with a change of quantum states between the two electrons. In the singlet state the space function is symmetric and the electrons have a tendency to be close to each other. In the triplet state the space function is antisymmetric and the electrons tend to avoid each other. Therefore the effect of the electrostatic repulsion is greater in the singlet state and it will be higher in energy, as shown in Fig. 6.3. The associate exchange energy $\Delta E = 2J$ corresponds to the singlet–triplet splitting.

The exchange energy $\Delta E = 2 J$ corresponds to the singlet-triplet splitting.

We can summarize this section as follows. We have seen above that the exchange interaction arises from two ingredients, the Coulomb interaction $e^2/(4\pi\epsilon_0 r_{ji})$ between two electrons and the requirement of a total antisymmetric wavefunction, the latter expressing the Pauli exclusion principle. Surprisingly, the Hamiltonian does not contain the spin at all!

The exchange interaction arises from the *Coulomb interaction* between electrons and the symmetrization postulate. The symmetrization postulate leads to either parallel or antiparallel spins.

- If J is *positive*, the spins point into the same direction and are aligned *parallel*.
- If J is negative, the spins are antiparallel.

While in He J is positive, we shall see below that for the H₂ molecule, J is negative.

6.3.2 Electron Exchange in Molecules

After Heisenberg's calculation of the He spectrum in 1926 [195] the importance of electron exchange in the bonding between atoms became clear in 1927 with the celebrated *Heitler–London (HL) calculation* [203] for the H₂ molecule. This calculation is of great historical importance for several reasons. From a *chemistry* point of view the calculation opened the door for a quantum mechanical understanding of chemical bonding. It linked the theory of the *electron pair bond*, developed in the early 1920s by Lewis [204], to the concept of the electron spin. More generally, it marked the beginning of quantum chemistry. From a *solid-state physics* point of view it influenced our thinking of whether electrons behave independently or are strongly correlated. These questions have remained at the forefront of condensed matter physics to this day. The calculation was particularly influential to the theoretical treatment of magnetism. It was the starting point for the Heisenberg Hamiltonian and pointed out the limitations of treating electrons independently, as later done in the *independent electron model*. It is for this reason that we shall discuss the Heitler–London calculation here.

In the last Sect. 6.3.1 we have discussed the electronic structure of the ground and excited states of He which is the "united" atom of H₂. Since the ground and excited states of He consist of singlet and triplet states, as summarized in Fig. 6.3, it is not obvious a priori whether the ground state is a singlet or a triplet when we bring two H atoms together with electrons in two different 1s orbitals. The HL calculation showed that the ground state is indeed a singlet. In the singlet ground state the spatial part of the two-electron wavefunction is localized between the atoms and forms an electron pair bond, and according to the Pauli principle the two electrons have opposite spins. In the following we shall discuss the IE and HL approaches in turn, using the H₂ molecule as our example.

Independent Electron Treatment

In order to appreciate the HL calculation we shall start by constructing a two-electron wavefunction for the H₂ molecule in the *independent electron (IE)* approximation. This is done by first considering the one-electron H_2^+ molecule and then adding the second electron. For convenience we show in Fig. 6.4a the relevant coordinates for H_2^+ . The Hamiltonian for the H_2^+ molecule is straightforward and given by

$$\mathcal{H}(\mathbf{r}) = \underbrace{\frac{\mathbf{p}^2}{2m_{\rm e}} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_1|}}_{\mathcal{H}_{\rm atom}} + \frac{e^2}{4\pi\epsilon_0} \left[-\frac{1}{|\mathbf{r} - \mathbf{R}_2|} + \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|} \right]. \quad (6.35)$$

Here $\mathcal{H}_{\text{atom}}$ is the central field Hamiltonian for a single H atom. The approximate solution of the corresponding molecular Schrödinger equation $\mathcal{H}(\mathbf{r})$ $\psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$ can be obtained from the solutions of the Schrödinger equation for two separate H atoms [205]. If we denote two one-electron atomic wavefunctions for the H atom as $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ and define an *overlap integral* between the two functions as

$$O = \langle \phi_1 | \phi_2 \rangle = \langle \phi_2 | \phi_1 \rangle , \qquad (6.36)$$

we can construct two normalized molecular orbital wavefunctions. They are often referred to as *linear combination of atomic orbitals* (LCAO) or *tight binding* wavefunctions. The LCAO *bonding function* is given by

$$\psi_B(\mathbf{r}) = \frac{1}{\sqrt{2(1+O)}} \left(\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})\right)$$
(6.37)

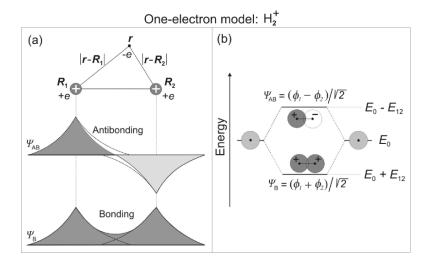


Fig. 6.4. Coordinates, wavefunctions, and energies for the one-electron H_2^+ molecule. In (a) we show the coordinates and the radial dependence of the molecular bonding and antibonding orbitals Ψ_B and Ψ_{AB} . In (b) we give the corresponding picture of the energies and wavefunctions of the bonding and antibonding molecular states, and show schematically, as done in chemistry textbooks, the combinations of the atomic 1s orbitals (*circles*) that lead to the bonding and antibonding molecular orbitals

and the LCAO antibonding function is

$$\psi_{AB}(\mathbf{r}) = \frac{1}{\sqrt{2(1-O)}} (\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})) .$$
 (6.38)

As the atoms are pushed together the overlap integral becomes unity and the bonding function $\psi_{\rm B}$ becomes the ground state function of the "united ion" He⁺ with *two* nuclear charges. It is an important point that the LCAO method has the proper united ion limit.

The two LCAO functions correspond to the eigenvalues

$$\epsilon_{\rm B} = \frac{E_0 + E_{12}}{1+O}, \qquad \epsilon_{\rm AB} = \frac{E_0 - E_{12}}{1-O}$$
(6.39)

and at the equilibrium distance the bonding function has the lower energy because $E_{12} < 0$, as shown in Fig. 6.4b. The quantities E_0 and E_{12} are the atomic energy

$$E_0 = \langle \phi_1 | \mathcal{H}(\boldsymbol{r}) | \phi_1 \rangle = \langle \phi_2 | \mathcal{H}(\boldsymbol{r}) | \phi_2 \rangle , \qquad (6.40)$$

and the interaction energy

$$E_{12} = \langle \phi_1 | \mathcal{H}(\boldsymbol{r}) | \phi_2 \rangle = E_{21} = \langle \phi_2 | \mathcal{H}(\boldsymbol{r}) | \phi_1 \rangle .$$
(6.41)

The interaction energy E_{12} and the overlap integral O decay exponentially to zero as $|\mathbf{R}_1 - \mathbf{R}_2|$ becomes large. For distances greater than the equilibrium bond length the two quantities are proportional to each other but have opposite signs, $E_{12} \propto -O$, and the atomic energy E_0 becomes the 1s binding energy (13.6 eV) of the H atom. The model is summarized in Fig. 6.4. It describes the formation of a covalent chemical bond as charge pile-up between the atoms in a "bonding" orbital. This orbital is singly occupied in the H_2^+ molecule and "glues" the atoms together. The higher energy antibonding orbital, if occupied, would lead to a repulsion between the atoms. The consequence is that the He₂ molecule, consisting of double occupation of both bonding and antibonding orbitals, does not exist.

Heitler-London Treatment

We now take the next step and consider the two-electron H_2 molecule. The relevant coordinates are illustrated in Fig. 6.5.

The H_2 Hamiltonian contains the typical kinetic energy, electron-nucleus and nucleus-nucleus Coulomb terms plus a term for the electron-electron interaction and is given by,

$$\mathcal{H}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) = \underbrace{\frac{\boldsymbol{p}_{1}^{2}}{2m_{e}} - \frac{e^{2}}{4\pi\epsilon_{0}}\frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{R}_{1}|}}_{\mathcal{H}_{atom}^{1}} + \underbrace{\frac{\boldsymbol{p}_{2}^{2}}{2m_{e}} - \frac{e^{2}}{4\pi\epsilon_{0}}\frac{1}{|\boldsymbol{r}_{2}-\boldsymbol{R}_{2}|}}_{\mathcal{H}_{atom}^{2}} \\ + \underbrace{\frac{e^{2}}{4\pi\epsilon_{0}}\left[-\frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{R}_{2}|} - \frac{1}{|\boldsymbol{r}_{2}-\boldsymbol{R}_{1}|} + \frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{r}_{2}|} + \frac{1}{|\boldsymbol{R}_{1}-\boldsymbol{R}_{2}|}\right]}_{\mathcal{H}'}.$$
 (6.42)

Here $\mathcal{H}^i_{\text{atom}}$ are the central field Hamiltonians for the two individual H atoms. We first try to find a solution of (6.42) by assuming an independent electron (IE) model. For this purpose we consider (6.42) without the electron– electron term $\mathcal{H}_{e-e} = -e^2/4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|$ and regroup the terms into two oneelectron molecular terms

$$\mathcal{H}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) = \underbrace{\frac{\boldsymbol{p}_{1}^{2}}{2m_{e}} - \left[\frac{e^{2}}{4\pi\epsilon_{0}}\frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{R}_{1}|} + \frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{R}_{2}|}\right]}_{\mathcal{H}_{\text{molecule}}^{1}} \\ + \underbrace{\frac{\boldsymbol{p}_{2}^{2}}{2m_{e}} - \frac{e^{2}}{4\pi\epsilon_{0}}\left[\frac{1}{|\boldsymbol{r}_{2}-\boldsymbol{R}_{2}|} + \frac{1}{|\boldsymbol{r}_{2}-\boldsymbol{R}_{1}|}\right]}_{\mathcal{H}_{\text{molecule}}} \\ + \frac{e^{2}}{4\pi\epsilon_{0}}\frac{1}{|\boldsymbol{R}_{1}-\boldsymbol{R}_{2}|}.$$
(6.43)

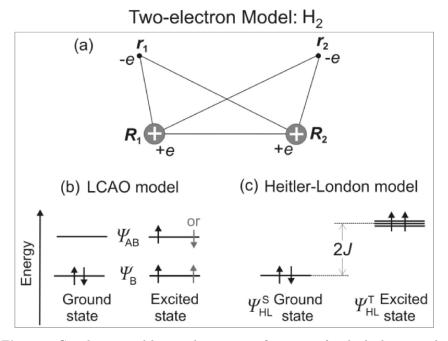


Fig. 6.5. Coordinates and lowest electronic configurations for the hydrogen molecule. In (a) we show the coordinates of the two-electron molecule. In (b) and (c) we compare the spin configurations in the ground and excited states in the LCAO and the Heitler–London models. In the LCAO model, shown in (b), the ground state and excited states are derived from the one-electron case shown in Fig. 6.4. The ground state is the singlet bonding state, the excited state is either a singlet or triplet with the same energy and with one electron in the antibonding orbital. In the HL model the ground state is a singlet and the excited state is necessarily a triplet. The singlet ground state $\Psi_{\rm HL}^{\rm S}$ corresponds to the bonding state and the triplet $\Psi_{\rm HL}^{\rm T}$ to the antibonding state. Their energy separation corresponds to the 4.476 eV dissociation energy of the H₂ molecule [206]. Note that optical transitions between the singlet and triplet states are forbidden

As for the H_2^+ molecule the solutions of the Schrödinger equations for the parts $\mathcal{H}_{molecule}^i$ can now be expressed as one-electron LCAO wavefunctions, similar to (6.37) and (6.38). These LCAO wavefunctions are good approximations to (6.43). They do not, however, satisfy the symmetrization postulate for a two-electron system. Yet we have learned in Sect. 6.2.2 how to create the appropriate two-electron singlet and triplet wavefunctions from one-electron orbitals and spin functions. By use of (6.18) we can therefore create the twoelectron singlet ground state as a product of two LCAO bonding (lowest energy) functions (6.37) according to

$$\Psi^{\rm S}(\boldsymbol{r}_1 \boldsymbol{s}_1; \boldsymbol{r}_2 \boldsymbol{s}_2) = \frac{1}{\sqrt{2}} \left[\psi_{\rm B}(\boldsymbol{r}_1) \, \psi_{\rm B}(\boldsymbol{r}_2) + \psi_{\rm B}(\boldsymbol{r}_2) \, \psi_{\rm B}(\boldsymbol{r}_1) \right] \, \chi_{\rm as}(\boldsymbol{s}_1, \boldsymbol{s}_2), \quad (6.44)$$

with $\chi_{as}(s_1, s_2)$ given by (6.19). Similarly, the *triplet* state solution is created from (6.20) and products of bonding, (6.37), and antibonding, (6.38), LCAO functions

$$\Psi^{\mathrm{T}}(\boldsymbol{r}_{1}\boldsymbol{s}_{1};\boldsymbol{r}_{2}\boldsymbol{s}_{2}) = \frac{1}{\sqrt{2}} \left[\psi_{\mathrm{B}}(\boldsymbol{r}_{1}) \psi_{\mathrm{AB}}(\boldsymbol{r}_{2}) - \psi_{\mathrm{B}}(\boldsymbol{r}_{2}) \psi_{\mathrm{AB}}(\boldsymbol{r}_{1}) \right] \chi_{\mathrm{sym}}(\boldsymbol{s}_{1},\boldsymbol{s}_{2}) ,$$
(6.45)

with $\chi_{\text{sym}}(\boldsymbol{s}_1, \boldsymbol{s}_2)$ given by (6.21).

The proper-symmetry two-electron spatial wavefunctions for the H_2 molecule consist of products of LCAO one-electron functions for the H_2^+ molecule, which are assembled into bonding and antibonding total spatial functions. The total antisymmetric wavefunctions are formed by products of the total spatial functions with the proper symmetry triplet and singlet spin functions.

The above functions provide a good approximation to the H₂ Hamiltonian (6.43). By inserting the LCAO one-electron orbitals (6.37), (6.38) and the spin functions (6.19) and (6.21) into equations (6.44) and (6.45), and renormalizing to the value of the *double overlap integral*

$$S = \langle \phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) | \phi_1(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_1) \rangle, \qquad (6.46)$$

we can rewrite the singlet state solution (6.44) in the IE approximation as

$$\Psi_{\rm IE}^{\rm S} = \frac{1}{2\sqrt{1+S}} \left[\phi_1(\boldsymbol{r}_1) \phi_2(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1) \phi_1(\boldsymbol{r}_2) \right] \left[\alpha_1 \beta_2 - \beta_1 \alpha_2 \right]}{\Psi_{\rm HL}^{\rm S}} + \frac{1}{2\sqrt{1+S}} \left[\phi_1(\boldsymbol{r}_1) \phi_1(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1) \phi_2(\boldsymbol{r}_2) \right] \left[\alpha_1 \beta_2 - \beta_1 \alpha_2 \right], (6.47)$$

where we have indicated a grouping of terms with the label $\Psi_{\rm HL}^{\rm S}$ for future reference. The triplet state is,

$$\Psi_{\rm IE}^{\rm T} = \frac{1}{\sqrt{2(1-S)}} \left[\phi_2(\boldsymbol{r}_1) \, \phi_1(\boldsymbol{r}_2) - \phi_1(\boldsymbol{r}_1) \, \phi_2(\boldsymbol{r}_2) \, \right] \chi_{\rm sym} \, . \tag{6.48}$$

The triplet spin functions χ_{sym} are given by (6.21). The IE two-electron function $\Psi_{\text{IE}}^{\text{S}}$ behaves properly as the atoms are pushed together because its components are LCAO functions that reduce to the "united" ion (He⁺) limit. However, $\Psi_{\text{IE}}^{\text{S}}$ behaves inappropriately at large distances. The reason is that it contains two ionic states $\phi_1\phi_1$ and $\phi_2\phi_2$, where two electrons are on the same atom. These states, corresponding to H⁺H⁻, enter on an equal footing with states $\phi_1\phi_2$ and $\phi_2\phi_1$ where a single electron is on each atom. When the atoms are pulled apart, the dissociation limit of H₂ should simply corresponds to two H atoms, yet the ionic terms in $\Psi_{\text{IE}}^{\text{S}}$ lead to a 50/50 mixture

of atoms and ions. Furthermore, if we calculated the expectation values of the full H₂ Hamiltonian (6.42), including the electron–electron term, with the singlet state $\Psi_{\text{IE}}^{\text{S}}$ and the triplet state $\Psi_{\text{IE}}^{\text{T}}$, the latter would be lower in energy at large distance, because it does not suffer from the additional contribution of the ionic states. Hence at large bond length the IE wavefunction would yield the incorrect triplet ground state.

This problem is overcome by the Heitler-London approximation

$$\Psi_{\rm HL}^{\rm S} = \frac{1}{2\sqrt{1+S}} \left[\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) \right] \left[\alpha_1 \,\beta_2 - \beta_1 \,\alpha_2 \right] \,, \ (6.49)$$

It is the independent electron wavefunction with the ionic terms omitted as indicated in (6.47). The electrons now belong to both atoms and the wavefunction is characteristic of a *covalent bond*. The HL *triplet* wavefunction is identical to that of the independent electron approximation given by (6.48), hence

$$\Psi_{\rm HL}^{\rm T} = \Psi_{\rm IE}^{\rm T} \ . \tag{6.50}$$

It is important to recognize the difference between the IE and HL singlet wavefunctions. The two-electron singlet state in the IE model is written as a product of symmetrized *molecular* LCAO wavefunctions, in line with the grouping of terms in (6.43). In contrast, the two-electron singlet in the HL model is written as a product of symmetrized *atomic* functions, reflecting the grouping of terms in (6.42). This causes the HL wavefunction $\Psi_{\rm HL}^{\rm S}$ to be a poorer representation than the IE representation at short bond length. We have seen that the IE function $\Psi_{\rm IE}^{\rm S}$ reduces to the proper united atom limit of He, with a doubly charged nucleus. In contrast, the structure of the HL wavefunction (6.49) corresponds to a two-electron wavefunction that is constructed from *atomic* functions $\phi_i(\mathbf{r}_i)$, corresponding to H nuclei with a single positive charge. This means that the atomic functions $\phi_i(\mathbf{r}_i)$ will be far too extended in space to be a good description of the united atom He with two positive charges in its nucleus. At the equilibrium molecular distance it is not clear a priori whether the IE or HL wavefunction is better, but it turns out the HL function is indeed a better approximation for H_2 .

6.3.3 Magnetism and the Chemical Bond

We conclude the discussion on exchange in molecules with a quick comparison of the ground and excited states in the independent electron and Heitler– London pictures, as illustrated in Fig. 6.5b, c. At the internuclear distance of H_2 the independent electron model gives a singlet ground state just like the correlated two-electron model. The first excited state consists of the excitation of one electron to the antibonding orbital, and both a parallel (triplet) or antiparallel (singlet) orientation of the two electrons have the same energy. In the Heitler–London model, the ground state is again a singlet. Similar to the one-electron model, this two-electron state is called the "bonding" state. The first excited state is the triplet with both electrons occupying the "antibond-ing" two-electron state. This fundamental concept linking the existence of a chemical bond with the existence of spin needs to framed and remembered.

The *Heitler–London* model links the occurrence of a "covalent" chemical bond with a correlated electron pair whose spatial orbitals overlap between the atoms and where, in accordance with the Pauli principle, the electrons have opposite spins.

Similar to the one-electron case one can express the singlet-triplet or bonding-antibonding splitting in closed form. The total Hamiltonian $\mathcal{H}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ for H₂ is given by (6.42) and it consists of atomic parts $\mathcal{H}^1_{\text{atom}}$ and $\mathcal{H}^2_{\text{atom}}$ and the extra potential energy terms \mathcal{H}' . By use of the Heitler–London singlet and triplet functions one obtains the energies [205]

$$E^{\rm S} = \frac{\langle \Psi_{\rm HL}^{\rm S} | \mathcal{H}(\boldsymbol{r}_1, \boldsymbol{r}_2) | \Psi_{\rm HL}^{\rm S} \rangle}{\langle \Psi_{\rm HL}^{\rm S} | \Psi_{\rm HL}^{\rm S} \rangle} = 2E_0 + \frac{C+X}{1+S} .$$
 (6.51)

and

$$E^{\mathrm{T}} = \frac{\langle \Psi_{\mathrm{HL}}^{\mathrm{T}} | \mathcal{H}(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}) | \Psi_{\mathrm{HL}}^{\mathrm{T}} \rangle}{\langle \Psi_{\mathrm{HL}}^{\mathrm{T}} | \Psi_{\mathrm{HL}}^{\mathrm{T}} \rangle} = 2E_{0} + \frac{C - X}{1 - S} .$$
 (6.52)

Here the double overlap function S is given by (6.46), E_0 is the atomic energy of the H atom, which is given by

$$E_0 = \langle \phi_1(\boldsymbol{r}_1) | \mathcal{H}^1_{\text{atom}} | \phi_1(\boldsymbol{r}_1) \rangle = \langle \phi_2(\boldsymbol{r}_2) | \mathcal{H}^2_{\text{atom}} | \phi_2(\boldsymbol{r}_2) \rangle , \quad (6.53)$$

C is the Coulomb integral

$$C = \langle \phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) | \mathcal{H}' | \phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) \rangle , \qquad (6.54)$$

and X is the exchange integral

$$X = \langle \phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) | \mathcal{H}' | \phi_1(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_1) \rangle .$$
(6.55)

Note that there are two equivalent terms C and X corresponding to exchange of coordinates \mathbf{r}_1 and \mathbf{r}_2 . Since the exchange integral links two-electron factors where each electron is attached to different nuclei it falls off similar to the double overlap function (6.46) and more rapidly than the Coulomb integral C. This point is of great importance for the magnetism of solids which is therefore based on a *short-range* interaction.

The *exchange integral* between two atoms falls off rapidly with increasing nuclear distance.

From (6.51) and (6.52) we obtain for the singlet-triplet splitting as

$$E^{\rm S} - E^{\rm T} = 2J = 2\frac{X - SC}{1 - S^2}$$
 (6.56)

Here we have defined the exchange constant J in accordance with that given by (6.32) for the He atom, i.e., we have taken the singlet-triplet splitting to be 2J, as shown in Fig. 6.5c. For the hydrogen molecule the singlet state is lower in energy than the triplet state and therefore the exchange constant J is *negative*. Note that for zero wavefunction overlap we have J = X.

The singlet-triplet splitting has indeed been observed as reviewed by Herzberg [206]. Since the triplet state corresponds to the unstable antibonding state the singlet-triplet energy separation corresponds to the dissociation energy of the H_2 molecule, which is 4.476 eV. We can therefore frame the following important result.

In the H_2 molecule the singlet-triplet excitation energy corresponds to the 4.476 eV dissociation energy of the molecule. The exchange coupling constant J has a value of 2.24 eV.

6.3.4 From Molecules to Solids

Because it emphasizes the importance of the singlet-triplet correlation for bonding, the Heitler-London function $\Psi_{\text{HL}}^{\text{S}}$ today is widely regarded in quantum chemistry as a prototype two-electron wavefunction for the description of *correlated or localized* electrons [194]. Historically it served as a quantum mechanical explanation for Lewis' electron-pair bond (written for H₂ as H:H) which was developed in the 1930s by Pauling and others into "valence bond theory" [204].

In contrast, the independent electron function $\Psi_{\text{IE}}^{\text{S}}$ represents a prototype wavefunction for *independent, delocalized, or itinerant* electrons. When the field experienced by a single electron is taken to arise from a spatial *average* over the positions of the other electrons (similar to (6.9)), which in practice is accomplished by the self-consistent field *Hartree–Fock* method, the IE approximation underlies *molecular orbital* (MO) theory and density functional theory (DFT). MO theory was developed by Hund [207], Mulliken [208], and Slater [209] and DFT was developed in the mid 1960s by Hohenberg, Kohn, and Sham [210, 211]. The latter approach is discussed in Sect. 7.4.4.

Despite the limitations of the independent electron approximation pointed out by the HL calculation, at the end of the 20th century the IE model had nevertheless assumed a dominant role in chemistry and solid-state physics. The success of this theory in chemistry is partly founded on the fact that it is easier to implement in calculations⁷ and partly on the recognition that most chemical bonds are relatively weakly correlated [194]. Correlation contributions can therefore be included through an extension of self-consistent field methods, as done in the *local-density approximation* (LDA) (see Sect. 7.4.4). The latter approximation has been equally important in chemistry and solid-state physics. It has had a major success in describing the magnetic ground state (zero temperature) properties of the elementary transition metals, despite the presence of correlation effects. On the other hand, we know to-day that the LDA fails for systems where correlation effects are strong as in rare earth systems or the transition metal oxides, in particular the important subclass of high-temperature superconductors [194]. Since it is designed as a ground state method the LDA also cannot describe finite temperature magnetism as discussed in Chap. 12.

In general, the HL and IE wavefunctions are only approximations and the true ground state lies in-between the two extremes. To this day the competition between the pictures of uncorrelated and correlated electrons has remained a central issue in solid-state physics and, in particular, in magnetism. Historically, in magnetism this dilemma led to the competing pictures of itinerant (meaning "traveling") versus localized behavior, the localized picture being favored by Van Vleck [212] and the itinerant idea by Slater [28, 29]. Because these concepts still dominate today's thinking and are at the very heart of magnetism we have discussed them here at length for the simple case of the He atom and H_2 molecule. For larger systems the description of the duality between localized and itinerant behavior still awaits a unifying theory.

Owing to the difficulties of establishing a first-principles theory it is common today to explore the magnetic properties of materials by means of model Hamiltonians. These Hamiltonians are constructed to give the correct result for simple cases, e.g., H_2 molecule, and to explore the rules for the electron– electron interactions and magnetic order in extended systems. The two most celebrated models are the Heisenberg and Hubbard models. The general solutions of these models have become research topics of their own. The *Heisenberg model* describes the exchange interaction by explicitly introducing the spin. Over the years it has been thoroughly explored to understand magnetic ordering in one, two, or three dimensions [213] and we shall see in Sect. 11.1.2 that it plays an important role today in describing the temperature dependence of the magnetization. The *Hubbard model* [214] has assumed particular importance in the description of the splitting of electronic states in correlated materials [194]. Such materials offer a rich phase diagram in terms of

⁷For example, the simplest HL wavefunction consists of two Slater determinants, in contrast to the single Slater determinant for the IE wavefunction in the self consistent field approximation [204].

their transport and magnetic properties. A particularly important subclass is formed by the high- $T_{\rm C}$ superconductors.

Because of the importance of the Heisenberg and Hubbard models in contemporary physics, in general, and their special educational role in understanding the complicated interplay between charge and spin we shall discuss them later. In particular, our modern understanding and language of exchange is strongly influenced by these two models. In order to appreciate the basic aspects of the two models we shall discuss them in the special context of the H_2 molecule where the two models can be solved exactly and, in certain limits, are found to be equivalent to each other. In particular, the Hubbard model provides the transition between the independent electron model and the HL model of correlated electrons.

It needs to be stressed up front that the Heisenberg and Hubbard Hamiltonians lack ab initio justification and simply constitute a convenient model Hamiltonian ansatz to circumvent the difficulties in establishing a firstprinciples theory.

6.3.5 The Heisenberg Hamiltonian

After his work on the He atom in 1926 and the Heitler–London calculation for H_2 in 1927, Heisenberg addressed the microscopic origin of exchange in solids and therefore the origin of ferromagnetism in 1928 [25]. He formulated an exchange model that formally builds on the HL model, the now famous *Heisenberg Hamiltonian*.

Heisenberg used the concepts of preferred parallel alignment to construct a new effective Hamiltonian which tries to hold the spins parallel (triplet) or antiparallel (singlet) depending on the sign of the exchange integral. The model thus required the existence of two states, a singlet and a triplet state, for the coupling of two spins with proper degeneracy and relative energy, as in the two electron HL model. The final result of the HL calculation is summarized in (6.51) and (6.52), and we see that there are three terms that determine the energies of the triplet and singlet electronic states. The effective Hamiltonian for H₂ can therefore be written in the form

$$\mathcal{H}_{\text{eff}} = 2\mathcal{H}_0 + \mathcal{H}_{\text{coul}} + \mathcal{H}_{\text{exch}} , \qquad (6.57)$$

where E_0 is the expectation value of atomic central field Hamiltonian \mathcal{H}_0 , the Coulomb energy C is the expectation value of \mathcal{H}_{coul} , and the exchange energies $\pm X$ are the singlet and triplet expectation values of the exchange Hamiltonian \mathcal{H}_{exch} . We have seen the remarkable result that the original Hamiltonian (6.42) does not include the spin at all. The spin enters in the solution only by dictating the symmetry of the spatial part of the wavefunctions. The fact that today we often associate the exchange interaction with the coupling of spins has its origin in rewriting the last term in (6.57) in an explicit spin dependent Heisenberg Hamiltonian $\mathcal{H} = A s_1 \cdot s_2$

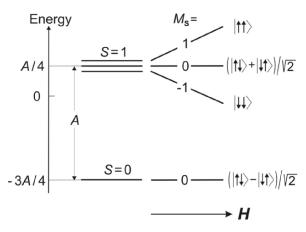


Fig. 6.6. States and energies resulting from a coupling of two spins s_1 and s_2 as assumed in the Heisenberg Hamiltonian of form $\mathcal{H} = A s_1 \cdot s_2$. The total splitting is |A|. If A > 0 the singlet state S = 0 is lowest, if A < 0 the triplet state S = 1 is lowest. The triplet state may be split by spin-orbit coupling, assumed to be zero, and a magnetic field H, as shown

form, the Heisenberg Hamiltonian. The model Hamiltonian that for H_2 gives the proper energies and wavefunctions is of the form

$$\mathcal{H}_{\text{exch}} = A \, \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 \tag{6.58}$$

where A is a constant. The spins $\mathbf{s}_1 = \pm 1/2$ and $\mathbf{s}_2 = \pm 1/2$ couple to a total spin according to $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, so that $\mathbf{S}^2 = (\mathbf{s}_1)^2 + (\mathbf{s}_2)^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2$ and their combination results in a triplet S = 1 or a singlet S = 0 state. By use of the operator expectation values $\langle \mathbf{S}^2 \rangle = S(S+1)$ and $\langle \mathbf{s}_i^2 \rangle = s(s+1) = 3/4$, the triplet state has an energy $\mathbf{s}_1 \cdot \mathbf{s}_2 = 1/4$ and the singlet state has an energy $\mathbf{s}_1 \cdot \mathbf{s}_2 = -3/4$, as shown in Fig. 6.6. The spin functions which follow from (6.19) and (6.21) are also shown. Comparison of Fig. 6.6 with Fig. 6.5c reveals the similarity of the results of the Heitler–London and the Heisenberg models, where A = -2J.

By extension of the two-spin Hamiltonian, the effective Heisenberg Hamiltonian for a many-electron system is usually written (see footnote 3)

$$\mathcal{H}_{\text{eff}} = -\sum_{i \neq j}^{N} J_{ij} \, \boldsymbol{s}_i \cdot \boldsymbol{s}_j = -2 \sum_{i < j}^{N} J_{ij} \, \boldsymbol{s}_i \cdot \boldsymbol{s}_j, \qquad (6.59)$$

where $J_{ij} = J_{ji}$ is symmetric so that we can sum over half the terms and multiply by a factor of 2, as indicated on the right. Our notation therefore corresponds to A = -2J in the two-electron case of (6.58). The *exchange integral* J_{ij} is defined similar to (6.34),

$$J_{ij} = \int \int \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \, \frac{e^2}{4\pi\epsilon_0 \, r_{12}} \, \psi_i^*(\mathbf{r}_2) \psi_j^*(\mathbf{r}_1) \, \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2. \tag{6.60}$$

The sign convention follows that of the original He calculation. If the spins are parallel we have a triplet state with $\mathbf{s}_i \cdot \mathbf{s}_j = 1/4 > 0$ (see Fig. 6.6), and $\langle \mathcal{H}_{\text{eff}} \rangle$ is a minimum (ground state) if J_{ij} is positive. This corresponds to *ferromagnetic* coupling. If the spins are *antiparallel*, i.e., antiferromagnetically coupled, we have a singlet state with $\mathbf{s}_i \cdot \mathbf{s}_j = -3/4 < 0$ and a minimum in energy corresponds to negative J_{ij} .

For the two-electron case the singlet–triplet splitting is given, as expected, by

$$\langle \mathcal{H}_{\text{eff}} \rangle^{\text{S}} - \langle \mathcal{H}_{\text{eff}} \rangle^{\text{T}} = -2 J_{12} \left(-\frac{3}{4} - \frac{1}{4} \right) = 2 J_{12} .$$
 (6.61)

Our definition of the Heisenberg Hamiltonian given by (6.59) is therefore consistent with the result for the exchange splitting in two-electron atoms and di-atomic molecules.⁸ We can summarize the Heisenberg model as follows,

The *Heisenberg model* accounts for the exchange interaction by explicitly couplings pairs of spins or atomic moments.

• The coupling energy constant J_{ij} is positive for ferromagnetic coupling, and negative for antiferromagnetic coupling.

- The coupling of individual spins, located on the same atom, is called *intra-atomic exchange*.
- The coupling of atomic moments (sums of spins) on different atoms is called *inter-atomic exchange*.

We shall discuss the differences between intra- and extra-atomic atomic exchange in more detail in Sect. 11.1.4.

The Heisenberg Hamiltonian has been extensively used for the discussion of magnetic order in one, two, and three dimensions [213]. In one dimension it reduces to the famous *Ising* expression

$$\mathcal{H}_{\text{eff}} = -2\sum_{i < j}^{N} J_{ij} \left(\boldsymbol{s}_{\boldsymbol{z}} \right)_{i} \left(\boldsymbol{s}_{\boldsymbol{z}} \right)_{j}.$$
(6.63)

The phenomenological Heisenberg Hamiltonian may be regarded as only the first term in an expansion of the exchange energy. The next higher term would be of the form

$$\sum_{i\neq j}^{N} J_{ij}' \left(\boldsymbol{s}_i \cdot \boldsymbol{s}_j \right)^2 \tag{6.64}$$

⁸We note that some authors define the Heisenberg Hamiltonian as

$$\mathcal{H}_{\text{eff}} = -\frac{1}{2} \sum_{i \neq j}^{N} J_{ij} \, \boldsymbol{s}_i \cdot \boldsymbol{s}_j = -\sum_{i < j}^{N} J_{ij} \, \boldsymbol{s}_i \cdot \boldsymbol{s}_j \,. \tag{6.62}$$

so that J_{ij} differs by a factor of 2.

and is called *biquadratic exchange*. When the exchange coupling constant is positive the $\cos^2 \theta$ dependence of the interaction on the angle θ between the two spins leads to a minimum energy that corresponds to *perpendicular coupling* of the spins. Such coupling can indeed be observed and has attracted attention for multilayer systems [215].

6.3.6 The Hubbard Hamiltonian

In the Heisenberg model the exchange term in the effective Hamiltonian (6.57) is rewritten explicitly in terms of spin operators. The *Hubbard Hamiltonian* rewrites the effective Hamiltonian in a different way. In accordance with the original electronic Hamiltonian it does not include a spin operator, although the spin is considered in the calculation of the matrix elements. The ideas behind it were independently developed by Gutzwiller [216], Hubbard [217] and Kanamori [218] in 1963, although the model is typically referred to under Hubbard's name alone. The central idea behind this model is to explore the interplay between two competing energies in the formation of the electronic states in a multiatom and multielectron system. One of the energies is the electrostatic Coulomb energy between electrons, the other the hopping energy of electrons from one atom to the next. The spin enters by imposing restrictions in accordance with the Pauli principle. We can summarize the basic features of the Hubbard model as follows,

The *Hubbard model* accounts for the magnetic ground state through a balance of two competing energies, under the constraint of the Pauli principle.

• The *hopping energy* involves motion of electrons of the *same spin between different atoms.* It favors *delocalized* or band-like behavior.

• The *Coulomb energy* experienced by electrons of *opposite spin on the same atom* keeps the electrons apart, confined to different atoms. It favors the formation of *localized moments*.

When applied to H_2 , the Hamiltonian (6.57) is rewritten in the following Hubbard form

$$\mathcal{H}_{\rm eff} = 2\mathcal{H}_0 + \mathcal{H}_{\rm Hub} , \qquad (6.65)$$

where the Hubbard Hamiltonian is given by [194, 214]

$$\mathcal{H}_{\text{Hub}} = -t \sum_{\sigma=\downarrow,\uparrow} \left(c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma} \right) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}).$$
(6.66)

The operator $c_{i\sigma}^{\dagger}$ creates an electron with spin σ on atom *i* and the operator $c_{i\sigma}$ annihilates an electron with spin σ on atom *i*. The action of the creation and annihilation operators, also called *ladder operators*, on the spin

orbitals follows the usual rules found in quantum mechanics books. For example, for the H₂ molecule with a maximum of one electron per spin per atom we have for a given atom $c_{i\sigma}^{\dagger}|\sigma'\rangle = |\sigma\sigma'\rangle$ and $c_{i\sigma}^{\dagger}|0\rangle = |\sigma\rangle$ and similarly $c_{i\sigma}|\sigma\sigma'\rangle = |\sigma'\rangle$ and $c_{i\sigma}|\sigma\rangle = |0\rangle$, where $\sigma' \neq \sigma$. The first term in (6.66) therefore describes the electron hopping from atom to atom without change of spin. The operator $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ in the second term is the number operator, counting the occupation on atom *i* for a given spin σ , and for H₂ we have for example $\langle \sigma | n_{i\sigma} | \sigma \rangle = 1$ and $\langle \sigma | n_{i\sigma} | \sigma' \rangle = \langle \sigma' | n_{i\sigma} | \sigma \rangle = 0$. The second term in (6.66) describes the Coulomb interaction U of electrons with opposite spin on the same atom. In summary, the hopping term involves the same spin and different atoms, the Coulomb term involves different spins on the same atom.

Our convention in (6.66) is such that both t and U are real, and t > 0while U may be positive or negative. Within this book we will only discuss the case $U \ge 0$. Knowing that the magnetic ground state will be determined by a minimum of the total energy $\langle \mathcal{H}_{\text{Hub}} \rangle$, we can view the relative influence of the two terms in (6.66) in the following two pictures.

- We may view the establishment of a minimum in total energy as a *competi*tion between minimizing two energies of the same sign, the kinetic energy and the Coulomb energy. We shall see below that -t is proportional to the kinetic energy $E_{\rm kin}$, so that the magnetic ground state is determined by minimizing (note signs) both the first term $-t \propto E_{\rm kin}$ (increasing t) and the second term U (decreasing U) in the most efficient way.
- One may also view the same process as a *balancing* of energies of opposite sign, hopping from atom to atom which gives an energy +t, and putting two electrons on the same site which costs a repulsion energy U.

It is important to realize that while the action of the operators in the Hubbard Hamiltonian depends on spin, the Hamiltonian does not contain an explicit spin operator, i.e., an operator that can flip spins. The hopping operator only moves spins but does not flip them while the Coulomb operator describes the energy between opposite spin electrons. Thus the Hamiltonian actually acts on the spatial part of the wavefunctions through coordinate changes while the spins are left alone. This is in contrast to the Heisenberg Hamiltonian (see below).

The Hubbard Hamiltonian does not allow spin flips. It acts on the spatial part of the wavefunctions through coordinate changes while preserving the spin.

6.3.7 Heisenberg and Hubbard Models for H₂

We now want to use the Hamiltonian (6.66) to calculate the electronic energy levels and functions for the H₂ molecule.⁹ In doing so we need to develop an appropriate set of basis functions which are used to diagonalize the Hamiltonian. In thinking about the basis functions we will also get an appropriate set for diagonalizing the Heisenberg Hamiltonian. This will allow us to avoid the semiclassical shortcut that we took in the last section and derive the result summarized in Fig. 6.6 by quantum theory.

In finding a suitable set of basis states one needs to remember that the symmetrization postulate for Fermions requires that the total wavefunction, consisting of radial, angular and spin parts, is antisymmetric. It is therefore convenient to start with basis functions that can be assembled to have the proper total symmetry. The key expressions for the structure of such wavefunctions for H₂ are (6.44) and (6.45) which by use of (6.19) and (6.21) may be written in short form as

$$\Psi^{\rm S} = \underbrace{(|R\rangle |R'\rangle + |R'\rangle |R\rangle)}_{\rm symmetric} \underbrace{(|\uparrow\rangle| \downarrow\rangle - |\downarrow\rangle| \uparrow\rangle)/\sqrt{2}}_{\rm antisymmetric} \tag{6.67}$$

and

$$\Psi^{\mathrm{T}} = \underbrace{(|R\rangle |R'\rangle - |R'\rangle |R\rangle)}_{\text{antisymmetric}} \underbrace{\begin{cases} |\uparrow\rangle|\uparrow\rangle\\ (|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle)/\sqrt{2}\\ |\downarrow\rangle|\downarrow\rangle}_{\text{symmetric}} \quad . \tag{6.68}$$

Here $R(\mathbf{r}_1)$ and $R'(\mathbf{r}_2)$ are one-electron LCAO bonding functions for the H⁺ molecule given by (6.37) and $|\uparrow\rangle$ and $|\downarrow\rangle$ are the one-electron spin functions. Since the central field and the Coulomb terms of the Hamiltonian are diagonal in the two-electron functions $|R\rangle |R'\rangle = |RR'\rangle$ they give the appropriate energies $2E_0$ and C in the effective Hamiltonian (6.57). We can therefore conveniently build our basis functions from these two-electron functions and two-electron spin functions of the form $|s\rangle |s'\rangle = |ss'\rangle$.

Since the central field and Coulomb terms of the effective Hamiltonian are diagonal in the functions $|RR'\rangle$, they are good basis functions for both the effective Hamiltonians in the Heisenberg and Hubbard formulations. What is not taken care of by these functions in the effective Hamiltonian (6.57) are the Heisenberg exchange term \mathcal{H}_{exch} given by (6.58) and the Hubbard hopping term in (6.66).

⁹Our calculation is somewhat different from the approach suggested as a problem (Chap. 32, problem 5) in Ashcroft and Mermin's book [219]. The solution of the problem can be found in Ref. [220].

Table 6.1. Rules for spin operators s_{α} ($\alpha = x, y$, or z) acting on spin-states $|\uparrow\rangle$ and $|\downarrow\rangle$, where we have assumed that z is the quantization axis. Eigenvalues are in units of \hbar

$ s_x \uparrow\rangle = \frac{1}{2} \downarrow\rangle$	$ s_y \uparrow angle = -rac{\mathrm{i}}{2} \downarrow angle$	$ s_z \uparrow angle = -rac{1}{2} \uparrow angle$
$ s_x \downarrow angle=rac{1}{2} \uparrow angle$	$ s_y \downarrow angle=-rac{\mathrm{i}}{2} \uparrow angle$	$s_z \downarrow\rangle = -\frac{1}{2} \downarrow\rangle$

Heisenberg Model Calculation

For the Heisenberg Hamiltonian the H_2 basis functions can simply be constructed by combining the $|RR'\rangle$ functions with a complete set of spin basis functions, which can be written as follows,

$$|\uparrow,\uparrow\rangle \quad |\downarrow,\downarrow\rangle \quad |\uparrow,\downarrow\rangle \quad |\downarrow,\uparrow\rangle \quad |\uparrow\downarrow,0\rangle \quad |0,\uparrow\downarrow\rangle.$$
(6.69)

The notation $|\mathbf{s}, \mathbf{s}'\rangle = |\mathbf{s}\rangle |\mathbf{s}'\rangle$ means that there is an electron with spin \mathbf{s} on one atom and with spin \mathbf{s}' on the other ($\mathbf{s}' = \mathbf{s}$ is allowed). States of the form $|\mathbf{ss}', 0\rangle = |\mathbf{ss}'\rangle |0\rangle$ have two electrons with opposite spins ($\mathbf{s}' \neq \mathbf{s}$, dictated by the Pauli principle) on one atom and no electron on the other. We can now calculate the matrix elements of the Hamiltonian (6.57) in the Heisenberg form,

$$\mathcal{H}_{\text{eff}} = 2\mathcal{H}_0 + \mathcal{H}_{\text{coul}} - 2J_{12}\,\boldsymbol{s}_1 \cdot \boldsymbol{s}_2 \,, \qquad (6.70)$$

In doing so we need to remember how the spin operator s acts on the spin functions, which is given in Table 6.1.

Table 6.1 shows that the spin operator can induce spin flips.¹⁰ By denoting the expectation values $\langle \mathcal{H}_0 \rangle = E_0$ and $\langle \mathcal{H}_{coul} \rangle = U$ we obtain the matrix in Table 6.2.

The energies of the form $\langle 0, \uparrow \downarrow | 2\mathcal{H}_0 + \mathcal{H}_{coul} - 2J_{12} \mathbf{s}_1 \cdot \mathbf{s}_2 | 0, \uparrow \downarrow \rangle = E^{+-}$ correspond to the ionic state $\mathrm{H}^+\mathrm{H}^-$ which is higher in energy and omitted in the Heitler–London calculation. The eigenvalues and eigenfunctions of the nontrivial 4 × 4 submatrix in Table 6.2 are given by a triplet and a lower energy singlet,

$$\begin{split} E_{\mathrm{T}} &= 2E_{0} + U + J_{12}/2 \qquad \Psi_{\mathrm{T}} = |\uparrow,\uparrow\rangle \\ E_{\mathrm{T}} &= 2E_{0} + U + J_{12}/2 \qquad \Psi_{\mathrm{T}} = |\downarrow,\downarrow\rangle \\ E_{\mathrm{T}} &= 2E_{0} + U + J_{12}/2 \qquad \Psi_{\mathrm{T}} = \frac{1}{\sqrt{2}} \left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\right) \\ E_{\mathrm{S}} &= 2E_{0} + U - 3J_{12}/2 \qquad \Psi_{\mathrm{S}} = \frac{1}{\sqrt{2}} \left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right). \end{split}$$

¹⁰The conditions for the experimental observation of spin flips are discussed in Sect. 12.7.1.

	$ \uparrow,\uparrow angle$	$ \downarrow,\downarrow angle$	$ \uparrow,\downarrow angle$	$ \downarrow,\uparrow angle$	$ \uparrow\downarrow,0 angle$	$ 0,\uparrow\downarrow angle$
$ \uparrow,\uparrow angle$	$2E_0 + U + \frac{J_{12}}{2}$	0	0	0	0	0
$ \downarrow,\downarrow angle$	0	$2E_0 + U + \frac{J_{12}}{2}$	0	0	0	0
$ \uparrow,\downarrow angle$	0	0	$2E_0 + U - \tfrac{J_{12}}{2}$	J_{12}	0	0
$ \downarrow,\uparrow angle$	0	0	J_{12}	$2E_0 + U - \frac{J_{12}}{2}$	0	0
$ \uparrow\downarrow,0 angle$	0	0	0	0	E^{+-}	0
$ 0,\uparrow\downarrow angle$	0	0	0	0	0	E^{+-}

Table 6.2. Matrix elements of the Heisenberg Hamiltonian for H_2 between the six possible spin orbitals of the molecule. The energy E^{+-} corresponds to the higherenergy ionic state H^+H^- which is omitted in the Heitler–London calculation

This is the same result as that shown in Fig. 6.6 since $A = 2J_{12}$. We have not written down the spatial parts of the wavefunctions. They can be constructed from symmetric and antisymmetric combinations of the $|RR'\rangle$ functions to make the total wavefunctions antisymmetric.

Hubbard Model Calculation

For the diagonalization of the effective Hamiltonian in the Hubbard form (6.65) we choose a basis of spatial functions that can be combined to give either symmetric or antisymmetric total spatial functions. The spin part of the wavefunction is only considered in the calculation of the matrix elements. The proper symmetry spin functions can be inserted in the end according to the symmetrization postulate. If the spatial wavefunction comes out to be symmetric the spin wavefunction needs to be antisymmetric, i.e., is a singlet, and if the spatial wavefunction is antisymmetric the spin wavefunction has to be symmetric, i.e., one of the triplet functions. Therefore, since the effective Hamiltonian does not contain the spin operator it is sufficient to diagonalize the corresponding matrix in the basis of spatial functions, only. By use of the two spatial functions $|R(\mathbf{r}_1)\rangle$ and $|R'(\mathbf{r}_2)\rangle$ we can now write down the possible combinations for the H₂ molecule. We write the spatial functions in the same form as the spin functions (6.69),

$$\underbrace{|R,R\rangle \quad |R',R'\rangle}_{\uparrow,\downarrow \text{ and }\downarrow,\uparrow} \quad \underbrace{|R,R'\rangle \quad |R',R\rangle}_{\uparrow,\uparrow \text{ and }\downarrow,\downarrow} \quad \underbrace{|RR',0\rangle \quad |0,RR'\rangle}_{\uparrow\downarrow,0 \text{ and }0,\uparrow\downarrow} \quad (6.71)$$

The notation $|R, R'\rangle$ means that there is an electron with function $|R\rangle$ on one atom and an electron with function $|R'\rangle$ on the other atom. For the first two basis functions R = R' and the electrons have the same spatial coordinates $r_1 = r_2$ and the spins are necessarily opposite because of the Pauli principle. This is indicated underneath the wavy brackets in (6.71). For the last two functions the notations $|0, RR'\rangle$ and $|RR', 0\rangle$ mean that there is no electron

Table 6.3. Matrix elements of the Hubbard Hamiltonian for H_2 between the six possible spin orbitals of the molecule

	R,R' angle	R',R angle	R,R angle	R',R' angle	RR',0 angle	0,RR' angle
R,R' angle	$2 E_0$	0	0	0	0	0
R',R angle	0	$2 E_0$	0	0	0	0
R,R angle	0	0	$2 E_0$	0	-t	-t
R',R' angle	0	0	0	$2 E_0$	-t	-t
RR',0 angle	0	0	-t	-t	$2E_0 + U$	0
$ 0,RR'\rangle$	0	0	-t	-t	0	$2E_0 + U$

on one atom and two electrons on the other atom. In this case the electrons also have opposite spins to satisfy the Pauli principle. For the middle two functions we have $R \neq R'$ and the electrons are allowed to have parallel spins.

The interaction matrix for the Hamiltonian (6.65) of the hydrogen molecule is given in Table 6.3.

We see that the hopping terms give rise to off-diagonal matrix elements because they can cause a change in the spatial function. For U > 0 the two highest energy eigenvalues of the matrix in Table 6.3 are given by,

$$E_6 = 2E_0 + \frac{U}{2} + \frac{U}{2}\sqrt{1 + \frac{16t^2}{U^2}}.$$

$$E_5 = 2E_0 + U$$

The lowest four eigenvalues and unnormalized eigenfunctions are,

$$\begin{array}{ll} E_4 = 2E_0 & \Psi_4 = |R, R'\rangle \\ E_3 = 2E_0 & \Psi_3 = |R', R\rangle \\ E_2 = 2E_0 & \Psi_2 = -|R, R\rangle + |R', R'\rangle \end{array}$$

with the ground state given by

$$E_{1} = 2E_{0} + \frac{U}{2} - \frac{1}{2}\sqrt{U^{2} + 16t^{2}}$$
$$\Psi_{1} = |R, R\rangle + |R', R'\rangle + \frac{-U + \sqrt{U^{2} + 16t^{2}}}{4t} \left(|RR', 0\rangle + |0, RR'\rangle\right). \quad (6.72)$$

The states $\Psi_2 - \Psi_4$ have antisymmetric spatial functions, hence need to have symmetric spin functions. They are thus *triplet* states. The lowest energy state Ψ_1 has a symmetric spatial function and hence must be a *singlet* spin state.

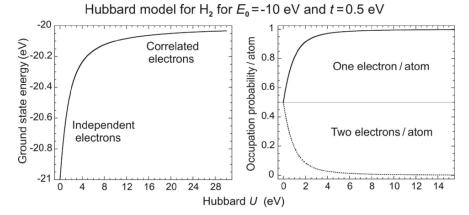


Fig. 6.7. Left: ground state energy for the hydrogen molecule according to (6.72) for the case $E_0 = -10 \text{ eV}$ and t = 0.5 eV as a function of Coulomb energy U. Right: The occupation probability per H atom for either 1 electron/atom or 2 electrons/atom as a function of U

The energies of the ground state and the probabilities for one or two electrons per atom calculated from (6.72) by assuming $E_0 = -10 \text{ eV}$ (chosen to be close to the ionization energy 13.6 eV of the H atom) are shown in Fig. 6.7.

The energy E_1 and wavefunction Ψ_1 given by (6.72) describe the ground state for all cases $U \ge 0$ and we can therefore discuss the interplay between the hopping energy and Coulomb energy. The case where the two energies are of comparable size is quite complicated but the limits of small t and large U represent familiar results.

In the limit $|U \gg t|$, the ground state energy and wavefunction are

$$E_1 = 2E_0 - \frac{4t^2}{U} \qquad \Psi_1 = |R, R\rangle + |R', R'\rangle + \frac{2t}{U} \left(|RR', 0\rangle + |0, RR'\rangle \right).$$
(6.73)

We find that the Hubbard model produces a singlet ground state and that the next higher state has a separation of $4t^2/U$ and is a triplet. This is the same level ordering as for the ab initio HL calculation and the Heisenberg model. As shown in Fig. 6.8 in this model the comparison of the singlettriplet splittings for the Heisenberg and Hubbard models gives the relationship $2J_{12} = -4t^2/U$, where the minus sign indicates antiferromagnetic coupling. In the literature this limit of the Hubbard model is called the t-J model. It plays an important role in conjunction with the transport properties of antiferromagnetic materials, for example the high $T_{\rm C}$ superconductors.

We see from (6.73) and Fig. 6.7 that in the limit $U \gg t$ the ground state energy converges toward the value $2E_0$ and the ground state wavefunction becomes a pure singlet state. In fact, for t = 0 we recover the HL calculation. In this limit the probability of finding two electrons on a single H atom goes

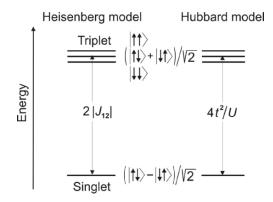


Fig. 6.8. Comparison of the lowest energy states for H₂ in the Heisenberg model and the Hubbard model in the limit $t \ll U$. Both models give a singlet or antiferromagnetic ground state, with a higher energy triplet state. Comparison of the two models shows that $2J_{12} = -4t^2/U$, the minus sign indicating the antiferromagnetic ground state

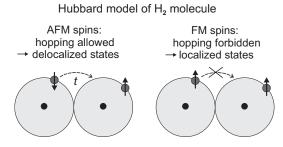


Fig. 6.9. Hubbard model for H_2 . If the spins are antiparallel, the electron may hop to the other atom but has to overcome the Coulomb repulsion U on this atom. For parallel spins, hopping is forbidden in the Hubbard model. The total energy is lower when hopping is allowed as discussed in the text

to zero as shown on the right side of Fig. 6.7. The electrons belong to both atoms and bond them together.

The preference for the *antiferromagnetic* alignment of spins in H_2 can be understood by the simple picture in Fig. 6.9. For *antiparallel* spins, hopping is allowed by the Hubbard Hamiltonian but, when on the new atom, the antiparallel electrons have to overcome the Coulomb repulsion U. For *parallel* spins, hopping is *not* allowed in the Hubbard model. The wavefunction with two electrons of the same spin on the same atom is disallowed in the Hubbard model for H_2 . The unrestricted hopping state, i.e., the antiferromagnetic state, is favored because it offers new degrees of freedom. The electrons can lower their kinetic energy by "delocalizing." Quite generally, the Heisenberg uncertainty relationship (3.45) tells us that the electron momentum and kinetic energy increase with decreasing distance. More specifically the effect of the electron kinetic energy is seen when the central field Schrödinger equation (6.9) is written in spherical polar coordinates. The kinetic energy term $p_i^2/2m_e$ then contributes a (positive) centrifugal term $E_{\rm kin} = l(l+1)\hbar^2/2m_er_i^2$ (see (7.4)). With our sign convention in the Hubbard Hamiltonian (6.66) we see that $-t \propto E_{\rm kin}$. Because of the $1/r^2$ dependence of the kinetic energy term, it is minimized when the electron wavefunction spreads out over more than one atom, i.e., if t becomes large. We will come back to this argument in conjunction with the phenomenon of superexchange discussed in Sect. 7.7.1.

In the Hubbard model the magnetic ground state is determined by the minimum in the total energy -t + U. This is accomplished by a competition between minimizing the Coulomb energy U and the kinetic energy $E_{\rm kin} = -t$.

In the limit $t \gg U$ the ground state energy and wavefunction in (6.72) become

$$E_1 = 2E_0 + \frac{U}{2} - 2t \qquad \Psi_1 = |R, R\rangle + |R', R'\rangle + |RR', 0\rangle + |0, RR'\rangle.$$
(6.74)

Now the ground state energy depends linearly on U and the wavefunction has an equal mixture of states corresponding to one and two electrons per atom. This is born out by the plots in Fig. 6.7. In the extreme limit U = 0the electrons would not interact with each other at all. The linear dependence of the electron interaction on U represents the *independent electron model*. It accounts for the interaction between electrons in some averaged way. It may be regarded as the first order (linear) term in the expansion of the Coulomb energy.

The ground state given by (6.74) is also obtained when the Hubbard Hamiltonian is written in the Hartree–Fock form where the Coulomb repulsion is taken into account in an averaged self-consistent fashion according to

$$\mathcal{H}_{\text{Hub}} = -t \sum_{i,j,\,\sigma=\downarrow,\uparrow} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} (\bar{n}_{i\uparrow} n_{i\downarrow} + n_{i\uparrow} \bar{n}_{i\downarrow} - \bar{n}_{i\uparrow} \bar{n}_{i\downarrow}) .$$
(6.75)

Here the entities \bar{n} indicate a thermodynamic average and they are determined self-consistently by an iterative process to minimize the ground state energy. We shall encounter this form again in the discussion of band structure effects in Sect. 7.6.3.

In Sect. 6.3.8 we will present a brief summary of what we have learned and try to generalize the H_2 case to extended systems.

6.3.8 Summary and Some General Rules for Electron Exchange

In practice, the whole topic of exchange boils down to a simple question. What determines the magnetic properties of the electronic ground state? Our discussion of the Hubbard model suggests that one can think about the origin of the magnetic ground state as a competition between two energies, the Coulomb energy U and the hopping energy t, or remembering that $-t \propto E_{\rm kin}$ we can also say the competition between the Coulomb energy and the kinetic energy.

In atoms, only the Coulomb contribution exists. For the He atom discussed above the 1s valence shell with l = 0 has no angular momentum degrees of freedom. A second electron in the 1s shell therefore has the same quantum numbers n, l, m and is given little choice but to invert its spin, according to the Pauli principle. In the Hubbard model this is reflected by the assumption that like spins cannot coexist on the same atom. The situation is quite different in bigger atoms like the transition metal atoms where the valence electrons have angular momentum l > 0 and there exists a 2l + 1 orbital degeneracy $-l \leq m \leq l$ which can be used to avoid antiparallel spin alignment. The filling of the degenerate suborbitals characterized by different m values with parallel-spin electrons to satisfy the Pauli principle is the basis for Hund's first rule. The Hubbard model is not designed to treat multielectron *atomic* physics. Hund's first rule favors parallel spin alignment, positive J, and a *ferromagnetic* ground state.

In molecules or larger systems either the Coulomb term or hopping term may dominate. For H₂ we find that in either case we obtain an *antiferromagnetic* ground state. While the case of H₂ constitutes a wonderful pedagogical example, one has to be careful in generalizing the results to extended systems. When cast into the framework of states extending over many atoms or bandstructure, the hopping term t becomes a measure of the band width. In the HL limit $U \gg t$ the hydrogen molecule would have a half-filled (narrow) band with a large band gap and therefore would be called an antiferromagnetic "insulator." In the IE limit $t \gg U$ hydrogen would be a "metal."

In extended systems ferromagnetism is indeed possible as born out by our observations of ferromagnetic materials. In Chap. 12 we will specifically discuss the ferromagnetic elemental metals Fe, Co, Ni and Gd. The H_2 calculation indicates an important fact, namely that antiferromagnetic spin alignment is more common and that ferromagnetic alignment is more the exception than the rule.

It is interesting to look at the problem of localized versus delocalized electron behavior in analogy with the dual nature of light. We may think of localized electrons as particle-like and delocalized electrons as wave-like, since we visualize a particle as localized in a small volume and waves as delocalized over a large volume. Through the development of quantum electrodynamics we feel comfortable today to deal with the dual nature of light. Yet we still have problems treating the dual nature of electrons. This is because electrons are Fermions and photons are Bosons. We run into problems as soon as we deal with more than a few electrons because we cannot keep track of the strong interactions between them. For this very reason we can only use approximations. The HL approximation, for example, emphasizes the particle-like electron behavior, the IE approximation the wave-like behavior. We shall come back to the dilemma of electron correlation in discussing the magnetic properties of metals in Chaps. 7 and 12. In these chapters we shall also encounter and discuss the concept of *indirect exchange*.

6.4 The Spin–Orbit Interaction

As the name suggests, the spin-orbit (SO) interaction describes the coupling of the spin s with the orbital angular momentum l to a new total angular momentum j = s + l. It is about a factor of 10–100 smaller than the exchange interaction and one might therefore expect it to be unimportant. However, we have already seen in the introductory Sect. 6.1 of this chapter that this is not so, and magnetism as we know it would not exist without the SO coupling. Here we shall take a closer look at this interaction. For atoms it may be readily understood with semiclassical concepts, while for solids its treatment is complicated by the effects of the ligand fields of neighboring atoms. Here we shall first discuss how the SO interaction was discovered, then give classical and quantum mechanical derivations of the SO Hamiltonian, and finally briefly review why the interaction is of such great practical importance.

6.4.1 Fine Structure in Atomic Spectra

Careful inspection of the prominent optical emission spectra of alkali metal atoms like Na, K, and Rb revealed lines that were split into doublets. The spacing of these doublets was found to increase with atomic number Z. This splitting was called "fine structure" and attracted considerable attention in the first quarter of the 20th century by the Bohr and Sommerfeld schools. The experimental spectra were carefully documented in Sommerfeld's book "Atombau und Spektrallinien" which all leading physicists studied and the book was always kept up-to-date. After the discovery of the spin in 1925 the "fine structure" was recognized to be due to spin–orbit coupling.

In the alkali atoms the valence shell contains one unpaired electron which can undergo electronic transitions that lead to visible light emission. Since all inner shells are filled and hence have zero spin and angular momentum, the spin-orbit coupling is due entirely to the valence states involved in the transition. For example, the strong yellow emission line of Na is due to an electronic transition from the first excited 3p state to the 3s ground state. In this case one observes a doublet which is due to the spin-orbit split 3pstate, resulting in two, $3p_{3/2} \rightarrow 3s_{1/2}$ and $3p_{1/2} \rightarrow 3s_{1/2}$, transitions to the unsplit $3s_{1/2}$ ground state. We shall come back to the Na spectrum later (see Fig. 6.16).

Spin-orbit splitting in He I

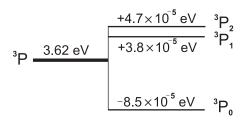


Fig. 6.10. Splitting of the ${}^{3}P_{J}$ multiplet for neutral He (He I) [202]. We give the binding energy of the ${}^{3}P_{J}$ triplet (compare Fig. 6.3) and also list the spin–orbit splitting for the J = 2, 1, 0 levels, relative to their center of gravity. Note the small size of the fine structure splitting because of the small atomic number of He. The ordering of the levels follows Hund's third rule

For atoms with more than one electron one often uses the so-called Russell-Saunders or L-S coupling scheme to describe the coupling of angular momenta. The individual electron spins are first coupled to a resultant S, the individual orbital momenta are coupled to a resultant L, and finally S and L are coupled to a total angular momentum J. Such coupled states, like the singlets and triplets in Fig. 6.3, are called *multiplets* and are labeled ${}^{2S+1}L_J$, where 2S + 1 is the multiplicity. We have seen in the previous section that for He I the electron–electron Coulomb interaction creates a splitting between the triplet ${}^{3}L_J$ and singlet ${}^{1}L_J$ states. However, the degeneracy in J is not lifted. For example, the ${}^{3}P_J$ state in Fig. 6.3 remains threefold degenerate with sublevels J = 2, 1, 0. This degeneracy is lifted by the spin–orbit coupling, as illustrated in Fig. 6.10, giving rise to the fine structure splitting in the atomic spectra.

The above explanation of SO splitting in spectra is based on a semiclassical vector coupling model. Let us take a closer look at this concept.

6.4.2 Semiclassical Model for the Spin–Orbit Interaction

We can picture the spin-orbit coupling in a magnetostatic model using classical concepts established earlier. From our knowledge about moments and fields we can derive an approximate expression for the interaction of a spin S with an orbital momentum L. We have used capital letters for S and L to indicate that they may already represent the sum of coupled momenta of several electrons. We picture the orbital momentum to arise from a current loop as shown in Fig. 6.11 and calculate the interaction energy as that of the corresponding magnetic field in the center of the loop $H_{\rm orb}$ with the spin moment, using the expression (3.15) for the magnetostatic energy,

$$E = -\boldsymbol{m}_s \cdot \boldsymbol{H}_{\rm orb} = -\boldsymbol{m}_s \, H_{\rm orb} \, \cos\theta. \tag{6.76}$$

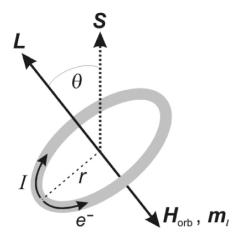


Fig. 6.11. Simple picture for deriving the spin-orbit coupling energy. The direction of L corresponds to the shown electron orbital motion, and the relationship $m_l = -\mu_{\rm B} L/\hbar$. Note that the electron motion is opposite to the direction of the current I

The spin moment is given by (3.13) as $\mathbf{m}_s = -2\mu_{\rm B}\mathbf{s}/\hbar = -e\mu_0\mathbf{S}/m_{\rm e}$, where S is in units of \hbar . The field at the center of the loop is given by the current and the radius of the loop as $H_{\rm orb} = I/2r$ according to (2.4). We can link the field to the orbital moment \mathbf{m}_l by means of (3.3), and the orbital moment and angular momentum L are related according to (3.9). Since the current is defined as a motion of a positive charge q = e, we just have to make sure that the directions of the fields and moments of the orbiting charge correspond to those of an orbiting electron with charge q = -e, as shown in Fig. 6.11. We then obtain

$$\boldsymbol{H}_{\rm orb} = \frac{\boldsymbol{m}_l}{2\pi\mu_0 r^3} = -\frac{e\boldsymbol{L}}{4\pi m_{\rm e} r^3} \ . \tag{6.77}$$

This allows us to obtain the following expression for the spin–orbit energy (using $\mu_0 = 1/\epsilon_0 c^2$)

$$E = -\boldsymbol{m}_{s} \cdot \boldsymbol{H}_{\text{orb}} = -\frac{e^{2}}{4\pi\epsilon_{0} \, m_{e}^{2} c^{2} \, r^{3}} \, \boldsymbol{L} \cdot \boldsymbol{S} \,, \qquad (6.78)$$

where L and S have units of \hbar . The orbital field \boldsymbol{H}_{orb} may be remarkably strong. If we assume a spin-1/2 moment $|\boldsymbol{m}_s| = -2\mu_{\rm B}\langle s_z \rangle/\hbar = \mu_{\rm B}$ we obtain a simple relation between the spin–orbit energy and the magnetic field strength,

$$E = \frac{\mu_{\rm B}}{\mu_0} \mu_0 H_{\rm orb} = \frac{\mu_{\rm B}}{\mu_0} B_{\rm orb} , \qquad (6.79)$$

and by use of the value (see (3.11))

$$\frac{\mu_{\rm B}}{\mu_0} = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \,\mathrm{eV} \,\mathrm{T}^{-1} \,\,, \tag{6.80}$$

we can derive $B_{\rm orb}$ in [T] from the spin orbit splitting energy E in [eV] according to

$$\frac{E}{B_{\rm orb}} = 5.788 \times 10^{-5} \,\mathrm{eV} \,\mathrm{T}^{-1} \,. \tag{6.81}$$

For the lighter atoms like H and He the spin–orbit splitting is very small, of order 5×10^{-5} eV, and therefore the orbital field is only of order of 1 T. However, as plotted in Fig. 6.12, the spin–orbit interaction rapidly increases with atomic number so that for heavier atoms the field $B_{\rm orb}$ may become quite large.

The quantum mechanical spin-orbit Hamiltonian which corresponds to (6.78) follows from the Pauli equation (6.3). We shall take a look at it now.

6.4.3 The Spin–Orbit Hamiltonian

The spin-dependent term \mathcal{H}_s in the Pauli equation contains the magnetic induction B^* which is created by a reference frame effect due to the relative motion of the electron and the nucleus. To the electron the nucleus appears to rotate around it and the moving nuclear charge or current j creates a magnetic induction according to Maxwell's equation

$$\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}. \tag{6.82}$$

However, when this simple picture is employed one obtains a size $B^* = -v \times E/c^2$, according to (4.6), which is too large by a factor of 2, relative to the Dirac result. The correct result is

$$\boldsymbol{B}^* = -\frac{\boldsymbol{v} \times \boldsymbol{E}}{2c^2} \ . \tag{6.83}$$

This factor of 2 has a long history and was one of the early puzzles when a nonrelativistic calculation of the fine structure (spin-orbit) splitting for atoms containing a single valence electron gave a value that was too large by a factor of 2 (see (6.86)). The discrepancy was first explained by L. H. Thomas in 1926 by a celebrated nonrelativistic calculation of the spin-orbit splitting that took into account the tricky reference frame effects between the electron and the nucleus [21]. The essence of the Thomas' calculation is that the picture where the electron is at rest and the nucleus is assumed to move involves a *noninertial* reference frame. The correct result can be obtained nonrelativistically by computing the energy of the stationary nucleus [221]. This reference frame correction is usually discussed in text books under the title *Thomas precession* or *Thomas correction*. We now know that it directly falls out of the Dirac equations. If we write

$$\boldsymbol{B}^* = -\frac{\boldsymbol{v} \times \boldsymbol{E}}{c^2} + \frac{\boldsymbol{v} \times \boldsymbol{E}}{2c^2} , \qquad (6.84)$$

we can think of B^* arising from the conventional transformed field $-v \times E/c^2$ in the electron's rest frame and another magnetic field $+(v \times E)/2c^2$

that points in the opposite direction. This illustrates the difficulty of classical descriptions to account for the quantum mechanical and relativistic concept of "spin".

With $\boldsymbol{E}(\boldsymbol{r},t) = -\nabla \boldsymbol{\Phi}(\boldsymbol{r},t)$ we can then rewrite (6.83) as

$$\boldsymbol{B}^* = \frac{1}{2m_{\rm e}c^2} (\boldsymbol{p} \times \nabla \Phi) \tag{6.85}$$

and when inserted into the Hamiltonian (6.7) this term leads to the spin orbit interaction. To see this we use the definition of the quantum mechanical orbital angular momentum $(\mathbf{r} \times \mathbf{p}) = \hbar \mathbf{l}$, and use the expression $\Phi(r) = Ze/(4\pi\epsilon_0 r)$ for the electrostatic potential of the nuclear charges +Ze, so that $\nabla \Phi(r) =$ $(\mathbf{r}/r) d\Phi(r)/dr$. This gives the familiar *spin-orbit interaction*

$$\mathcal{H}_{\rm so} = \frac{e\hbar}{2m_{\rm e}^2c^2}\,\boldsymbol{s}\cdot(\boldsymbol{p}\times\nabla\Phi) = -\frac{e\hbar^2}{2m_{\rm e}^2c^2}\,\frac{1}{r}\,\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r}\,\boldsymbol{s}\cdot\boldsymbol{l} = \xi_{nl}(r)\,\boldsymbol{s}\cdot\boldsymbol{l}\,. \tag{6.86}$$

Since $d\Phi(r)/dr$ is negative, $\xi_{nl}(r)$ is positive. The expectation value

$$\zeta_{nl} = \langle \xi_{nl}(r) \rangle = \int_0^\infty R_{nl}(r) \,\xi_{nl}(r) \,R_{nl}^*(r) \,r^2 \,\mathrm{d}r \tag{6.87}$$

is called the *spin-orbit parameter* or *coupling constant*. If we use the expression $\Phi(r) = Ze/(4\pi\epsilon_0 r)$ for the electrostatic potential, we have $\xi_{nl}(r) = Ze^2\hbar^2/8\pi\epsilon_0 m_e^2c^2r^3$ which is smaller by a factor of 2 than the classical expression (6.78) due to the Thomas factor.

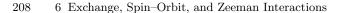
Theoretical values for the spin-orbit parameter ζ_{nl} , obtained by the relativistic Hartree-plus-statistical-exchange method [182] are plotted in Fig. 6.12 for the valence shell ground state configurations of the neutral atoms. Apart from a strong Z dependence, ζ_{nl} also depends strongly on the radius of the atomic shell as indicated by the subscript n.

The *spin-orbit interaction* Hamiltonian is given by

$$\mathcal{H}_{\rm so} = \xi_{nl}(r) \, \boldsymbol{s} \cdot \boldsymbol{l} \,, \tag{6.88}$$

The expectation value $\zeta_{nl} = \langle \xi_{nl}(r) \rangle$, which is positive, is called the *spin*-orbit coupling constant or *spin*-orbit parameter with dimension [energy].

We see from Fig. 6.12 that the spin-orbit interaction energy is rather small for the important 3d transition metals. Its value of the order of 10–100 meV is considerably weaker than the exchange interaction ($\sim 1 \text{ eV}$) and also the ligand field interaction (a few eV). We shall see in Sect. 11.2 that this accounts for the small orbital magnetic moment of Fe, Co, and Ni. In contrast, the spinorbit interaction is considerably larger for the rare earths and this together with the smaller ligand field effects for the shielded 4f electrons leads to large orbital magnetic moments for the lanthanides.



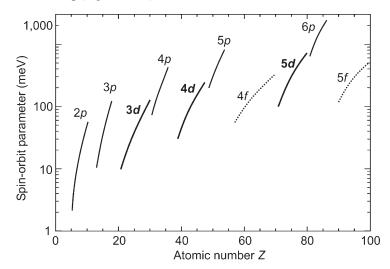


Fig. 6.12. Values for the spin-orbit parameter ζ_{nl} , defined in (6.87), for the valence shells of neutral atoms in their ground state, calculated by Cowan [182]

The spin orbit coupling, discussed in Sect. 6.4, produces the observed doublet in the atomic spectra because it lifts the degeneracy by creating two states with $j = l \pm s$. The energy of these two states are obtained by writing j = l + s and using the expression $j \cdot j = l \cdot l + 2l \cdot s + s \cdot s$ to rewrite the spin-orbit Hamiltonian,

$$H_{\rm so} = \xi_{nl}(r) \ \boldsymbol{l} \cdot \boldsymbol{s} = \frac{\xi_{nl}(r)}{2} \left[\boldsymbol{j} \cdot \boldsymbol{j} - \boldsymbol{l} \cdot \boldsymbol{l} - \boldsymbol{s} \cdot \boldsymbol{s} \right] \ . \tag{6.89}$$

The eigenstates of this Hamiltonian are the functions $|R_{n,l}; j, m_j, l, s\rangle$ and we obtain the eigenvalues as

$$\langle R_{n,l}; j, m_j, l, s | H_{\rm so} | R_{n,l}; j, m_j, l, s \rangle = \frac{\zeta_{nl}(r)}{2} [j(j+1) - l(l+1) - s(s+1)].$$
(6.90)

(6.90) Therefore the substates with $j_+ = 3/2$ experience an energy shift $E_{j_+} = \zeta_l/2$ and the substates with $j_- = 1/2$ are shifted by $E_{j_-} = -\zeta_l$, with the separation given by the Landé interval rule $E_{j_+} - E_{j_-} = \zeta_l j_+$.

In our derivation of the spin-orbit Hamiltonian we have tacitly assumed that the spin s and angular momentum l are those of a single electron. The formalism is more general, however, as already mentioned in Sect. 6.4.1. In multielectron systems the Coulomb and exchange interaction couple the spins of the individual electrons to a resultant spin according to $S = \sum_i s_i$ and the individual orbital momenta to a coupled orbital momentum $L = \sum_i l_i$. This so-called *Russell-Saunders* or *L-S*-coupling scheme therefore creates states that are usually denoted as *terms* or *multiplets* and written as ${}^{2S+1}L$. As for a one-electron systems the effect of the spin-orbit coupling is to couple the total spins and angular momenta according to J = L + S and the one-electron formalism above equally applies to a multielectron system. The coupled multielectron states are written as ${}^{2S+1}L_J$ with $L-S \leq J \leq L+S$. This is the origin of the labels in Figs. 6.3 and 6.10.

6.4.4 Importance of the Spin–Orbit Interaction

According to the definition of the magnetostatic energy $E = -\boldsymbol{m}_s \cdot \boldsymbol{H}_{orb}$ in Sect. 3.4, the energy given by (6.78) corresponds to the energy gain one experiences if the spin \boldsymbol{S} is turned from a perpendicular to a parallel orientation to \boldsymbol{L} , as illustrated in Fig. 6.11. If we now imagine that the orbital moment prefers to lie along a specific bonding or lattice direction, i.e., is "locked-in" by the lattice, the energy expressed by (6.78) is exactly the energy difference between the favored (L and S parallel) and unfavored (L and S perpendicular) spin directions. It is therefore the magnetocrystalline anisotropy energy. We are led to the following important conclusion.

In solids, the spin–orbit interaction determines the magnetocrystalline anisotropy.

Despite this simple intuitive picture, it is all but trivial to develop a detailed understanding of the magnetic anisotropy phenomenon for a given solid. Even more difficult is a reliable calculation of the magnetocrystalline anisotropy energy and the prediction of the easy magnetization axis [222]. The magnetocrystalline anisotropy is a key parameter in the design of all magnetic materials, ranging from transformer and electromagnet cores to magnetic recording media. It is discussed in more detail in Sects. 7.9 and 11.2.

6.5 Hund's Rules

The exchange and spin orbit interactions are at the origin of the famous empirical rules suggested by Friedrich Hund (1896–1997) in 1925 for the energetic ordering and filling of electronic states in atoms and molecules. *Hund's rules* determine the lowest multiplet term or electronic ground state for a given electronic configuration.

Hund's Rules for a given electronic configuration:

- 1. The lowest electronic term has maximum spin S.
- 2. The lowest term has maximum angular momentum L.
- 3. The lowest term has the largest total angular momentum J if the shell
- is more than half full, and the smallest J if the shell is less than half full.

210 6 Exchange, Spin–Orbit, and Zeeman Interactions

Octahedral ligand field splitting and filling of d orbitals

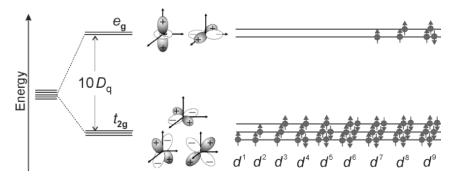


Fig. 6.13. Splitting of the *d* shell in an octahedral ligand field into doubly degenerate $e_{\rm g}$ and triply degenerate $t_{2\rm g}$ states. Also shown is the filling of the energy levels for the case that the $e_{\rm g}$ - $t_{2\rm g}$ splitting is large relative to the exchange interaction [204]. The resulting ground states for $d^4 - d^7$ are called the *low-spin* configurations (see Sect. 7.5.1)

Hund's first rule is about *spin-spin coupling*. The electronic ground state corresponds to a minimum of the Coulomb repulsion. This is achieved by spatially keeping the electrons apart. The corresponding wavefunction according to the symmetrization postulate of Sect. 6.2.2 is then antisymmetric in space and symmetric in the spin, corresponding to maximum S.

Hund's second rule is about *orbit-orbit coupling*. The basis for this rule is that electrons orbiting in the same direction meet less often than electrons orbiting in opposite directions. Electrons that orbit in the same direction therefore minimize their Coulomb repulsion and they have parallel angular momenta, corresponding to maximum L.

Hund's third rule is about *spin-orbit coupling*. According to (6.78) the lowest spin-orbit energy corresponds to the same direction of S and L since the prefactor is negative. When the shell is more than half full, S and L point in the same direction the highest value of J is lowest in energy. For atoms with less than half-filled shells, S and L are antiparallel and the energy is positive. Now the lowest value of J has the lowest (positive) energy.

An examples of the effect of Hund's rules is shown in Fig. 6.13. It shows the consecutive d electron filling of ligand field energy levels for a transition metal in octahedral environment. The ligand field states are the well-known dorbitals (see Appendix A.3), and they are spit into a e_g doublet and t_{2g} triplet. We see that because of Hund's first rule electrons with parallel spins are filled in first. This maximizes the total spin S. If the ligand field splitting becomes smaller, the e_g state gets filled sconer. It can then happen, for example, that a d^5 configuration consists of five parallel spins with S = 5/2. This is a socalled "high-spin" configuration. In contrast, the shown d^5 configuration with S = 1/2 is called "low-spin."

 d^2 and d^8 Energy Levels according to Hund's Rules

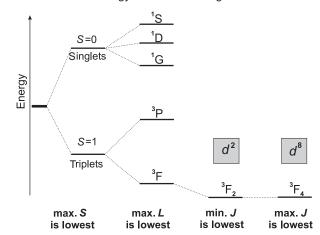
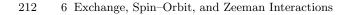


Fig. 6.14. Order of the multiplet terms of the *d*-shell containing two electrons (e.g., Ti^{2+}) or eight electrons (e.g., Ni^{2+}), according to Hund's three rules. Note that the *d* shell has a maximum occupancy of 10 electrons and the cases d^n and d^{10-n} have the same multiplet terms. The lowest term or electronic ground state, however, differ because of Hund's third rule

An application of all three of Hund's rules is shown in Fig. 6.14, where we consider the multiplet terms of a two electron (d^2) or eight electron (d^8) configuration [181]. Because the maximum number of d electrons is 10, the d^8 electron configuration is equivalent to a two hole d^2 configuration.¹¹ The change of sign between an electron or hole configuration leaves the allowed multiplet terms unchanged but it introduces an inverted order in J according to Hund's third rule. This has the important consequence that the lowest term or electronic ground state is different and so will be the magnetic properties.

An example of a d^8 configuration is Ni²⁺ in NiO, and we shall discuss this interesting antiferromagnet later in the context of "exchange bias." In general, we will see in Chap. 10 that multiplet structure plays an important role in the X-ray absorption spectra of transition metal oxides. Although it complicates the spectra through peak splittings, it also gives rise to large linear magnetic dichroism effects and is therefore of great importance.

¹¹The origin of this equivalence lies in two facts. First, full shells have zero spin and orbital momenta. Second, for a given shell l we have for the number of electrons N and the number of holes $N_{\rm h}$ the relationship $N+N_{\rm h}=O=(2s+1)(2l+1)=2(2l+1)$, where O is the maximum possible occupation number. This allows us to treat the Coulomb and exchange interactions which couple the individual angular momenta l and s to L and S in equivalent electron and hole pictures.



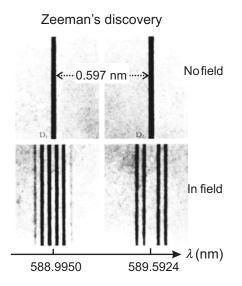


Fig. 6.15. Emission spectrum of Na atoms recorded by Pieter Zeeman in 1896 without (top) and in the presence of (below) a magnetic field that is perpendicular to the observation direction. In the presence of the field the prominent Na doublet in the yellow part of the spectrum (2.1 eV) splits into a quartet and sextet of lines. This splitting is called the Zeeman effect

6.6 The Zeeman Interaction

In discussing the third important magnetic interaction we shall, as before, first take a historical perspective which naturally leads to the proper theory of the Zeeman effect. We will then discuss why the Zeeman interaction is so important in magnetism to this day. Finally we point out the distinction between the effect of a "real" external magnetic field and the internal molecular or exchange field on electronic level splittings. This proves of great importance in modern X-ray dichroism.

6.6.1 History and Theory of the Zeeman Effect

In 1896 Pieter Zeeman examined the emission spectrum of a flame that contained Na. In the absence of a magnetic field the Na spectrum consists of a bright spin–orbit split doublet in the yellow part of the spectrum, the so-called Na *D*-lines at 588.9950 and 589.5924 nm wavelength. Zeeman discovered that in the presence of a magnetic field the doublet splits into a characteristic pattern as shown in Fig. 6.15.

Zeeman's result is readily explained by means of modern quantum theory, as illustrated in Fig. 6.16. The Na atom has a ground state electronic configuration $[(1s)^2 (2s)^2 (2p)^6]$ 3s. The inner filled shells indicated by square brackets

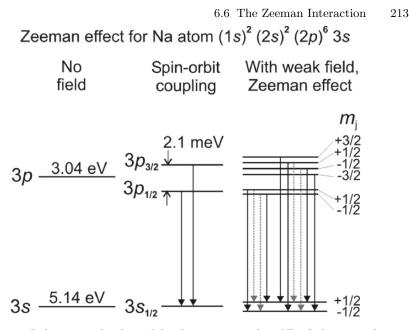


Fig. 6.16. Left: energy levels and binding energies (in eV) of the ground state $[(1s)^2 (2s)^2 (2p)^6] 3s$ and first excited state $[(1s)^2 (2s)^2 (2p)^6] 3p$ configurations of the Na atom. Center: level scheme after inclusion of spin orbit coupling, shown with an exaggerated splitting. Right: level splitting in the presence of an additional weak external magnetic field, giving rise to the Zeeman splitting. For a given field, the Zeeman splittings are determined by the Landé g-factor which is $g_j = 2$ for $3s_{1/2}$, $g_j = 2/3$ for $3p_{1/2}$ and $g_j = 4/3$ for $3p_{3/2}$. On the right we also show all transitions allowed by the dipole selection rule $\Delta j = 0, \pm 1$ and we have indicated that the transitions with $\Delta m_j = 0$ (dashed lines) and $\Delta m_j = \pm 1$ (solid lines) have different polarizations

have zero spin and angular momentum so that the magnetic properties are entirely determined by the outer electron. The emission spectrum of Na in the visible range is dominated by the de-excitation of the outer electron from the first excited 3p state to the 3s ground state, by emission of a photon of 2.1 eV, producing an intense yellow spectral line. As discussed in Sect. 6.4.3 the 3pstate occupied by one electron and quantum numbers $\ell = 1$ and s = 1/2will be subject to spin orbit splitting, whereas the 3s state has $\ell = 0$ and its magnetic properties are therefore entirely determined by the spin alone. This gives the level structure shown in Fig. 6.16 and the yellow emission line will be spin orbit split by 2.1 meV. This is indeed the observed pattern in Fig. 6.15 in the absence of a magnetic field.

In order to calculate the pattern in the presence of the field we first have to establish the appropriate interaction Hamiltonian and its approximate size. The Hamiltonian corresponds to the interaction energy (3.15) of a magnetic dipole with an external magnetic field and is given by 214 6 Exchange, Spin–Orbit, and Zeeman Interactions

$$\mathcal{H}_{\text{Zee}} = -\boldsymbol{m} \cdot \boldsymbol{H}. \tag{6.91}$$

Since the total magnetic moment is the sum of the spin and orbital parts according to (3.14) we have the following general result.

The Zeeman Hamiltonian for a magnetic moment $m = -\mu_{\rm B}(\ell + 2s)/\hbar$ in a magnetic field H is given by

$$\mathcal{H}_{\text{Zee}} = \frac{\mu_{\text{B}}}{\hbar} \boldsymbol{H} \cdot (\boldsymbol{\ell} + 2\boldsymbol{s}) . \qquad (6.92)$$

In order to estimate the size of the Zeeman interaction we take a typical case $\ell = 1$ and s = 1/2 and with the magnetic field \boldsymbol{H} taken along the z-axis we obtain

$$\langle \mathcal{H}_{\text{Zee}} \rangle = 2\,\mu_{\text{B}}\,H = 2\,\frac{\mu_{\text{B}}}{\mu_{0}}\,B$$
 (6.93)

By use of (6.80) we see that the Zeeman interaction has a typical size of $\sim 0.1 \text{ meV}$ for a field $B = \mu_0 H = 1$ T. Thus for Na we have the case that the spin orbit interaction of 2.1 meV is much larger than a typical Zeeman interaction.

In order to calculate the eigenvalues of the Zeeman Hamiltonian and hence the Zeeman splitting it is convenient to use a general formalism derived by Landé in the early 1920s [223]. Landé's result takes care of the vector coupling of spin and angular momenta which exists in the case of spin orbit coupling, as for the case of Na discussed above. Today Landé's formula, originally derived using semiclassical vector coupling concepts [181], readily emerges from a quantum mechanical treatment of vector coupling. This theory allows the calculation of the expectation value of the Zeeman Hamiltonian by use of wavefunctions that are either written in terms of the individual spin S and angular momenta L functions $|L, S, M_L, M_S\rangle$ or the spin–orbit coupled functions $|L, S, J, M_J\rangle$, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$.¹² For brevity we shall state here just the basic result.

Landé's formula for the Zeeman-split energy levels includes the three basic cases where the magnetic moment is due either to the spin S, the orbital

$$|L, S, J, M_J\rangle = \sum_{M_L, M_S} C_{M_L, M_S; J, M_J} |L, S, M_L, M_S\rangle$$
, (6.94)

where the $C_{M_L,M_S;J,M_J}$ are the famous Clebsch–Gordon coefficients, written in Slater's notation [225] (see Table A.5).

 $^{^{12}}$ The matrix elements of the Hamiltonian for the spin–orbit coupled functions $|L, S, J, M_J\rangle$ can be expressed in terms of the uncoupled functions $|L, S, M_L, M_S\rangle$ by use of the Wigner–Eckart theorem [147] (see Appendix A.5). An equivalent way is by directly relating the wavefunctions before calculation of the matrix elements according to

6.6 The Zeeman Interaction 215

angular momentum L or the coupled angular momentum J = S + L. The latter case arises in the presence of spin-orbit coupling. Here we have used capital letters for the angular momenta to indicate that they may represent sums of individual electron angular momenta, e.g., $S = \sum_i s_i$. By generalizing the concept of the g-factor we may then use the following formulation for the Zeeman Hamiltonian for the three cases,

$$\mathcal{H}_{\text{Zee}} = g_S \frac{\mu_{\text{B}}}{\hbar} \boldsymbol{H} \cdot \boldsymbol{S}, \qquad (6.95)$$

$$\mathcal{H}_{\text{Zee}} = g_L \frac{\mu_{\text{B}}}{\hbar} \boldsymbol{H} \cdot \boldsymbol{L}, \qquad (6.96)$$

$$\mathcal{H}_{\text{Zee}} = g_J \frac{\mu_{\text{B}}}{\hbar} \boldsymbol{H} \cdot \boldsymbol{J}.$$
(6.97)

By choosing a coordinate system with z in the direction of the external field H we readily see that the magnetic field lifts the degeneracy of the substates of the angular momenta and the energy splittings are given by

$$\Delta E(M_S) = g_S \,\mu_{\rm B} \,H \,S_z = g_S \,\mu_{\rm B} \,H \,M_S,\tag{6.98}$$

$$\Delta E(M_L) = g_L \,\mu_{\rm B} \,H \,L_z = g_L \,\mu_{\rm B} \,H \,M_L, \qquad (6.99)$$

$$\Delta E(M_J) = g_J \,\mu_{\rm B} \,H \,J_z = g_J \,\mu_B \,H \,M_J. \tag{6.100}$$

All that is needed for the calculation of the size of the respective splittings are the g-factors. We already know the answer for the first two factors, namely, $g_S = 2$ and $g_L = 1$. Landé provided the result for the third, called the Landé g-factor,

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} .$$
 (6.101)

In fact, (6.97) and (6.100) constitute a general result that includes the other two cases. This is readily seen by evaluating (6.101) for J = S and L = 0 which gives $g_J = g_S = 2$ and for J = L, S = 0 we obtain $g_J = g_L = 1$.

It is now straightforward to predict the Zeeman line pattern for Na, as illustrated in Fig. 6.16. Since this case corresponds to a single electron we shall use small letters for the momenta. The spin orbit states have the following Landé g-factors: $g_j = 2$ for $3 s_{1/2}$, $g_j = 2/3$ for $3p_{1/2}$ and $g_j = 4/3$ for $3p_{3/2}$ and they give rise to different Zeeman splittings, as schematically indicated in Fig. 6.16. The observed optical transitions follow from the dipole selection rule $\Delta j = 0, \pm 1$ (see Sect. 9.5.5), and the polarization of the lines is different for $\Delta m_j = 0$ (dashed lines) and $\Delta m_j = \pm 1$ (solid lines), as indicated [181, 198].

With modern tools the explanation of Zeeman's discovery is therefore straightforward. Historically, the full explanation of the original spectra took about 30 years. One needs to remember that at the time of Zeeman's discovery the electron had not yet been discovered, which happened only a year later in 1897 by J. J. Thomson (and independently about the same time by Wiechert [13]). By means of additional studies of the field splitting of the sodium doublet and through a more detailed analysis, Zeeman and Lorentz demonstrated in the following years that the magnetic splitting could be

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associated with the charge-to-mass ratio $e/m_{\rm e}$ of the electron. This was the first direct demonstration that electrons were involved in the production of spectral line emissions. The full explanation of the observed splitting, how-ever, had to await the discovery of the spin in 1925 and the development of quantum theory in the late twenties.

The slow historical interpretation of the magnetic field splitting of Na led to a somewhat confusing terminology. Since the splitting in Na could not be understood for a long time because of the missing concept of the spin, it was called "anomalous," and the associated Zeeman effect has since gone under the historical name anomalous Zeeman effect. Today there is nothing anomalous about the effect! In contrast, when the magnetic field splitting of the strong red $n = 3 \rightarrow n = 2$ line ($\lambda = 656.3 \,\mathrm{nm}$ or $1.89 \,\mathrm{eV}$) for the simplest atom, hydrogen, was studied a much simpler three line pattern was observed. This three line magnetic pattern was called "normal," because scientists thought they understood its origin. It was attributed to the fact that the states with principal quantum number n are composed of degenerate angular momentum states $n \ell m_{\ell}$ with $0 \leq \ell \leq n-1$ and $-\ell \leq m_{\ell} \leq \ell$ and that the splitting indicated the lifting of the degeneracy of the states with magnetic quantum numbers m_{ℓ} (hence the name "magnetic quantum number" for m_{ℓ}). It turns out that this is only half of the story because the effect of the spin remained hidden as we shall discuss now.

The strong red $n = 3 \rightarrow n = 2$ line in hydrogen with a wavelength of $\lambda = 656.3 \text{ nm} (1.89 \text{ eV})$ arises from transitions from the excited n = 3 state with an energy -1.511 eV below the vacuum level to the lower energy n = 2 state at -3.400 eV. The states with principal quantum number n are composed of degenerate angular momentum states $n\ell$ with $0 \leq \ell \leq n - 1$, e.g., for n = 3 we have $\ell = 0(s), 1(p), 2(d)$, and the red line arises from three allowed dipole transitions $3s \rightarrow 2p, 3p \rightarrow 2s$ and $3d \rightarrow 2p$ which are energetically degenerate [181,226]. In hydrogen the spin–orbit splitting is very small, similar to that of He in Fig. 6.10. For example, the $2p_{3/2} - 2p_{1/2}$ spin–orbit splitting is only 4.5×10^{-5} eV. In the early part of the 20th century this small splitting was in fact already known and had an important impact. It was used by Uhlenbeck and Goudsmit, the latter having studied spectroscopy with Paschen and Back, to predict the existence of the electron spin with a half integer angular momentum [18–20].

Under application of a magnetic field the red line was found to split into three components whose separation was larger than the small spin-orbit splitting. Thus we have the opposite case from that of the Na atom in that the Zeeman splitting is larger than the spin-orbit splitting. In order to simplify things we shall neglect the spin-orbit splitting in our discussion. This leads to the picture of the "normal" Zeeman effect in H illustrated in Fig. 6.17.

The origin of the splitting is readily understood from the eigenvalues of the Hamiltonian (6.92), and by use of (6.98) and (6.99) we obtain

$$\Delta E_{\text{Zee}} = \mu_{\text{B}} H \left(2m_s + m_\ell \right). \tag{6.102}$$

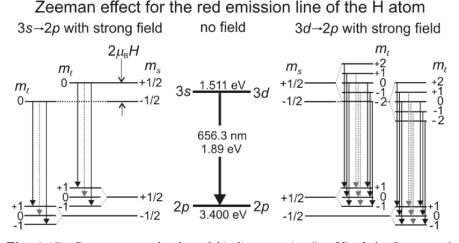


Fig. 6.17. Center: energy levels and binding energies (in eV) of the first n = 2and second n = 3 excited shells of atomic hydrogen. Within each shell n all other quantum numbers ℓ, s, m_ℓ, m_s are degenerate. The strong red emission line in the H spectrum of 656.3 nm wavelength (1.89 eV) corresponds to three allowed dipole transitions $3s \to 2p$, $3p \to 2s$ and $3d \to 2p$, of which we only show two cases for simplicity. The spin-orbit splitting of the states in H is small, and it is neglected in our diagram. On the left and right sides we show how the levels split in an external magnetic field H. In all cases the levels exhibit a spin splitting into $\pm m_s = \pm 1/2$ states with a separation $2\mu_{\rm B}H$. Each spin state is further split into orbital states $-\ell \leq m_\ell \leq +\ell$ with a splitting of $\mu_{\rm B}H$ between adjacent m_ℓ states. For a given field, the allowed optical transitions follow the dipole selection rule $\Delta \ell = 1, \Delta m_\ell =$ $0, \pm 1, \Delta m_s = 0$. This gives rise to a triplet splitting of the emission line with the central transitions with $\Delta m_j = 0$ (dashed lines) and the outer transitions $\Delta m_j = \pm 1$ (solid lines) having different polarizations

Since for H we may neglect the spin-orbit coupling in strong external fields (say 30 T or so) the spin and orbital angular momentum are decoupled and this leads to the form of (6.102) and splitting patterns as shown in Fig. 6.17. We can now understand why the resulting three line pattern could be understood before the spin was discovered. The spin splitting, which is twice the orbital splitting, simply leads to two degenerate triplet patterns. Thus the effect of the spin remained hidden and the three line pattern could be understood simply on the basis of orbital angular momentum splitting.

With our modern knowledge we would distinguish the H and Na cases simply by the relative strength of the spin–orbit and Zeeman interactions. In particular, one often calls the case where the Zeeman energy is larger than the spin–orbit energy the *Paschen–Back limit*.

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6.6.2 Zeeman Versus Exchange Splitting of Electronic States

The essence of the Zeeman interaction is the action of a magnetic field onto the spin and orbital angular momentum. It is important to realize that the magnetic field must be a "real" field, that is an Oersted field produced by current flow or by a permanent magnet. We shall later see in Sect. 11.1.2 that the concept of "field" is also used in conjunction with the exchange interaction. In magnetic materials the exchange interaction may be thought to give rise of an effective field called the *exchange field*, *molecular field* or *Weiss field*. This field, however, is distinct form a "real" field in that it acts only on the spin, not the orbital magnetic moment. The effect of the Weiss field H_W on an electronic state of an atom is therefore given by a Hamiltonian of the form

$$\mathcal{H}_{\rm ex} = \frac{2\mu_{\rm B}}{\hbar} \, \boldsymbol{H}_{\rm W} \cdot \boldsymbol{s} \tag{6.103}$$

in contrast to the Zeeman Hamiltonian for a real field ${\cal H}$

$$\mathcal{H}_{\text{Zee}} = \frac{\mu_{\text{B}}}{\hbar} \boldsymbol{H} \cdot (\boldsymbol{\ell} + 2\boldsymbol{s}) . \qquad (6.104)$$

This has important consequences in X-ray dichroism spectroscopy (see Chap. 10). In X-ray absorption measurements electrons are excited from core shells to unoccupied valence states. In magnetism research transitions from the 2p core shell to the 3d valence shell are of particular importance. For the magnetic metals Fe, Co and Ni the 2p core shell is SO split by an energy of about 15 eV, giving rise to the so-called L₃ $(2p_{3/2})$ and L₂ $(2p_{1/2})$ edges. If we consider how the two SO core states split further under the influence of a weak Weiss field or a real field, we obtain the results shown in Fig. 6.18.

We see that the energies of the m_j substates for the $p_{1/2}$ state are inverted for the two types of fields. In order to derive this we use the eigenfunctions $|\ell, s, j, m_j\rangle$ of the spin-orbit Hamiltonian and calculate the eigenvalues for the Hamiltonians (6.103) and (6.104) by first order perturbation theory. The new eigenvalues are simply given by the diagonal matrix elements of the two Hamiltonians calculated with the $|\ell, s, j, m_j\rangle$ functions, and for the field aligned along the z quantization axis we obtain from (6.103)

$$E_{\rm ex}(m_j) = \frac{2\mu_{\rm B}}{\hbar} H_{\rm W} \langle \ell, s, j, m_j | \mathbf{s}_z | \ell, s, j, m_j \rangle$$
(6.105)

and similarly from (6.104),

$$E_{\text{Zee}}(m_j) = \frac{\mu_{\text{B}}}{\hbar} H \left\langle \ell, s, j, m_j \right| \boldsymbol{\ell}_z + 2\boldsymbol{s}_z \left| \ell, s, j, m_j \right\rangle .$$
(6.106)

The matrix elements are most easily calculated by expressing the spin-orbit functions $|\ell, s, j, m_j\rangle$ in terms of basis states $|\ell, m_\ell, s, m_s\rangle = Y_{\ell, m_\ell}\chi \pm$ where $\chi^{\pm} = |s, \pm m_s\rangle$. The expansion coefficients are the Clebsch–Gordon coefficients and for convenience we simply state the result for the two $p_{1/2}$ substates of

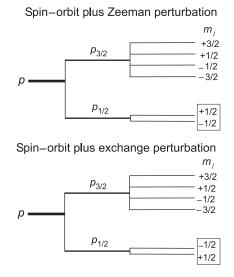


Fig. 6.18. Splitting of an atomic p state under the influence of the spin-orbit interaction and a weaker Zeeman interaction (top) or exchange interaction (bottom) which are treated as a perturbation. Note that the energetic order of states for the $p_{1/2}$ states is inverted for the two cases

interest. The substates have quantum numbers $\ell = 1$, $s = \frac{1}{2}$, $j = \frac{1}{2}$, and $m_j = \pm \frac{1}{2}$, and we shall write them in short as $|m_j = \pm \frac{1}{2}\rangle$. The relevant expansions are (see Table A.5),

$$|m_j = +\frac{1}{2}\rangle = \frac{1}{\sqrt{3}} \left[-Y_{1,0} \chi^+ + \sqrt{2} Y_{1,+1} \chi^- \right] ,$$
 (6.107)

$$|m_j = -\frac{1}{2}\rangle = \frac{1}{\sqrt{3}} \left[-\sqrt{2} Y_{1,-1} \chi^+ + Y_{1,0} \chi^- \right] .$$
 (6.108)

With the usual rules $\ell_z Y_{\ell,m_\ell} = m_\ell \hbar$ and $s_z \chi^{\pm} = \pm \frac{1}{2} \hbar$ we obtain¹³

$$E_{\rm ex}(\pm m_j) = \mp \frac{\mu_{\rm B} H_{\rm W}}{3} \tag{6.110}$$

and

$$E_{\text{Zee}}(\pm m_j) = \pm \frac{\mu_{\text{B}} H}{3}.$$
 (6.111)

¹³The same result is obtained by use of the Landé formula (6.100) with the appropriate value $g_j = 2/3$ for $\ell = 1, s = 1/2$, and j = 1/2. In fact, the Landé formula is derived from the requirement [147]

$$\langle \ell, s, j, m_j | \ell + 2s | \ell, s, j, m_j \rangle = g_j \langle \ell, s, j, m_j | j | \ell, s, j, m_j \rangle.$$
(6.109)

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This reveals the opposite energetic ordering of m_j states shown in Fig. 6.18. Similarly, it can be shown by using the wavefunction transformations in Table A.5 that for the $p_{3/2}$ state the Zeeman and exchange energy perturbations lead to the same ordering of m_j states, which is also illustrated in Fig. 6.18.

6.6.3 Importance of the Zeeman Interaction

We have seen that the Zeeman effect played an important role in the first quarter of the 20th century toward the development of quantum theory. In particular, it helped in understanding the fine structure or spin-orbit splitting of the spectra. The same interaction that leads to the splitting of spectroscopic lines is also responsible for our ability to magnetize materials. This is probably the most important application of the Zeeman interaction and it has been used throughout history. In the absence of a magnetic field the magnetization, referred to as the *spontaneous magnetization* naturally breaks up into domains with different magnetization directions that cancel on a macroscopic scale, as discussed in Sect. 11.3. The application of a magnetic field is therefore required to induce a well-defined magnetic direction which makes the magnetic material useful. In the early days of magnetism, the Zeeman interaction was used to align iron compass needles by the magnetic field of loadstones found in nature, which in turn had been magnetized by the earth's magnetic field during the process of cooling or by the field of a lightning bolt. Today, we all use the Zeeman effect daily as we "save" information in our computers. This is accomplished by using the current induced Oersted field from a recording head to write "0" and "1" magnetic bits into the recording media in our "hard drives."

The Zeeman interaction is also used to study the magnetic properties of materials and improve them. For example, by measurement of a magnetization loop (see Sect. 11.4) it allows the determination of the *coercivity*, which is the field required to completely align the material along its *easy axis* of magnetization, the axis favored by the crystal structure. When applied perpendicular to the easy axis, along the so-called *hard axis*, one can determine what field is required to rotate the magnetization by 90° away from the easy axis. This determines the magnetocrystalline anisotropy which is a measure of how strong the spin is locked into a special lattice direction by the spin–orbit coupling as briefly discussed in Sect. 6.4.4. This will be discussed in more detail in Sect. 7.9.

7.1 Chapter Overview

In the previous chapter we have looked at the three main magnetic interactions largely from a historical point of view which naturally is based on the electronic and magnetic structure of atoms and small molecules. We have seen that the interplay of charge and spin degrees of freedom is already quite complicated in atoms. It is therefore expected that in solids the first principle description of the interactions between charges under the constraint of the antisymmetrization postulate must be a monumental challenge. Indeed, it has taken the better part of the 20th century to make some headway in this direction and, as of today, we still do not possess a first principles theory that satisfactorily explains the behavior of different solids such as the transition metals and their oxides. Nevertheless, in this chapter we aim to discuss some important concepts underlying our present understanding. Our emphasis will be on the 3d transition metals and their compounds but we shall also consider the rare earths in comparison. From a magnetism point of view we shall concentrate on the intrinsic magnetic interactions: exchange and spin-orbit.

We start this chapter in Sect. 7.2 by taking a look at the important concept of charge "localization" which is one of the key ingredients in modern solid state physics. In the language of modern condensed matter physics, one distinguishes localized or correlated electron behavior from delocalized, band-like or itinerant behavior. One of the important contributions to the localization problem is the very behavior of the atomic valence electrons in the central atom potential. This will be demonstrated by comparing the atomic *potential barrier effects* for the 3d and 4f valence shells of magnetic atoms.

In the next Sect. 7.3 we then give an overview of the relative strength of intra-atomic interactions and extra-atomic interactions for the same 3d and 4f systems. This overview is essential in understanding the different magnetic behavior of transition metal and rare earth materials.

The next two sections are devoted to band and ligand field (LF) methods for the calculation of the electronic ground state. For the ground state it is

7

typically sufficient to consider the lowest-energy configurations $4f^n$ and $3d^n$. only. In particular, Sect. 7.4 reviews the concepts of band structure. It deals with the most important model for the understanding of ferromagnetism, the Stoner band model. This model underlies our modern understanding of the magnetic structure of metals. In the context of the Stoner model we shall also review the basic concepts underlying the wave-vector dependent band structure and briefly outline the foundations of modern band calculations, density functional theory (DFT) and the local (spin) density approximation (L(S)DA). In Sect. 7.5 we explore the concepts of LF theory because of its importance for understanding the electronic and magnetic structure of ionic transition metal compounds, such as the oxides and halides. We discuss both the strong bonding limit which can be treated by an independent-electron LF theory, and make contact with molecular orbital theory. We then treat the weak bonding limit where a localized cluster or multiplet model that emphasizes the intra-atomic correlation of the central transition metal ion needs to be used.

The following Sect. 7.6 illustrates the importance of excited states, in particular for our modern understanding of correlated materials. We discuss both theoretical and experimental concepts underlying their understanding. We give a short review of important concepts used in the classification of materials, such as the correlation energy U and the charge transfer energy $\Delta_{\rm c}$. We then show how photoemission and inverse photoemission spectroscopies hold the key to the electronic structure of correlated materials. We point out why independent electron theories, like band theory, fail for the description of correlated systems and mention remedies like the LSDA+U method.

In Sect. 7.7 we take a closer look at the magnetic interactions in transition metal oxides. We discuss two forms of *indirect exchange* in the form of *super-exchange* and *double exchange*, and use a simple Hubbard model to derive the respective antiferromagnetic and ferromagnetic ground states for the two cases. We then discuss two important magnetic oxides, both governed by double exchange, the perovskite-type manganites of the LaMnO₃-family and magnetite, Fe₃O₄. Both exhibit fascinating phase transitions and unusual and fascinating properties, such as colossal magnetoresistance (manganites) and half metallic behavior (magnetite).

In Sect. 7.8 we discuss another form of indirect exchange, the Ruderman-Kittel-Kasuya-Yosida or RKKY exchange and use it to discuss the magnetic exchange coupling in magnetic multilayers.

The final section discusses the effect of the small but important spinorbit interaction on the magnetic properties of solids. We shall see that it is the origin of the magneto-crystalline anisotropy (MCA) and therefore of great practical importance. We shall give a conceptually simple model for the origin of the MCA, based on the anisotropy of the orbital magnetic moment and support our picture by a model calculation.

7.2 Localized versus Itinerant Magnetism: The Role of the Centrifugal Potential

In the central field approximation discussed in Sect. 6.2.1, the inner atomic electrons are bound by the nuclear charge and form an electrostatic potential in which the outer electrons move. We will now show that the form of the central potential depends on angular momentum and that electrons can become more "trapped" or "localized" as their angular momentum increases. This picture explains important aspects of the localization properties of the d electrons in transition metals and especially of the 4f electrons in the rare earths.

The atomic potential is obtained by solution of the time-independent Schödinger equation with the central field Hamiltonian (6.9)

$$\mathcal{H}^0(\boldsymbol{r}) = \frac{\boldsymbol{p}^2}{2m_{\rm e}} + V(\boldsymbol{r}). \tag{7.1}$$

When the electron coordinates \boldsymbol{r} and the electron momentum operator $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$ are written in spherical polar coordinates we have

$$\boldsymbol{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r \sin \theta \cos \phi \\ r \sin \theta \sin \phi \\ r \cos \theta \end{pmatrix}$$
(7.2)

and

$$\boldsymbol{p}^{2} = -\hbar^{2} \boldsymbol{\nabla}^{2} = \underbrace{-\frac{\hbar^{2}}{r} \frac{\partial^{2}}{\partial r^{2}} r}_{p_{r}^{2}} \underbrace{-\frac{\hbar^{2}}{r^{2} \sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}\right) - \frac{\hbar^{2}}{r^{2} \sin^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}}}_{p_{\phi}^{2}}, \quad (7.3)$$

where on the right side we have indicated the correspondence with the classical kinetic energy, which when written in spherical coordinates has a radial (p_r^2) and angular (p_{ϕ}^2) part. The Schödinger equation corresponding to (7.1) separates into angular and radial parts with the radial equation given by

$$-\frac{\hbar^2}{2m_{\rm e}}\frac{{\rm d}^2 P_{n\ell}(r)}{{\rm d}r^2} + \underbrace{\left[V(r) + \frac{\ell(\ell+1)\hbar^2}{2m_{\rm e}r^2}\right]}_{V_{\rm eff}}P_{n\ell}(r) = E P_{n\ell}(r), \qquad (7.4)$$

where $P_{n\ell}(r) = rR_{n\ell}(r)$ is the radial part of the total central potential eigenfunction $\psi_{n,\ell,m}(\mathbf{r}) = R_{n,\ell}(r) Y_{\ell,m}(\theta,\phi)$ given by (6.11). We see that the effective potential V_{eff} in (7.4) consists of two terms. The first term is the true three dimensional potential energy V(r). It is negative (see later) and corresponds to a force pointed toward the atomic center. The second term arises from the

angular momentum part of the kinetic energy, considering that the quantum mechanical angular momentum operator L^2 has eigenvalues $\hbar^2 \ell(\ell + 1)$. This energy is positive and corresponds to the centrifugal force directed away from the atomic center.¹ For an electron orbiting with the angular frequency ω at a distance r from the nucleus we can calculate this force semiclassically by identifying the angular momentum as $m_e^2 r^4 \omega^2 = L^2 = \hbar^2 \ell(\ell + 1)$, i.e.,

$$F = -m_{\rm e}a = -m_{\rm e}r\omega^2 = -\frac{m_{\rm e}^2 r^4 \omega^2}{m_{\rm e}r^3} = -\frac{\ell(\ell+1)\hbar^2}{m_{\rm e}r^3} .$$
 (7.5)

Hence the term $\ell(\ell+1)\hbar^2/2m_{\rm e}r^2$ in (7.4) is referred to as the centrifugal potential.

In practice, the calculation of the potential V(r) in (7.4) is complicated and in the development of electronic structure calculations much effort has been devoted to this task. A nice review of the different approximations used in solving the radial wave equation is given by Cowan [182]. An electron in an outer or valence shell of an atom has a probability distribution that is peaked at some distance (the shell radius) from the nucleus but quantum mechanically has a finite probability over a range of distances. Close to the nucleus, the electron with charge $q_{\rm e} = -e$ will experience the full nuclear charge $q_N = Ze$, hence

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{7.6}$$

while at very large distances, all nuclear charges but one are screened by the core electrons, hence

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}.$$
(7.7)

The potential V(r) has to fulfill the correct boundary conditions near the nucleus and far away from it but has a more complicated form at intermediate distances. The determination of the potential in this intermediate region requires approximations. The different methods all assume an effective potential of the general form

$$V_{\rm eff}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + V_{\rm ee}(r) + \frac{\ell(\ell+1)\hbar^2}{2m_{\rm e}r^2} , \qquad (7.8)$$

where $V_{ee}(r)$ is the electron–electron term. It is typically calculated by approximations such as the Hartree, Hartree-Fock-Slater, or Hartree-plus-statisticalexchange methods. One of the simplest methods to somewhat account for the screening effect was suggested by Slater. In this formalism one simply sets

¹The centrifugal force has its classical analogue in Keplerian motion where for a stable orbit the central gravitational force is compensated by the centrifugal force.

 $V_{\rm ee}(r) = \sigma e^2/(4\pi\epsilon_0 r)$ so that the Coulomb part of the potential only depends on an effective nuclear charge $Z^* = Z - \sigma$, where σ is called a screening constant [227, 228]. Using this approach the total effective potential in (7.4) is given by

$$V_{\rm eff}(r) = -\frac{Z^* e^2}{4\pi\epsilon_0 r} + \frac{\ell(\ell+1)\hbar^2}{2m_{\rm e}r^2}.$$
(7.9)

With the definition $a_0 = 4\pi\epsilon_0\hbar^2/m_{\rm e}e^2 = 0.0529$ nm = 0.529 Å for the Bohr radius we can write as follows,

The *effective potential* for an atom with effective nuclear charge Z^* is given by

$$V_{\rm eff}(r) = E_{\rm R} \left[-\frac{2Z^* a_0}{r} + \frac{\ell(\ell+1)a_0^2}{r^2} \right] , \qquad (7.10)$$

where $E_{\rm R} = m_{\rm e} e^4/2(4\pi\epsilon_0)^2 \hbar^2 = 13.606 \,\text{eV}$ is the Rydberg energy, and $a_0 = 0.0529$ nm is the Bohr radius.

The effective potentials for s, p, d, and f electrons in the hydrogen atom $(Z^* = Z = 1)$ are plotted in Fig. 7.1.

If we solve the radial Schrödinger equation (7.4) with the hydrogenic potential (7.10) we can obtain analytical solutions for the radial parts of the valence

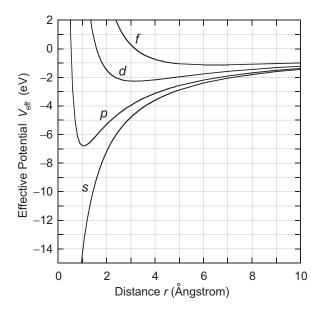


Fig. 7.1. The effective potential $V_{\text{eff}}(r)$ given by (7.10) plotted for s ($\ell = 0$), p ($\ell = 1$), d ($\ell = 2$), and f ($\ell = 3$) electrons in the hydrogen atom ($Z^* = Z = 1$). The effect of the centrifugal term in the effective potential is clearly revealed

electron wavefunctions $P_{n\ell}(r)$. With the notation $\rho = r/a_0$ the normalized² wavefunctions $P_{n\ell}(r) = rR_{n\ell}(r)$ for the 3d, 4s, 4p, and 4f electrons are given by [181, 182, 229]

$$P_{3d}(r) = \frac{4}{81\sqrt{30}} \sqrt{\frac{Z^*}{a_0}} (Z^*\rho)^3 e^{-Z^*\rho/3}, \qquad (7.11)$$

$$P_{4s}(r) = \frac{1}{4} \sqrt{\frac{Z^*}{a_0}} \left(Z^* \rho \right) \left(1 - \frac{3Z^*\rho}{4} + \frac{(Z^*\rho)^2}{8} - \frac{(Z^*\rho)^3}{192} \right) e^{-Z^*\rho/4}, \quad (7.12)$$

$$P_{4p}(r) = \frac{\sqrt{5}}{16\sqrt{3}} \sqrt{\frac{Z^*}{a_0}} (Z^*\rho)^2 \left(1 - \frac{Z^*\rho}{4} + \frac{(Z^*\rho)^2}{80}\right) e^{-Z^*\rho/4}, \quad (7.13)$$

$$P_{4f}(r) = \frac{1}{768\sqrt{35}} \sqrt{\frac{Z^*}{a_0}} (Z^*\rho)^4 e^{-Z^*\rho/4}.$$
 (7.14)

The situation for a typical transition metal atom with 1–9 electrons in the 3d shell and two electrons distributed over the 4s and 4p shells is shown in Fig. 7.2.

On top we have plotted the radial probability distribution function or charge density $P_{n\ell}^2(r) = r^2 R_{n\ell}^2(r)$ as a function of the distance r from the atomic center, obtained with the wavefunctions (7.11)-(7.13) using a value of $Z^* = 10$. The corresponding effective potentials $V_{\rm eff}(r)$ given by (7.10) with the same Z^* value are plotted underneath. The value of Z^* was chosen to approximately match the radial extent of the wavefunctions and the potential to those obtained for Fe (Z = 26) with the ab initio Hartree-plus-statisticalexchange (HX) method [182] (see Fig. 7.3 later). The 3d wavefunction is seen to be trapped in the potential well formed by the Coulomb and centrifugal contributions to the effective potential. The maximum charge densities of the 4s and 4p electrons are seen to be located further from the atomic center with the 4p electrons residing slightly closer to the nucleus than the 4s electrons, contrary to the expected "shell" structure. This effect is due to the centrifugal part of the potential for p or $\ell = 1$ electrons which is absent for s or $\ell =$ 0 electrons. The shown atomic charge density supports the notion that the 3d valence electrons are more "localized" than the other 4s and 4p valence electrons, which therefore can assume more "itinerant" character.

The centrifugal part of the potential is often associated with a "centrifugal barrier". Typically this barrier corresponds to a positive energy region of the potential at some distance which helps to keep the wavefunction trapped. Because centrifugal barriers can assume positive energies they have played an important role in spectroscopy since they can trap excited electrons, e.g., photoelectrons that are excited to energies just above zero potential energy,

We have $\int_0^\infty |P_{n\ell}(r)|^2 dr = \int_0^\infty |R_{n\ell}(r)|^2 r^2 dr = 1$ and with our form of wavefunctions the normalization is readily evaluated by means of the integral $\int_0^\infty r^m e^{-ar} dr = m!/a^{m+1}$.

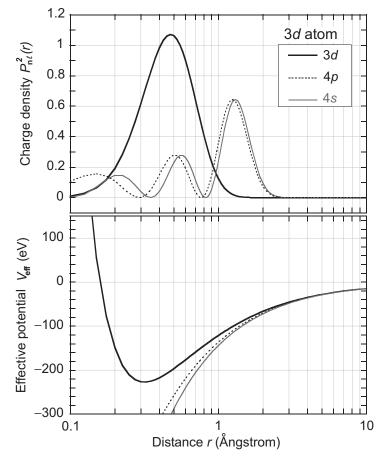


Fig. 7.2. Representative charge density $P_{n\ell}^2(r) = r^2 R_{n\ell}^2(r)$ and effective potential $V_{\text{eff}}(r)$ for a 3*d* transition metal atom. We have used (7.10) and the wavefunctions (7.11)–(7.13) with $Z^* = 10$ to account for screening of the inner shells. The potential and wavefunctions resemble those calculated for Fe (Z = 26) by means of the Hartree-plus-statistical-exchange (HX) method shown in Fig. 7.3 [182]. Note that the centrifugal potential term moves the charge of the "outermost" 4p shell inside the 4s shell

the so-called "vacuum level". Well known examples are molecular shape resonances which are due to centrifugal barriers in the molecular potential when it is written in the center-of-mass coordinate system [189]. In atoms centrifugal barriers exist for heavy elements and states with high angular momentum. This is illustrated in Fig. 7.3 for Fe and Yb. In each case the effective potential given by (7.8) consists of two regions. At small distances from the nucleus the potential is similar to the full nuclear potential corresponding to (7.10) with $Z^* = Z$ while at larger distances it has the shape of the hydrogen potential with $Z^* = 1$, shown as the dashed line in Fig. 7.3.

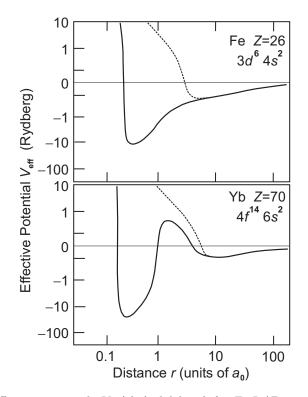


Fig. 7.3. Effective potentials $V_{\text{eff}}(r)$ (solid lines) for Fe I (Z = 26) and Yb I (Z = 70) atoms, calculated by means of the Hartree-plus-statistical-exchange (HX) method, taken from Cowan [182]. The ordinate is in Rydberg units (1 Rydberg = 13.606 eV), the abscisse is in units of the Bohr radius ($a_0 = 0.529$ Å). The dashed curves correspond to the hydrogenic (Z = 1) effective potentials. Their residual presence causes the appearance of an "outer well" in the atomic potentials. The 3d wavefunction in Fe and the 4f function in Yb are trapped in the "inner well". In the case of Yb this well is clearly separated from the outer well by a centrifugal barrier of positive energy

The formation of the transition metal and lanthenide series is closely associated with centrifugal effects, leading to 3d and 4f wavefunction trapping in a potential well. As Z increases from K (Z = 19) through Ca (Z = 20) to Sc (Z = 21) the 3d charge density moves from being centered near the minimum of the hydrogen-like potential well (outer well) into the deep inner well and a ground state configuration 3d electron appears, signifying the beginning of the 3d transition metal series [182]. Similar effects are observed at higher Z values with the formation of the 4d and 5d transition metals series. For all dtransition metals the d wavefunction is localized in the deep inner well. Note that the angular momentum of the d electrons is not quite high enough to give rise to a pronounced centrifugal barrier.

The situation is different for the rare earths, where the effective potential actually contains a pronounced centrifugal barrier as seen in Fig. 7.3. Now the potential contains pronounced inner and outer wells, the outer well again being due to the hydrogenic part of the potential. When Z increases from Ba (Z = 56) through La (Z = 57) to Ce (Z = 58) the 4f charge density moves from the outer into the inner well [182]. The 4f wavefunction collapses into the inner well around Z = 57 and similarly the 5f wavefunction collapses around Z = 90 then lead to the formation of the lanthanide and actinide series, respectively. Figure 7.3 beautifully demonstrates that the centrifugal barrier causes the strong localization of the 4f function. The localization is seen even more clearly in the plot of the radial charge density shown in Fig. 7.4 for the Gd^{+1} ion which has the outer electron configuration $4f^7 5s^2 5p^6 6s^2$. The 4fshell is seen to be quite localized in the atom and is shielded on the outside by the eight $5s^2 - 5p^6$ and the $6s^2$ valence electrons. It is interesting that for the rare earths the spatial collapse of the 4f wavefunction into the inner well is not accompanied by a significant increase in the 4f electron binding energy $E_{\rm B}$ which remains "valence-shell like" with $E_{\rm B} \leq 10 \, {\rm eV}$. In contrast, the outer 5s and 5p shells have higher binding energies in the ranges $32 \le E_{\rm B} \le 52 \, {\rm eV}$, and $16 \leq E_{\rm B} \leq 26 \, {\rm eV}$, respectively.

The more the valence electrons in atoms are localized the more their atomic properties are conserved in the solid state. As a consequence the magnetic moments in the rare earths are strongly localized in the 4f shell, the magnetic properties of the 3d transition metals are predominantly localized in the 3d shell with smaller (of order 10%) contributions from the s and p electrons. Yet

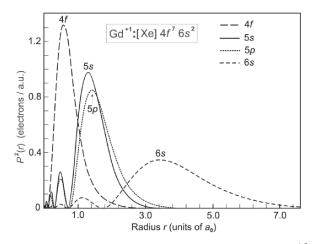


Fig. 7.4. Radial charge density in units of $[\text{electrons}/a_0]$ for the Gd^{+1} ion $(4f^7 6s^2)$ calculated by Freeman and Watson [230] for the 4f, 5s, 5p, and 6s orbitals. The figure shows that the 4f orbitals are actually located well inside the outer shells which screen them from the extra-atomic environment

stronger localization causes lower magnetic ordering temperatures because there is decreased exchange with the neighbors. For this reason all rare earths (lanthenides) are paramagnetic at room temperature with ferromagnetic Gd having a Curie point ($T_{\rm C} = 289 \,\mathrm{K}$) close to room temperature. For the 3*d* metals, the balance is just right for Fe, Co, and Ni. We can summarize this as follows.

For the ferromagnetic transition metals Fe, Co, and Ni the localization of the 3d electrons is high enough to generate a sizable magnetic moment yet low enough to provide overlap with the neighbors. This fortunate balance leads to sizeable Curie temperatures.

Coupling to the neighbors may occur indirectly via s and p electrons as well. But this coupling mostly produces antiferromagnetic ordering and is typically much weaker than in the ferromagnetic case (see Sects. 12.2.2 and 12.3, below).

7.3 The Relative Size of Interactions in Solids

The description of the bonding between atoms depends on the relative size of the intra-atomic and bonding interactions and one therefore needs to use different methods, depending on the system. For molecules, independent-electron theories in the form of molecular orbital theory and density functional theory have proven very successful, owing to relatively small correlation effects. In metals, one typically uses a spin dependent *band structure* approach which is also based on the density functional approach. In such systems, the overlap of the wavefunctions on neighboring atoms and the periodic structure lead to a strong dependence of the energy of a given electronic state on the electron momentum k, and this leads to a "band" of energies as a function of k. In ionic systems, like transition metal oxides, one instead uses an approach called ligand field theory. This theory concentrates on the bonding of a given 3d or 4f ion to its neighbors, the ligands. Because it emphasises the local bonding, around a transition metal ion embedded in a relatively small cluster, LF theory can be formulated in either an independent electron or a correlated electron model. We shall discuss these various approaches later.

The aim of the above theories is typically to determine the energetic ground state of the system which determines many properties of solids and tells us the favorite way atoms like to be positioned with respect to each other and how electrons and spins like to be distributed. The great success of density functional theory (DFT) is related to the importance of the electronic ground state. As we shall see later, it gives a good account of the electronic ground state at zero temperature for systems that are not "correlated". For "correlated" (yet to be defined) systems, however, a new way of thinking is required. This new way of thinking started with a simple question: why are so many oxides insulators? As early as 1937, de Boer and Verwey [231] recognized that the newly developed band theory which was first applied to magnetic systems around 1935 by Mott [27], Slater [28,29], and Stoner [30,31], could not account for the insulating nature of many oxides. Later in 1937, Mott [232] took up this puzzle, following a suggestion by Peierls about the fundamental importance of the strong electron–electron correlation on the transport in these materials. A broader understanding of the formation of insulators through the electron correlation phenomenon was developed by Mott in a series of papers starting in 1949 [233]. Mott's work constituted the birth of the broad field of correlated electron physics, which because of the rich and complex behavior of correlated systems remains at the core of condensed matter physics research to this day, as reviewed by Imada, Fujimori, and Tokura [234].

Mott realized that for the transition metal oxides one can no longer think in the ground-state-like picture of the band model, where the transport can easily be envisioned by small excitations around the Fermi level. Obviously, in an insulator higher energy excitations are required to transport an electron through the lattice. Hence one needs to consider excited states that lie above the ground state by energies up to several eV. The insulator problem therefore boils down to understanding the nature of excited states!

Such large energy excitations are intimately linked to the Coulomb repulsion, i.e., the Hubbard U, when an electron is removed from one atomic site and added to another. Any electron motion through the crystal, which may be envisioned as hopping from metal to oxygen to metal etc., where the hopping parameter is proportional to the band width W, has to overcome the Uon a given metal site. One thus obtains an insulator if $U \gg W$. The relative size of these two quantities also serves as a criterion whether a material is "correlated" ($U \gg W$) or not ($W \gg U$). It is this concept which lies at the heart of correlated electron physics and that needs to be incorporated into modern treatments of interactions in solids.

In order to get a handle on the size of various interactions we shall start by taking a look at the electronic structure of the 4f valence electrons of rare earth ions and 3d electrons of transition metal ions in crystals such as oxides and halides. We use these systems because they have been thoroughly studied by optical and paramagnetic resonance techniques [140, 228, 235, 236]. The relative sizes of important interactions emerging from such studies are summarized in Fig. 7.5.

We have indicated both the energetic splitting within a particular $4f^n$ $(1 \le n \le 14)$ and $3d^n$ $(1 \le n \le 10)$ free ion ground state, and also shown approximate excitation energies from these ground state configurations by adding or removing an electron. We will see later that these energies are very important in correlated materials and that they can be measured by photoemission and inverse photoemission.

It is important to realize that excitations from the ground state, defined as the lowest energy state within the lowest energy configuration, may involve

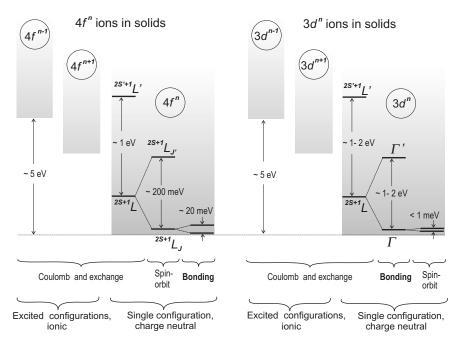


Fig. 7.5. The approximate size of three important interactions in solids for the $3d^n$ shell in transition metal ions and the $4f^n$ shell in rare earth ions, illustrated by the observed splittings in spectra of the ions in crystals [140, 235]. Note the opposite relative size of the bonding and the spin-orbit splittings for the 3d and 4f systems. We also indicate the size of noncharge conserving excitations, $n \to n \pm 1$, leading to excited configurations where electrons have been removed or added, as measured in photoemission and inverse photoemission

either an *intraconfiguration excitation* that preserves the charge state of the bonded ion, or by an *extraconfigurational excitation* that changes the charge state by adding or removing an electron from an atom in the sample. We have already encountered an excitation of the latter kind in the discussion of the Hubbard model, where an electron may hop on or off an atom, and from this it is evident that the Hubbard U must be associated with an extraconfigurational excitation. We shall later see that in the modern classification of correlated materials another energy is of great importance. This so-called charge transfer energy actually corresponds to an intraconfiguration excitation.

Let us now take a look at the relative size of interactions within the electronic ground state configuration. As discussed in Chap. 6 the Coulomb and exchange interaction leads to the coupling of the spins and angular momenta of the individual n electrons in the d or f shell to terms ${}^{2S+1}L$. For both the 3d and 4f ions the size of the intra-atomic coupling is given by the separation between the terms and we have indicated an order of magnitude estimate in Fig. 7.5.

state	$(\text{element})^{3+}$	$^{2S+1}L_J$	state	$(\text{element})^{2+}$	$^{2S+1}L_J$
		ground state		· · ·	ground state
$4f^1$	Ce	${}^{2}F_{5/2}$	$3d^1$	\mathbf{Sc}	${}^{2}D_{3/2}$
$4f^1 \\ 4f^2 \\ 4f^3 \\ 4f^4 \\ 4f^5 \\ 4f^6 \\ 4f^7 \\ 4f^8$	\Pr	${}^{3}H_{4}$	$3d^2$	Ti	${}^{3}F_{2}$
$4f^3$	Nd	${}^{4}I_{9/2}$	$3d^3$	V	${}^{4}F_{3/2}$
$4f^4$	\mathbf{Pm}	${}^{5}I_{4}$	$3d^4$	Cr	$^{\circ}D_{0}$
$4f^5$	Sm	${}^{6}H_{5/2}$	$3d^5$	Mn	${}^{6}S_{5/2} \\ {}^{5}D_{4}$
$4f^6$	$\mathbf{E}\mathbf{u}$	${}^{7}F_{0}$	$3d^6$	Fe	${}^{5}D_{4}$
$4f^{7}$	Gd	^{8}S	$3d^7$	Co	${}^{4}F_{9/2}$
$4f^{8}$	$^{\mathrm{Tb}}$	${}^{7}F_{6}$	$3d^8$	Ni	${}^{3}F_{4}$
$4f^{9}$	Dy	${}^{6}H_{15/2} \\ {}^{5}I_{8}$	$3d^9$	Cu	$^{2}D_{5/2}$
$4f^{10}$	Но	${}^{5}I_{8}$	$3d^{10}$	Zn	${}^{1}S_{0}$
$4f^{11}$	\mathbf{Er}	${}^{4}I_{15/2}$			
$4f^{12}$	Tm	${}^{3}H_{6}$			
$4f^{13}$	Yb	${}^{2}F_{7/2}$			

Table 7.1. f^n ground states of trivalent rare earth ions and $3d^n$ ground states for divalent transition metal ions in crystals [219]. For d^n ground states also see Table 7.7

For the 3*d* ions the second important interaction is the bonding interaction which is of comparable size as the Coulomb and exchange interaction. The reason is that the 3*d* electrons participate in the bonding with the ligands, and overlap with the oxygen 2*p* orbitals. In contrast, the spin–orbit interaction is much smaller than the other two interactions. In fact, it is smaller than the spin–orbit parameter ($\zeta_{nl} \sim 30$ meV, see Fig. 6.12) because the orbital angular momentum is broken up by the crystal field so that the effective spin–orbit splitting is only about 1% of ζ_{nl} , as discussed in Sect. 7.9.3 later.

The 4f shell is more like an inner than a valence shell as discussed in detail in Sect. 7.2. Its compact radius and the relative large atomic number of the rare earths causes the spin-orbit coupling constant to be quite large $(\zeta_{nl} \sim 0.2 \,\text{eV}, \text{ see Fig. 6.12})$. Because of the localized nature of the 4f electrons they are not directly involved in bonding and therefore the LF splitting is quite small, about a factor of 10 less the spin-orbit splitting. The LF splitting in the rare earths, often called the *Stark splitting*³ can be measured by optical spectroscopy [235] while the larger spin-orbit and multiplet splittings may be observed in photoemission spectroscopy [237, 238]. For later use, we list in Table 7.1 the multiplet ground states for the various $4f^n$ and $3d^n$ configurations.

Figure 7.5 shows that we need to treat the 3d and 4f systems quite differently. The 4f compounds are dominated by extra- and intraconfiguration correlation energies and therefore are prototype correlated electron systems. Ligand field effects can be treated as a perturbation.

 $^{^3\}mathrm{This}$ goes back to the idea that it arises from the "crystal electric field" set up by the ligands.

For the ionic 3d compounds, we need to treat bonding and correlation effects on an equal footing. This means that we should expect the band width W due to bonding and the extra- and intra-configuration correlation energies to be of comparable size. This is the key reason why transition metal compounds are not adequately treated by band calculations, and why they offer rich phase diagrams and their properties remain full of surprises and puzzles. In the next two sections we shall look at two fundamental methods of treating the interactions of charges and spins in solids.

7.4 The Band Model of Ferromagnetism

7.4.1 The Puzzle of the Broken Bohr Magneton Numbers

It is well known that the spin and orbital magnetic moments of atoms are multiples of the Bohr magneton according to $\mathbf{m} = (2\mathbf{s} + \mathbf{l})\mu_{\rm B}/\hbar$. One would therefore naively expect that the magnetic moments of the magnetic metals Fe, Co, and Ni should also be even multiples of $\mu_{\rm B}$. For example, in the 3*d* metal atoms one has the number of 3*d* and 4*s* valence electrons listed in Table 7.2.

Table 7.2. Number of 3d and 4s electrons in the free transition metal atoms

	Κ	Ca	\mathbf{Sc}	Ti	\mathbf{V}	Cr	Mn	Fe	Co	Ni	Cu	Zn
N_{3d}	0	0	1	2	3	5	5	6	7	8	10	10
N_{4s}	1	2	2	2	2	1	2	2	2	2	1	2
N_{3d+4s}	1	2	3	4	5	6	7	8	9	10	11	12

Since the metals are charge neutral in the atomic spheres one would expect similar numbers of unpaired electrons in the metals as for the atoms. This allows us to calculate the expected magnetic moments. For Fe there are six 3d and two 4s electrons, relative to a total of 12 possible electrons if both shells were completely filled. Because there are 4 unfilled "holes", Hund's rule would predict 4 unpaired electrons and therefore a magnetic spin moment equivalent to 4 spins or $m_s = 4\mu_{\rm B}$. Similar considerations lead to predicted spin moments of $3\mu_{\rm B}$ for Co and $2\mu_{\rm B}$ for Ni. If one wanted to include the orbital moment one would estimate the moment per atom from Hund's rules, maximizing S, L, and J, as listed in Table 7.3 for the expected atomic delectron configurations. If one neglected the outermost s electron and assumed that the magnetic moment arises from the d shell one would be led to a model where the electronic ground state corresponds to the respective ${}^{2S+1}L_J$

Table 7.3. Occupation of 3*d* orbitals with quantum numbers m_{ℓ} for some atomic d configurations d^5 , d^6 (Fe atom and metal), d^7 (Co atom and metal), d^8 (Ni atom and metal), and d^9 . We use the convention $s_z = -1/2 = \downarrow$. We also list the angular momenta $S = |\sum s_z|$, $L = |\sum l_z|$, and J and the terms ${}^{2S+1}L_J$ from Hund's rules. Note that J = L + S for a more than half filled shell. The magnetic moment m_{J_z} is the d shell moment expected for an atom with Hund's rule ground state and occupation of the lowest state $J_z = -J$, only, i.e., $m_{J_z} = g_J J \mu_{\rm B}$, where g_J is the Landé g-factor given by (6.101)

$m_\ell \rightarrow$	+2	+1	0	-1	-2	S	L	J	$^{2S+1}L_J$	g_J	$m_{J_z}^a$
d^5	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	$\frac{5}{2}$	0	$\frac{5}{2}$	${}^{6}S_{5/2}$	2	5
d^6	$\uparrow \downarrow$	\downarrow	\downarrow	\downarrow	\downarrow	2	2	4	${}^{5}D_{4}$	$\frac{3}{2}$	6
d^7	$\uparrow \downarrow$	$\uparrow \downarrow$	\downarrow	\downarrow	\downarrow	$\frac{3}{2}$	3	$\frac{9}{2}$	${}^{4}F_{9/2}$	$\frac{4}{3}$	6
d^8	$\uparrow \downarrow$	$\uparrow \downarrow$	↑↓	\downarrow	\downarrow	1	3	4	${}^{3}F_{4}$	$\frac{5}{4}$	5
d^{9}	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	\downarrow	$\frac{1}{2}$	2	$\frac{5}{2}$	${}^{2}D_{5/2}$	$\frac{6}{5}$	3

^{*a*} Moments are in units of $[\mu_{\rm B}]$.

manifolds listed in Table 7.3. The exchange field would split this ground state,⁴ leaving only the lowest state with $J_z = -J$ occupied and one would expect the listed moments $m_{J_z} = g_J J \mu_{\rm B}$, where g_J is the Landé g-factor given by (6.101). All such atomic scenarios result in integer magnetic moments.

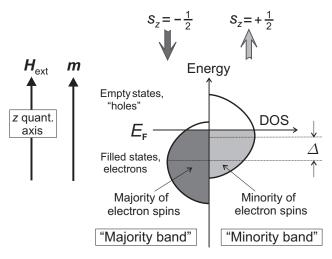
If one measures the spontaneous magnetization M in Fe, Co, and Ni and divides it by the number of atoms, one discovers that the atomic moments $m_{\rm exp} = 2.216\mu_{\rm B}$ for Fe, 1.715 $\mu_{\rm B}$ for Co, and 0.616 $\mu_{\rm B}$ for Ni are not multiples of the Bohr magneton but rather odd fractions of it. This shows that the 3d electrons are not strictly localized. The values listed in Table 7.3 also show that inclusion of an atomic-like orbital moment gives a value that is much higher than the experimental value and that expected from the spin moment, only. This indicates that the atomic model severely overestimates the orbital moments. As discussed in Sect. 11.2.2 in solids the orbital moment is indeed largely quenched by the bonding which we have completely neglected in our above discussion. These considerations show that a different approach is needed to account for the measured values for the magnetic moments of the transition metals, the key being a proper treatment of the effects of the bonding in the metallic lattice.

7.4.2 The Stoner Model

The puzzle about the broken Bohr magneton numbers in the ferromagnetic metals was solved through the development of band theory, which was first applied to magnetic systems around 1935 by Mott [27], Slater [28, 29], and

⁴Although the exchange field acts only on S, the J manifold would nevertheless split. With the exchange field along +z and for J = L + S the lowest energy state would be $-J_z$. Note that for coupling J = L - S the lowest state would be $+J_z$!

Stoner [30, 31]. The simplest band-like model of the ferromagnetic metals is often called the Stoner-model or the Stoner-Wohlfarth-Slater-model (SWS-model) of metallic ferromagnetism.



Stoner model for 3d band and nomenclature

Fig. 7.6. The Stoner model of ferromagnetic transition metals, illustrated for the 3d shell, and nomenclature used for the band description of magnetism. Filled electron states below the Fermi energy $E_{\rm F}$ are shown shaded, "hole" states above $E_{\rm F}$ are shown unshaded. The spin states with the largest number of electrons are called "majority spins" and the corresponding band is the "majority band", and the term "minority" is used for the other electron spins and band. The centers of the majority and minority d bands, assumed to be reasonably localized as shown, are separated by the exchange splitting Δ . The labels "spin-up" and "spin-down" only have a meaning in conjunction with a quantization direction, which in our case is taken to be the direction of the external field $H_{\rm ext} \parallel M$. It is good to remember that the minority spins always point in the direction of M. The magnetic moment |m| in units of $\mu_{\rm B}$ is determined by the difference in the number of majority and minority states, as discussed in the text. The density of states generated by the *s*-*p* electrons is not shown for clarity

The assumption behind the SWS-model is that the bonding interaction between the 3d electrons causes a smearing of their energy into a band which can be described from physics [205, 219] or chemistry [239] points of view. The periodicity of the atomic positions leads to the formation of characteristic periodic variations of the individual energy states and their band width increases with the inverse lattice constant, i.e., with the electron momentum q. For now it is sufficient to consider the average finite energy width of the valence band states and we approximate the density of states (DOS) by a simple semicircle as shown in Fig. 7.6. In the presence of a Weiss field the centers of gravity of the states characterized by opposite spins exhibit an energy separation, the exchange splitting Δ .

At T = 0 all states are filled up to the Fermi energy $E_{\rm F}$ and we speak of the filled states as "electron states" and of the empty states as "hole states". The spin states with the larger electron population are called the *majority states*, those with the smaller population the *minority states*, and the same labels are used for the respective bands.

The two bands associated with different spin orientations are labeled according to their relative *electron* population as "majority band" and "minority band".

The often used labels "spin-up" and "spin-down" by themselves are arbitrary and only have a meaning relative to a quantization direction. Therefore they provide a valuable concept in theory, where it is easy to define a quantization direction, typically labelled z. Then "up" is along z and "down" along -z. The spin-up states, labelled $|\uparrow\rangle = |+\rangle$, have the eigenvalue $s_z = +\hbar/2$, and the spin-down states, labelled $|\downarrow\rangle = |-\rangle$, have the eigenvalue $s_z = -\hbar/2$.

In Fig. 7.6 we have taken the quantization direction as the direction of an external magnetic field H_{ext} , used to align the magnetization M of the sample. Then the magnetic moment is also in the up direction and because the moment is defined as $m = -g\mu_{\text{B}}s$, the moment and spin have opposite directions. So in this case the majority states have spin-down, the minority states have spin-up. For a "down" field the labels spin up and down are reversed.

In experiments it is not trivial to determine and keep track of the true field direction and therefore the terms "up" and "down" lose their physical meaning. Instead, one uses the terms minority and majority spins. As discussed in Sect. 2.6 and also shown in Fig. 7.6, by convention, the magnetization M and the atomic moments m point in the same direction as H_{ext} .

In modern magnetism research the flow of electrons and spins in transport measurements or the transmission of spin polarized electron beams through a magnetic sample are of key importance. In such experiments, a central theme in later chapters of our book, we therefore distinguish the role of the majority and minority spins. Since the minority spins have states below and above the Fermi level as shown in Fig. 7.6, they turn out to be more important than the majority spins for the description of spin transport. Throughout this book we will repeatedly use the following unique definition, which should be remembered.

The minority spins always point into the direction of M.

Historically the magnetic properties of materials within the band model have been discussed in terms of the electron, i.e., the filled states. More recently however, in particular in conjunction with the development of inverse

photoemission and X-ray magnetic circular dichroism techniques, attention has also been paid to the hole states because these techniques probe transitions to the empty states and the measured intensities are therefore directly determined by the spin dependent hole states. In principle it should be equivalent to use the electron or hole states (by taking care of the different sign) for the quantitative description of the magnetic moment because the total number of filled and empty states, i.e., the number of electrons and holes, needs to add up to the maximum occupation number of a given shell with angular momentum ℓ , which is $2\ell + 1$ for each spin.⁵ Thus by knowing the number of electrons we also know the number of holes. Using this simple concept we can then derive an expression for the magnetic moment in either the electron or hole picture.

From the spin dependent density of states $D^{\uparrow}(E)$ and $D^{\downarrow}(E)$ we can determine the number of states by an appropriate energy integration. For example, the number of spin-down electron states is given by

$$N_{\rm e}^{\rm maj} = N_{\rm e}^{\downarrow} = \int_{-\infty}^{E_{\rm F}} D^{\downarrow}(E) \,\mathrm{d}E.$$
(7.15)

Because of the negative charge of the electron, the atomic magnetic moment is given by $\mathbf{m} = -2\mu_{\rm B}\mathbf{s}/\hbar$ according to (3.13), where s is in units of $[\hbar]$. The absolute value of \mathbf{m} is then given by the expectation value of the electron spin $\langle s_z \rangle$, relative to a quantization axis z. With $H_{\rm ext}$ defining the direction of z, we see from Fig. 7.6 that

$$\langle s_z \rangle = \langle +\frac{1}{2} | s_z | +\frac{1}{2} \rangle N_{\mathrm{e}}^{\mathrm{min}} + \langle -\frac{1}{2} | s_z | -\frac{1}{2} \rangle N_{\mathrm{e}}^{\mathrm{maj}}$$
$$= \frac{\hbar}{2} \left(N_{\mathrm{e}}^{\mathrm{min}} - N_{\mathrm{e}}^{\mathrm{maj}} \right) = \frac{\hbar}{2} \left(N_{\mathrm{e}}^{\uparrow} - N_{\mathrm{e}}^{\downarrow} \right).$$
(7.16)

The maximum number of electrons in the d shell cannot exceed (2s+1)(2l+1) = 10 according to Pauli's exclusion principle. If the total number of 3d electrons is $N_{\rm e}$ and the number of holes is $N_{\rm h}$ we have $N_{\rm e} + N_{\rm h} = 10$. Similarly, if we call the number of holes in the minority band $N_{\rm h}^{\rm min} = N_{\rm h}^{\uparrow}$ and in the majority band $N_{\rm h}^{\rm maj} = N_{\rm h}^{\downarrow}$, respectively, we have $N_{\rm e}^{\downarrow} + N_{\rm h}^{\downarrow} = 5$ and $N_{\rm e}^{\uparrow} + N_{\rm h}^{\uparrow} = 5$ and therefore

$$\langle s_z \rangle = \frac{\hbar}{2} \left(N_{\rm e}^{\uparrow} - N_{\rm e}^{\downarrow} \right) = -\frac{\hbar}{2} \left(N_{\rm h}^{\uparrow} - N_{\rm h}^{\downarrow} \right) = -\frac{\hbar}{2} \left(N_{\rm h}^{\rm min} - N_{\rm h}^{\rm maj} \right).$$
(7.17)

Since the magnetic moment $|\boldsymbol{m}|$ is related to the expectation value of the spin according to $|\boldsymbol{m}| = -2\mu_{\rm B} \langle s_z \rangle / \hbar$, we can summarize our discussion above in the following statement about the origin of the magnetic moment.

 $^{^5 \}mathrm{In}$ practice the situation is slightly more complicated as discussed in Sect. 12.2.2 later.

The magnetic moment $|\mathbf{m}|$ is given by the difference in the number of electrons or holes in the majority and minority bands, defined in Fig. 7.6, according to,

$$|\mathbf{m}| = \mu_{\rm B} \left(N_{\rm e}^{\rm maj} - N_{\rm e}^{\rm min} \right) = \mu_{\rm B} \left(N_{\rm h}^{\rm min} - N_{\rm h}^{\rm maj} \right).$$
 (7.18)

In the band picture the number of majority and minority states is noninteger and the magnetic moments are noninteger multiples of the Bohr magneton.

The simple relation (7.18) between electron and hole moments is exact only if the band states are well defined in their energy spread about the Fermi level as assumed in Fig. 7.6. In practice, this is only approximately so for the 3d transition metals as discussed in more detail in Sect. 12.2.2 later. One finds that through hybridization of the d states with the s-p states some small dcharacter is found even at energies more than 10 eV above the Fermi level. Therefore, as pointed out by Wu and Freeman [240, 241], the number of dholes and the magnetic d hole moment are slightly reduced relative to the values expected from the filled electron states.

The exchange field H_{ex} generating the splitting Δ of the electronic states is not a true magnetic field. It produces no electromagnetic induction and no Lorentz force or eddy currents. However, just like a magnetic field, it is axial and in two respects it can be treated as if it were a magnetic field. First, in accordance with (3.15), we can use it to describe the origin of the exchange splitting as $\Delta = 2\mathbf{m} \cdot \mathbf{H}_{\text{ex}}$. Secondly, following (3.28), it also exerts a torque $\mathbf{T} = \mathbf{m} \times \mathbf{H}_{\text{ex}}$ on the electron spins. The energy and the torque $|\mathbf{T}| = \Delta/2$ correspond to a giant value for the effective exchange field of 10^3 T, as discussed in Sect. 11.1.2.

The exchange field does not act on the orbital moment or on the nuclear magnetic moment. This is of great importance because in the presence of the exchange interaction the spin system still remains independent from the orbital system which is locked to the crystal lattice. Once the electron spin polarization and hence the spin moment is established by the exchange interaction, the coupling of the spin moment to the orbital moment is established through the weaker spin–orbit interaction. It is this coupling which leads to the magnetocrystalline anisotropy by locking the spin to the orbital moment which itself is locked to the lattice, as discussed in Sect. 7.9.3.

The ratio of the orbital moment to spin moment may be obtained from the measurement of the g-factor according to (3.44). Today a more powerful method is the separate measurement of the spin and orbital moments by means of X-ray magnetic circular dichroism, discussed in Chap. 10. The orbital moment is small in the case of the 3d-ferromagnets, but approaches the atomic value in the case of the 4f ferromagnets where the ligand field acting

on the magnetic levels is largely screened by the outer closed shells in most cases.

7.4.3 Origin of Band Structure

In the Stoner model we have ignored the detailed dependence of the band structure on the electron wavevector \mathbf{k} and simply integrated over all \mathbf{k} states to obtain the energy dependent DOS. We have further assumed that the DOS has a simple form, represented by a semicircle. In reality, the DOS typically varies strongly with energy and consists of peaks and valleys. Since it is important to understand the origin of the density of states and the underlying \mathbf{k} dependent band structure we shall now illustrate the origin of band structure in a simple chemistry based picture, as given by Hoffmann [239] and Harrison [242].

In order to simplify our discussion we shall consider the bonding and resulting band structure for a one-dimensional chain of atoms bonded through their d orbitals as illustrated in Fig. 7.7. Magnetic effects are introduced into our model in a Stoner-like fashion by assuming the existence of a molecular magnetic field that splits the electron states into spin-states with orientation parallel (spin-up) and antiparallel (spin-down) to the molecular field direction.

The bonding of the atoms in our chain, shown in Fig. 7.7a is assumed to originate from the *d* electrons as in the Stoner model. Each atom has 10 *d* electrons, whose electronic states are described by five angular momentum functions, taken as the well known real *d* orbitals $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{3z^2-r^2}$, given in Table A.2, and either a spin-up $s_z = +1/2$ or spin down $s_z = -1/2$ function. For later use we have also listed in Table A.2 the form of *s* and *p* orbitals.

The real d_j orbitals can be conveniently visualized in terms of the charge density $|d_j|^2$, as shown in Fig. 7.7b for selected orbitals. The individual orbital lobes along specific directions are marked as + or - or simply by color, according to the sign of the wavefunction. For example $d_{xz} \propto xz$ is positive (dark shaded) along the directions $(\pm x, \pm z)$ and negative (white) along the directions $(\pm x, \mp z)$. In molecular orbital theory the bonding is then simply pictured as directional overlap between the d_j orbital densities with recognition of the signs. The bonding is strong when orbitals with the same sign overlap and a bonding orbital is formed. When the sign is opposite an antibonding orbital is formed. Electrons in bonding orbitals act as glue, those in antibonding orbitals as a repulsive spring.

In band theory the process of combining orbitals on different atoms corresponds to the formation of Bloch functions, which for the case of our chain is written as

$$\phi_j(k) = \sum_n d_j^{(n)} e^{i \, n \, k \, a}, \qquad (7.19)$$

where the index j labels the five Bloch functions or bands per spin, composed of the orbitals $d_i^{(n)}$ on different atoms n. We have for k = 0 7.4 The Band Model of Ferromagnetism 241

$$\phi_j(0) = \sum_n d_j^{(n)} \tag{7.20}$$

and for $k = \pi/a$

$$\phi_j(\pi/a) = \sum_n d_j^{(n)} e^{i n \pi} = \sum_n (-1)^n d_j^{(n)}.$$
(7.21)

The Bloch functions at k = 0 and $k = \pi/a$ therefore are superpositions of the $d_j^{(n)}$ orbitals on different atoms n with different phase factors +1 or -1. As shown in Fig. 7.7b the resulting Bloch functions at k = 0 and $k = \pi/a$ are simply bonding or antibonding combinations of the $d_j^{(n)}$ orbitals. Bonding combinations are always lower in energy than antibonding combinations and this determines whether the bands run down or up from k = 0 to $k = \pi/a$, as shown in Fig. 7.7c. The width of a particular sub-band depends on the d_j

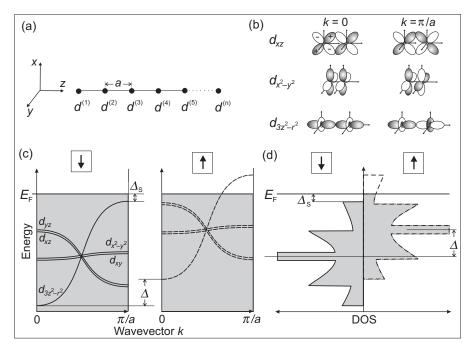


Fig. 7.7. Origin of band structure for a chain of *d*-orbital bonded atoms and assuming that one spin band, the majority band, is completely filled. (a) defines the geometry of atoms in a chain with atomic spacing a, (b) gives a simple chemistry based picture how *d* orbitals on different atoms combine at points k = 0 and $k = \pi/a$ to form a band state, (c) gives the band structure corresponding to a *d*-orbital bonded atomic chain, assuming a splitting Δ between the spin-up and spin-down bands caused by a molecular field in the up direction, (d) gives the density of states that follows by summing over all states in (c). The separation of the top of the majority band to the Fermi level, $\Delta_{\rm S}$ is called the Stoner gap

orbital overlap, which in our case is largest for the $d_{3z^2-r^2}$ orbitals that are directed along the atomic chain.

A spin dependent valence band state $\psi_i(\mathbf{k}, r)$, labelled by a band index $i \ (1 \leq i \leq 10)$, can then be written in terms of the five d_j orbital basis functions centered on the atoms and wave-vector (**k**), position (r) and spin $(\alpha = \chi^+ = \uparrow, \beta = \chi^- = \downarrow)$ dependent terms [243]

$$|\psi_i(\mathbf{k}, r)\rangle = |R_{n,d}(r)\rangle \sum_{j=1}^5 a_{i,j}(\mathbf{k}) |d_j \chi^+\rangle + b_{i,j}(\mathbf{k}) |d_j \chi^-\rangle .$$
 (7.22)

We can also write a band state in terms of $Y_{l,m} = |l m\rangle$ (l = 2) basis functions

$$|\psi_{i}(\mathbf{k},r)\rangle = |R_{n,l}(r)\rangle |\phi_{i}(\mathbf{k})\rangle$$

= $|R_{n,l}(r)\rangle \sum_{m=-l}^{+l} c_{i,m}(\mathbf{k}) |l m \chi^{+}\rangle + e_{i,m}(\mathbf{k}) |l m \chi^{-}\rangle$. (7.23)

The above wavefunctions are written in a Slater-Koster tight binding formalism [244] and describe a band state in the presence of both exchange and spin-orbit interactions (see Sect. 7.9.2 later). We have assumed that the radial part $R_{n,l}(\mathbf{k}, r) = R_{n,l}(r)$ is the same for all basis functions $Y_{l,m}$ or d_j and is independent of \mathbf{k} , which is a reasonable approximation. The spin-up coefficients $a(\mathbf{k}), c(\mathbf{k})$ and spin-down ones $b(\mathbf{k}), e(\mathbf{k})$ are determined by a suitable band structure calculation, and obey the normalization condition

$$\langle \phi_i(\mathbf{k}) | \phi_i(\mathbf{k}) \rangle = \sum_{m=-2}^{+2} |c_{i,m}(\mathbf{k})|^2 + |e_{i,m}(\mathbf{k})|^2 = \sum_{j=1}^{5} |a_{i,j}(\mathbf{k})|^2 + |b_{i,j}(\mathbf{k})|^2 = 1 .$$
(7.24)

When summed over all possible k values in the Brillouin zone, corresponding to the reciprocal space of the unit cell or Wigner-Seitz cell of the lattice, one gets the DOS shown in Fig. 7.7d. The DOS is largest where the bands are flat since at these energies many k points contribute. The electron states are filled up to the Fermi energy.

If we only consider band states with energies above the Fermi energy $E_{\rm F}$ and we sum over all **k**-dependent states in the Brillouin zone, we obtain the number of empty states or holes $N_{\rm h}$,

$$N_{\rm h} = N_{\rm h}^{\uparrow} + N_{\rm h}^{\downarrow} = \sum_{m=-2}^{+2} N_m = \sum_{m=-2}^{+2} \sum_{\substack{E>E_{\rm F}\\i,k}} |c_{i,m}(\mathbf{k})|^2 + |e_{i,m}(\mathbf{k})|^2$$
$$= \sum_{j=1}^5 N_j = \sum_{j=1}^5 \sum_{\substack{E>E_{\rm F}\\i,k}} |a_{i,j}(\mathbf{k})|^2 + |b_{i,j}(\mathbf{k})|^2 .$$
(7.25)

Here N_m and N_j are the number of d holes, projected for the different states $Y_{l,m}$ or orbitals d_j .

7.4.4 Density Functional Theory

Now that we have developed a basic understanding of the origin of k dependent bands, we shall briefly give an introduction to the basic assumption underlying modern band theoretical calculations, *density functional theory*. For more thorough reviews the reader is referred to various reviews available on the topic [222, 245–248].

A band structure calculation starts from a certain atomic geometry, given by the atomic positions in the crystal lattice. The real space is typically partitioned into regions around the atoms and interstitial regions and different functions are used in the two regions to describe the electronic states. For example, in the regions around the atoms the wavefunctions may consist of radial functions and spherical harmonics while plane waves may be used in the interstitial regions. The functions are made continuous by appropriate boundary conditions. One now constructs the potentials in the two regions for solving the time-independent Schrödinger equation using one-electron wavefunctions. The total Hamiltonian is written within the Born-Oppenheimer approximation which assumes that the electronic and nuclear parts can be separated, and the motions of the nuclei are neglected with respect to those of the electrons. The electronic Hamiltonian has the general form of (6.6) and the Coulomb part is of the form

$$\mathcal{H}_{\rm C}(\boldsymbol{r}) = \frac{e^2}{4\pi\epsilon_0} \left[-\sum_i \frac{Z_i}{|\boldsymbol{r} - \boldsymbol{R}_i|} + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,\mathrm{d}\boldsymbol{r}' \right].$$
(7.26)

Here \mathbf{R}_i are the atomic coordinates, \mathbf{r} specifies the electron coordinates and $\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r})$ is the total electron charge density. The potential (7.26) may be obtained by solving Poisson's equation in each of the two regions. The exchange-correlation potential resulting from the symmetrization postulate (or Pauli principle) is added to (7.26) and for magnetic materials it is charge and spin dependent

$$\mathcal{H}_{xc}[\rho(\boldsymbol{r}),\sigma(\boldsymbol{r})]$$
, (7.27)

where $\sigma(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$ is the spin density.

In practice, approximations have to be made in the calculation since it is currently not possible to solve the many-body problem for the electrons in the solid. The main idea of the important density functional theory (DFT) is to describe the system of the N interacting electrons by its density $\rho(\mathbf{r})$ and not via a many-body wavefunction. This means that the description of the system depends on three spatial coordinates and the spin, only, rather than on N times more degrees of freedom. The use of a spin dependent density results in two sets of single-particle wavefunctions, one for spin-up and one for spin-down, as in the independent electron model. One may say that this approach maps the many-body problem onto a system of noninteracting fictitious particles with a certain density. The most successful first principles band

theory today is based on DFT pioneered by Hohenberg-Kohn-Sham [210,211]. The theory is based on two theorems that can be stated together as follows,

Density functional theory expresses the total energy of an atomistic system as a function of its electron density ρ . It can then be shown that:

• $E(\rho)$ is at its minimum for the ground state density, that is a T = 0.

• $E(\rho)$ is stationary with respect to first order variations in the density.

Because of the theorems above, DFT is well suited only for the treatment of ground state properties. One cannot expect it a priori to apply to excited states, as well. A very successful and widely used approximation for magnetic systems is DFT, expressed in the local (spin) density approximation or L(S)DA. In this case the exchange correlation energy of an inhomogeneous system is assumed to depend only on that of an electron gas evaluated at the local electron density of each volume element, and the exchange-correlation potential, given by (7.27), is expressed as an analytic function of $\rho(\mathbf{r})$ and $\sigma(\mathbf{r})$. Several forms of this approximation exist in the literature. The basic assumption underlying L(S)DA is a delocalized or itinerant behavior of the valence electrons. Only with this assumption can one hope to replace the detailed orbital-dependent atomic exchange-correlation potential with the averaged one-electron potential for the homogeneous electron gas.

The results obtained by means of band theory for the electronic states of solids may be compared to the band dispersion measured by means of angle resolved photoemission [237, 249]. A celebrated case of the success of band theory is Cu, as extensively discussed by Hüfner [237] and shown in Fig. 7.8.

The question arises why the calculated band dispersion for the electronic ground state agrees so well with the results of photoemission which measures the difference between the ground state and an excited state where an electron has been removed from the solid. The answer is that such a comparison only works if the correlation between the electrons is indeed negligible. This is of course the assumption made in the independent electron model. If we take an electron out of a band in Cu we change the electronic density of order 10^{-23} . If the electrons are truly independent their wavefunctions may be viewed as being delocalized over the whole crystal and therefore each atom in the crystal carries only a 10^{-23} part of the hole left behind. Thus the states probed by photoemission are indistinguishable from those calculated in an independent electron approximation.

Solids that are well described by band theory give photoemission spectra that accurately reflect the electronic ground state.

Unfortunately, the agreement for magnetic metals is not as good [237, 249–251], owing to the presence of significant correlation effects, as will be discussed in Sect. 7.6.3 later and in Chap. 12.

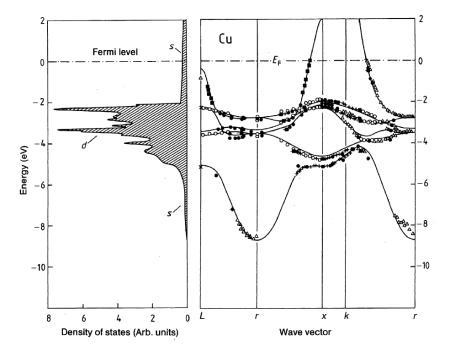


Fig. 7.8. Calculated band structure of Cu metal in comparison with experimental results obtained by angle resolved photoemission. Figure taken from Ibach and Lüth [205] after data compiled by Hüfner [237]

7.5 Ligand Field Theory

Ligand field (LF) theory aims to explain the electronic states and energies of transition metal ions when surrounded by other atoms, which are referred to as ligands [140, 228, 252–254]. In contrast to band theory or molecular orbital theory (see Fig. 7.12, below), LF theory does not treat the electronic states on the central atom and on the ligands on an equal footing. The wavefunctions or orbitals of the ligands do not enter at all. Only the splitting of states on the central atoms is considered. The effect of the ligands is entirely taken into account by symmetry and the strength of the "field" produced by them.

The theory originates from work by Bethe in 1929 [255] and van Vleck [256] in 1935. It was originally referred to as "crystal field theory" and the original idea was to use a pure electrostatic point charge model to calculate the local electrostatic interaction between the negative charges on the ligands (neighbors) and a valence shell electron on a central transition metal ion. It was quickly recognized that a pure point charge model gave orbital splittings on the metal atoms that were an order of magnitude smaller than those observed.

Following ideas of van Vleck [256], modern ligand field theory therefore includes the missing overlap of the valence electrons, e.g., that of the O 2p with the metal 3d states. Fortunately this does not require a completely new theory but rather one uses the electrostatic form of the Hamiltonian which correctly describes the symmetry and simply fits certain ligand field parameters to fit the experimentally observed orbital splitting.

The treatment of the magnetic properties of the transition metal oxides is complicated by the fact that, for a given ionic configuration, one has to consider two competing interactions of comparable strength (of the order of 1– 2 eV, see Fig. 7.5). One interaction is the intra-atomic Coulomb and exchange interaction between the *d* electrons which in the free ions give rise to coupled multiplet states ^{2S+1}L through the coupling of the spins and orbital momenta of the individual electrons in the *d* shell (L–S coupling). The other interaction arises when the free ion is subjected to interactions with its neighbors in a molecule or a solid. In transition metal compounds this inter-atomic interaction is modeled by a ligand field approach [140,228,252–254]. In the literature the topic of "ligand field theory" is typically treated by distinguishing two cases. The case where the LF energy is smaller than the correlation energy is called the *weak field* limit. When the LF interaction is stronger than the electron–electron correlation one speaks of the *strong field* limit [140,204,228].

In modern calculations, the weak and strong field cases are treated by two different approaches. In the weak field limit the most important interaction is the intra-atomic Coulomb and exchange interaction between the electrons. Thus one uses an atomic multiplet theory that properly accounts for intra-atomic correlation effects. The inter-atomic bonding modelled by the weaker ligand field is accounted for by its symmetry and a scalable interaction strength.

In practice, the advanced calculations are often carried out for a cluster and include the ground state configuration with n electrons, excitations within the ground state configuration, and higher energy configurations such as $n \pm 1$ through a configuration interaction scheme. Within the configurations the bonding is treated by LF concepts. As an example we cite the calculations for the negatively charged cluster (NiO₆)⁻¹⁰ [257–259].

In the strong field case the inter-atomic bonding is considered of prime importance. It is treated in a LF approach which emphasizes the symmetrydependent interactions between one-electron orbitals, typically taken as the real p and d orbitals. The weaker interactions between electrons are treated by an averaged exchange correlation potential similar to molecular orbital theory or a band structure approach.

In the following discussion we will not use the terms "weak" and "strong" field theory, but instead use a terminology that emphasizes the way the calculations are done in practice, namely *independent electron LF theory* and *multiplet LF theory*. The two models may be summarized as follows.

Independent electron LF theory starts with five one-electron d orbitals and describes their splitting in terms of the symmetry and strength of the LF of the neighbors.

• The orbitals are filled with electrons under observation of the Pauli principle, and an ad hoc assumption of the size of the correlation (Coulomb and exchange) energy relative to the LF splitting.

• A large correlation energy favors a high spin ground state, and a small correlation energy a low spin ground state.

Multiplet LF theory starts with the correlated multiplet states ${}^{2S+1}L$ of the free ion, resulting from the Coulomb and exchange interactions.

• The symmetry group of the LF then determines the splitting of the multiplets into irreducible representations (IRs).

• The energetic splitting of the IRs depends on the LF to correlation energy ratio, and is given by a so-called Tanabe-Sugano diagram [253,260].

7.5.1 Independent-Electron Ligand Field Theory

In the independent electron LF approach one uses the three real p_i orbitals and/or five real d_i -orbitals given in Table 7.4, as basis functions.

The reasons for the extensive use of the p_i and d_i orbitals are:

- Since the spin–orbit coupling is small, the ligand field can be assumed to act on the orbital degrees of freedom only, described by the p_i or d_i orbitals.
- The orbitals are real and can therefore be used to picture bonding in the three-dimensional real world.
- The pure orbitals are eigenfunctions of the LF Hamiltonian for most cases of interest (see later).

As the spherical symmetry for the free ion is lowered to the appropriate symmetry in the solid, the orbital degeneracy is lifted. Initially the calculation of the splitting was based on the point charge crystal electric field approach and the Hamiltonian was constructed for such a point charge model. The matrix elements were calculated using an *operator equivalence method* developed by Stevens and this approach dominated the literature for many years [140]. Today one uses the elegant spherical tensor algebra developed by Racah [181, 182] which is related to Stevens' method [254]. In the spherical tensor notation, the LF Hamiltonian has the form

$$\mathcal{H}_{\rm LF} = \sum_{k}^{\infty} \sum_{q=-k}^{k} B_q^k \ C_q^{(k)} \ . \tag{7.28}$$

	· [· · -		ιI	-,,
s	=	$\frac{1}{\sqrt{4\pi}}$	=	$Y_{0,0}$
p_x	=	$\sqrt{\frac{3}{4\pi}}\frac{x}{r}$	=	$\frac{1}{\sqrt{2}}(Y_{1,-1} - Y_{1,+1})$
p_y	=	$\sqrt{\frac{3}{4\pi}}\frac{y}{r}$	=	$rac{i}{\sqrt{2}}(Y_{1,-1}+Y_{1,+1})$
p_z	=	$\sqrt{rac{3}{4\pi}rac{z}{r}}$	=	$Y_{1,0}$
d_{xy}	=	$\sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$	=	$rac{i}{\sqrt{2}}(Y_{2,-2}-Y_{2,+2})$
d_{xz}		$\sqrt{\frac{15}{4\pi}}\frac{xz}{r^2}$	=	$\frac{1}{\sqrt{2}}(Y_{2,-1} - Y_{2,+1})$
d_{yz}		$\sqrt{\frac{15}{4\pi}\frac{yz}{r^2}}$	=	$\frac{i}{\sqrt{2}}(Y_{2,-1}+Y_{2,+1})$
$d_{x^2-y^2}$		$\sqrt{\frac{15}{16\pi}} \frac{(x^2 - y^2)}{r^2}$	=	$\frac{1}{\sqrt{2}}(Y_{2,-2}+Y_{2,+2})$
$d_{3z^2-r^2}$	=	$\sqrt{\frac{5}{16\pi} \frac{(3z^2 - r^2)}{r^2}}$	=	$Y_{2,0}$

Table 7.4. Mathematical description of s, p, and d orbitals, pictured in Figs. 7.9 and A.3, in terms of spherical harmonics $Y_{l,m_l} = |l, m\rangle$. The orbitals are real^a

^aThe orbitals o_i are normalized according to $\int o_i^* o_i \, \mathrm{d}\Omega = \int_0^{2\pi} \int_0^{\pi} o_i^* o_i \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$ = $\langle o_i | o_i \rangle = 1$.

The LF symmetry dictates which k, q values contribute to the sum. The "crystal field parameters" or ligand field coefficients B_q^k depend on the positions \mathbf{R}_i and charges of the *neighbor atoms* (ligands) and in practice are treated as adjustable. Racah's spherical tensor operators $C_q^{(k)}$ depend on the angular coordinates of the electrons on the *central atom*. They are listed in Table A.3 and are related to the spherical harmonics according to

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2l+1}} Y_{k,q} . (7.29)$$

The matrix elements $\langle l, m | C_q^{(k)} | l', m' \rangle$ are given by the Clebsch-Gordon coefficients or 3 - j symbols [181, 254]. Nowadays they are readily calculated by standard computer programs, e.g., mathematica.

When for a certain LF symmetry the Hamiltonian (7.28) is diagonalized in the d_i (or p_i) orbital basis, the Hamiltonian is found to be diagonal for all but the lowest symmetries. The eigenvalues associated with different d_i eigenfunctions then form certain degenerate sets that correspond to the IR of

Table 7.5. Abbreviated character tables for the cubic group O. We only show the irreducible representations, their degenéracy given by the character of the identity operation E, the coordinates (important for p orbitals), and their squares and binary products (important for d orbitals) [183]. The brackets mean that the functions together transform like the representation. For example, the functions $2z^2 - x^2 - y^2 = 3z^2 - r^2$ and $x^2 - y^2$ together transform like the E representation. They are therefore inseparable and degenerate and form the basis of E. In older texts [140] the irreducible presentations are sometimes labelled in the Bethe notation which is linked to that of Mullikan according to $\Gamma_1 \equiv A_1$, $\Gamma_2 \equiv A_2$, $\Gamma_3 \equiv E$, $\Gamma_4 \equiv T_1$, $\Gamma_5 \equiv T_2$

0	E	
A_1	1	$x^2 + y^2 + z^2$
A_2	1	
E	2	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	(x, y, z)
T_2	3	(xy,xz,yz)

the LF symmetry group. The link between the IRs of a given symmetry group and the degenerate eigenvalue sets of the LF Hamiltonian provides a powerful tool to predict the splitting of the d_i orbitals from group theoretical symmetry arguments alone. The relevant information is contained in the character tables, which decompose the group into its IRs [183, 228, 253]. The character tables also conveniently link the IRs with the specific p_i or d_i -orbitals. As an example we give in Table 7.5 an abbreviated character table for the cubic group O. Throughout this book we shall use the IR notation of Mulliken as is common in most texts today, and denote the IRs in an independent electron model by small letters (e.g., t_{2g}) and the IRs of multielectron configurations by capital letters (e.g., T_{2g}).

Table 7.5 identifies the p_x, p_y , and p_z orbitals, which transform like x, y, and z, with the IR T_1 and the bracketed symbol (x, y, z) means that the orbitals p_x, p_y, p_z together transform like the T_1 representation and are hence degenerate and inseparable and not split by the cubic LF symmetry.

The orbitals d_{xy}, d_{xz}, d_{yz} form the basis of the IR T_2 and the orbitals $d_{3z^2-r^2}, d_{x^2-y^2}$ form the basis of the IR E. Thus in cubic symmetry the 3d orbitals split into threefold degenerate T_2 and twofold degenerate E states. The splitting between the irreducible representations is determined by the parameterized interaction strength and is commonly denoted $10D_q$. The LF splitting of the pure d orbitals for some symmetries is shown in Fig. 7.9. Note that the tetragonal symmetries D_{4h} corresponding to different in-plane and out-of-plane coordinations are representative of geometries encountered at surfaces or in thin films, as discussed in Sect. 7.9.2 later.

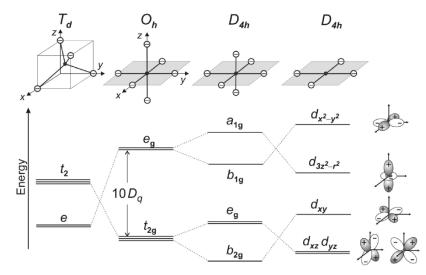


Fig. 7.9. Ligand field splitting of energy levels for a single d electron in fields of different coordination and symmetry. For the cases shown the central 3d ion is assumed to be coordinated by electronegative ligands such a oxygen. On the left we compare the splitting in the tetrahedral (T_d) and octahedral O_h cubic symmetries. For octahedral O_h and tetragonal D_{4h} symmetries we have assumed equal interaction strengths in the x - y plane and varied the interaction along z, as illustrated. On the right are plotted the orbital densities $(d_i)^2$ of the LF eigenfunctions d_i and the numerical sign of d_i wavefunction lobes are indicated on top of the charge densities

The character tables also reveal when the individual pure p_i and d_i orbitals can mix and cease to be good eigenfunctions [183]. The most important rule is,⁶

Two orbitals $|o_l\rangle$ and $|o_n\rangle$ can only be mixed by a ligand field if they belong to the same irreducible representation of the symmetry group.

Inspection of the character tables shows that the p_i orbitals are good eigenfunctions for all symmetries higher than monoclinic C_{2h} , that is for all cases with rectangular unit cell axes. Similarly one finds from the character tables that the $d_{x^2-y^2}$ and d_{xy} orbitals can mix when the point group symmetry is lowered from C_{4v} to C_{4h} . When the symmetry is lowered to the highest orthorhombic point group D_{2h} , two things happen. First, all degeneracies are lifted since the yz and xz orbitals now belong to different irreducible representations. Second, the functions $3z^2 - r^2 = 2z^2 - x^2 - y^2$ and $x^2 - y^2$ now belong

⁶Note that this does not apply to IRs that in the character tables are listed in brackets, since they together transform like the representation and are inseparable and degenerate.

to the same A_g representation and they can mix. The $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals cease to be good eigenfunctions of the LF and the new eigenfunctions are linear combinations of the two.

In general, one can write the independent electron LF eigenfunctions as a linear combination of d-orbitals and by use of Table 7.4 they maybe written in the general forms (ignoring spin)

$$|\phi_d\rangle = R_{n,d}(r) \sum_{i=1}^5 a_i \, |d_i\rangle = R_{n,d}(r) \sum_{m=-l}^{l=2} b_m \, Y_{l,m}.$$
 (7.30)

Here the complex coefficients a_i and b_m fulfill the normalization condition $\sum_m |b_m|^2 = \sum_i |a_i|^2 = 1$. There will be 2l + 1 LF states for a given l value if spin is neglected. If we include spin, each LF state can contain two electrons, so when the shell l is full it will contain 2(2l + 1) electrons, e.g., there are a maximum of 2s electrons, 6p electrons, 10d electrons, 14f electrons etc. We shall use the wavefunctions in (7.30) in either basis, depending on the problem. The general form of the LF wavefunctions reveals what will turn out to be of great importance in our later discussion of the spin–orbit interaction in solids (Sect. 7.9 later). It can be stated as follows.

In the independent electron LF model, the LF eigenfunctions contain mixtures of different m values, and therefore m ceases to be a good quantum number.

The tetrahedral T_d and octahedral O_h symmetries are of particular importance because the effect of lower symmetries can often be treated as a perturbation of these two basic symmetry types. From Fig. 7.9 we see that in T_d symmetry the triplet is higher in energy than the doublet while the opposite holds in O_h symmetry. This can be explained by the original point charge concept of the LF. In this model Fig. 7.9 depicts an atom with a single d electron in the field of negatively charged ligands, and we therefore expect the central atom orbitals that are pointed toward the ligand positions to be higher in energy than those orbitals that avoid the ligand positions.⁷ In O_h symmetry the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals point directly to the ligand positions and are therefore higher in energy because of electrostatic repulsion effects. In T_d symmetry the ligands lie along the body diagonals of the cube shown in Fig. 7.9. The $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals of the central atom point toward the centers of the cube faces and the d_{xy}, d_{xz}, d_{yz} orbitals point toward the centers of the cube edges. The latter points are closer to the ligands by a factor $\sqrt{2}$ and the d_{xy}, d_{xz}, d_{yz} orbitals are therefore higher in energy. If all

⁷When this argument is applied to a hole rather than an electron in the d shell, one sees that an electron configuration d^n and the corresponding hole configuration d^{10-n} should have inverted energy level schemes.

Spin states of Fe in octahedral field

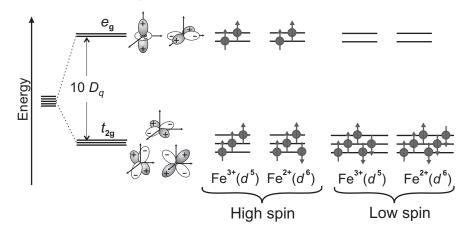


Fig. 7.10. Ligand field splitting of d orbitals in an octahedral (O_h) ligand field, resulting in lower energy t_{2g} and higher energy e_g orbitals. On the right we show the filling of the orbitals for the cases of Fe³⁺ (d^5) and Fe²⁺ (d^6) , under two assumptions. An exchange energy larger than the $t_{2g} - e_g$ splitting favors parallel spin alignment and we obtain a high spin ground state. If the exchange energy is smaller than the $t_{2g} - e_g$ splitting we obtain a low spin ground state

other things are equal the tetrahedral splitting is smaller, with a value of 4/9 of than the octahedral one. We can make the following general statement.

Metal d orbitals that point more toward the ligand positions are higher in energy.

The LF approach is based on considering the possible states of a single d electron in a LF and is therefore based on a *one-electron model*. Interactions between electrons are only considered in an ad hoc fashion in a second step. One distinguishes two important cases corresponding to a "high spin" or "low spin" ground state. If the exchange interaction is large relative to the LF splitting, all five LF levels are consecutively filled with electrons of the same spin, and only then are electrons with opposite spin added, as shown in Fig. 7.10 for the case of octahedral symmetry O_h and Fe^{3+} (d^5) and Fe^{2+} (d^6). This corresponds to a filling of the energy levels according to Hund's first rule as discussed in Sect. 6.5.

In contrast, if the exchange interaction is small relative to the LF splitting, as assumed previously in Fig. 6.13 and shown for Fe on the right side of Fig. 7.10, then the fourth and fifth electrons are not in the high-energy e_g state but instead are also located in the lower t_{2g} state. Since the Pauli principle requires them to be of opposite spin than the first three electrons we obtain a low spin ground state. For Fe³⁺ (d^5) we are left with only one uncompensated spin and hence S = 1/2. For Fe²⁺ (d^6) all spins are compensated and S = 0. The ground states for the configurations $d^4 - d^7$ may therefore consist of either a low-spin or high spin configuration. We can summarize as follows.

For the $d^4 - d^7$ configurations, the electron filling of the 10 possible d spinorbitals leads to two distinct ground states, depending on the relative size of the electron correlation energy relative to the LF splitting.

• If the electron correlation energy is larger (or "high"), the ground state has *high-spin*.

• If the electron correlation energy is smaller (or "low"), the ground state has *low-spin*.

Jahn–Teller Effect

Sometimes the filling of the orbitals with electrons according to the Pauli principle may also affect the local structure around the transition metal ion,

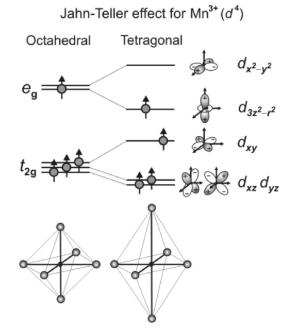


Fig. 7.11. Jahn–Teller effect for Mn^{3+} (3d⁴). The Mn^{3+} ion (black) is located in the center of an oxygen octahedron, as shown in the lower part of the figure. When the octahedral symmetry is distorted into the shown tetragonal symmetry, the energy of the $d_{3z^2-r^2}$ orbital which points along the elongated bond direction (z) is lowered in energy (compare Fig. 7.9). Since the lower $d_{3z^2-r^2}$ orbital is filled and the higher $d_{x^2-y^2}$ orbital is empty the system can lower its energy. Since both of the split t_{2g} states are filled and the center of gravity is preserved the t_{2g} states do not contribute to the overall energy saving

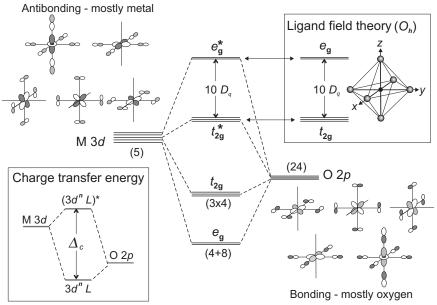
a phenomenon known as the Jahn–Teller effect. A prominent Jahn–Teller ion is Mn^{3+} . When the ion in the high-spin configuration, shown in Fig. 7.11, is placed in an octahedral LF it contains a single electron in the upper e_g state. The system can lower its energy by a tetragonal distortion which causes a level splitting. The lowering in total energy is due to the lowering of one of the e_g orbitals, as shown for the case of a bond lengthening along the z axis, which causes the singly filled $d_{3z^2-r^2}$ orbital to drop in energy below the empty $d_{x^2-y^2}$ orbital. The filled lower t_{2g} state also splits but retains its center of gravity without any net change in energy. In contrast, for Mn^{4+} (d^3), the e_g state is empty and the distortion would yield no net gain in energy. Hence no Jahn–Teller distortion occurs.

Molecular Orbital Theory

LF theory focuses on the energy splitting of the orbitals on a chosen atom under the influence of the "field" from the ligands. It is largely empirical in nature and allows the description of experimental data in terms of a few parameters. In contrast, molecular orbital theory is an ab initio theory that properly describes the overlap and mixing of the wavefunctions of bonded atoms. For 3d transition metal oxides, for example, we have seen that LF theory describes the splitting and filling of the 3d orbitals on the central transition metal atom in the "field" of the oxygen neighbors. We did not consider the oxygen orbitals at all. In contrast, molecular orbital theory considers in detail the orbitals on the central transition metal atom and the oxygen neighbors.

This is illustrated in Fig. 7.12 for a 3d atom surrounded by six oxygen atoms in an octahedral arrangement. The inset shows the typical LF picture, where the 3d states are split into lower energy t_{2g} and higher energy e_g states. In molecular orbital theory one starts with the five atomic d_i orbitals on the central metal atom and three p_i orbitals (see Table 7.4) on each O neighbor. Since only orbitals belonging to the same irreducible representation can mix, we can form linear combinations of a given d_i orbital and symmetry adapted combinations of p_i orbitals on the oxygen ligands, as done in Fig. 7.12. In all cases the total symmetry of the combined p_i orbitals on the oxygen neighbors is either e_{g} or t_{2g} and matches the symmetry of the central d_{i} orbital. The e_{g} orbitals form σ bonds and the t_{2g} orbitals π bonds, as revealed by the orientation of the p orbitals parallel (σ) and perpendicular (π) to the interatomic O–M axes. By forming bonding (matching phases) and antibonding (opposite phases, denoted with an asterisk) combinations of the d_i orbitals with the symmetry adapted p_i orbitals we obtain the energy level diagram shown in Fig. 7.12. In constructing the diagram we have assumed that the metal 3dstates lie higher in energy than the O 2p states.

The composition of the bonding and antibonding wavefunctions depends on the amount of hybridization. If the hybridization, i.e., the 2p - 3d mixing is small, the lower-energy bonding states are mainly oxygen 2p in character while the higher-energy antibonding states are mostly 3d like. This is, in



Molecular orbital theory of octahedral MO₆ cluster

Fig. 7.12. Illustration of molecular orbital theory for a central metal atom, surrounded by a six oxygen atom octahedron. The coordinate system is specified in the top right inset. The bonding is caused by orbital overlap of the central atom 3d orbitals with a symmetry adapted combination of oxygen 2p orbitals. The bonding orbitals have mostly oxygen character and the antibonding orbitals (marked with an asterisk) consist of mostly metal orbitals. We also show the correspondence between the $e_{\rm g}^*$ and $t_{2\rm g}^*$ molecular orbitals and the $e_{\rm g}$ and $t_{2\rm g}$ orbitals in a ligand field picture in the upper right inset. The number of oxygen p states is given in brackets. Note that the symmetry adapted p states that mix with $d_{3z^2-r^2}$ contains 8 p_i orbitals, because along z two p orbitals are needed to match the $3z^2 - r^2 = 2z^2 - x^2 - y^2$ symmetry. In the lower left inset we define the charge transfer energy Δ_c as the average energy required to excite an electron from the ligand-like bonding to the metal-like antibonding state

fact, the typical situation and we can therefore identify the $e_{\rm g}^* - t_{\rm 2g}^*$ separation with the LF *d* orbital splitting $10D_q$, as indicated in the top right inset. A more complete picture would include 4s and 4p states on the transition metal atom but we shall neglect them here and simply assume that the electrons are transferred to the oxygen 2p states because of the large electronegativity of oxygen. The oxygen 2p states are therefore completely filled with 6 electrons/atom and the metal 3d electrons fill the $e_{\rm g}^*$ and $t_{\rm 2g}^*$ orbitals, in agreement with the LF model.

We also show in the bottom left inset another basic feature of the molecular orbital model. If we ignore the splitting into $e_{\rm g}$ and $t_{\rm 2g}$ states the antibonding and bonding states are separated by an energy $\Delta_{\rm c}$. By using the label L for

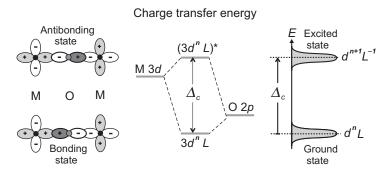


Fig. 7.13. Illustration of the charge transfer concept. We show the bonding and antibonding states in a molecular orbital picture and also the corresponding configurational energy picture

ligand we can denote the filled bonding states $3d^nL$ and the partially filled antibonding states with $(3d^nL)^*$. Because for weak hybridization the bonding state is mostly ligand-like and the antibonding state mostly metal-like, we see that the energy Δ_c can be thought of as an electron excitation that creates a hole in the ligand-like bonding state and adds an electron in the metallike antibonding state. For this reason, Δ_c is called the (ligand to metal) charge transfer energy and the excitation $3d^nL \to (3d^nL)^*$ maybe pictured in terms of a configurational energy diagram [261] as illustrated in Fig. 7.13. It is important to distinguish the molecular orbital picture which shows the ground state level diagram and the configuration picture which gives the energies of the ground state and excited state configurations.

The charge transfer energy Δ_c involves an excitation from the ground state $3d^nL$ with energy $\varepsilon(3d^nL)$ to an excited state with energy $\varepsilon(3d^{n+1}L^{-1})$ according to

$$\varepsilon(3d^nL) + \Delta_{\rm c} = \varepsilon(3d^{n+1}L^{-1}) . \tag{7.31}$$

In the final state there is a hole in the ligand-like bonding state and an added electron in the 3d-like antibonding state.

We shall come back to the important charge transfer concept later in Sect. 7.6.2.

7.5.2 Multiplet Ligand Field Theory

In independent electron LF theory discussed earlier, we have first constructed an energy level scheme appropriate for a single electron. We have then simply filled other electrons into this scheme by assuming that the interactions between them are weak and that only the Pauli principle needs to be taken care of. This approach is similar to that taken in a band structure calculation, where the exchange correlation potential is treated in some averaged fashion, and the Stoner splitting takes care of the Pauli principle. Similar to independent electron band theory, the independent electron LF theory fails if the correlation between the electrons is strong.

In contrast to band theory, it is possible in LF theory to accurately account for strong electron correlation effects. This is facilitated by a cluster approach where one only calculates the correlation for a central atom without considering the long range k-dependent details of the band structure. The LF approach can be viewed as a flat-band model, where the dispersion throughout the Brillouin zone is very weak and the bonding interactions are localized around individual atoms. Because of this simplifying assumption one can work out in detail the intra-atomic d-d interactions in the valence shell and then introduce the effect of bonding as a mixing and splitting of the free ion terms ${}^{2S+1}L$ by the ligand field. This is done using the powerful concepts of group theory. We shall refer to this multielectron interaction model as multiplet LF theory. The development of this theory was pioneered by Tanabe, and Sugano in 1954 [260] and expanded in the book of Sugano, Tanabe, and Kamimura [253] published in 1970. Today, calculations are often carried out using the LF multiplet program developed by Thole et al. [262, 263], which combines Cowan's atomic Hartree-Fock program [182, 264] and the general group theoretical program by Butler [265]. Calculation procedures are described in more detail by de Groot [266, 267].

The procedure is as follows. One assumes a certain ligand field symmetry and then uses group theory to see how the free ion terms ${}^{2S+1}L$ split into the IRs of the LF symmetry group. The situation is simplified by the fact that the spin orbit coupling is weak relative to the d-d correlation and the LF energy as shown in Fig. 7.5. This means that the orbital (charge) and spin degrees of freedom to first order remain uncoupled and there is no mechanism for the electrostatic LF to talk to the spin. Therefore in first order one only needs to consider the effect of the LF on the orbital angular momentum L. The general group theoretical decomposition of the angular momenta $L = 0, \ldots, 6$, corresponding to the terms S, \ldots, I , into the IRs for cubic symmetry is given in Table 7.6.

\overline{L}	term	IRs
0	S	A_1
1	P	T_1
2	D	$E + T_2$
3	F	$A_2 + T_1 + T_2$
4	G	$A_1 + E + T_1 + T_2$
5	H	$E + 2T_1 + T_2$
6	I	$A_1 + A_2 + E + T_1 + 2T_2$

 Table 7.6. Splitting of orbital terms into irreducible representations (IRs) for a cubic ligand field

Table 7.7. d^n (n = 1, ..., 10) ground states of transition metal ions in high and low spin configurations. For the free ions we list the lowest energy ${}^{2S+1}L$ terms and for the ions in an octahedral (O_h) ligand field we list the irreducible representation of the lowest energy state. The degeneracies of the irreducible representations are 1 for A, 2 for E and 3 for T

state	free ion	octahedral	configuration
	$\operatorname{term}(s)$	ground state	-
high spin			
$3d^1$	^{2}D	${}^{2}T_{2}$	$(t_{2 ext{g}}^{\uparrow})^1$
$3d^2$	${}^{3}F$	${}^{3}T_{1}$	$(t_{2g}^{\uparrow})^2$
$3d^3$	4F	${}^{4}A_{2}$	$(t_{2\sigma}^{\uparrow})^3$
$3d^4$	^{5}D	${}^{5}E$	$(t_{2g}^{\uparrow})^3 \ (e_{\mathrm{g}}^{\uparrow})^1$
$3d^5$	6S	${}^{6}A_{1}$	$(t_{2g}^{\uparrow})^3 \ (e_{\mathrm{g}}^{\uparrow})^2$
$3d^6$	^{5}D	${}^{5}T_{2}$	$(t_{2\sigma}^{\uparrow})^3 \ (e_{g}^{\uparrow})^2 \ (t_{2\sigma}^{\downarrow})^1$
$3d^7$	4F	${}^{4}T_{1}$	$(t_{2g}^{\uparrow})^3 \ (e_{g}^{\uparrow})^2 \ (t_{2g}^{\downarrow})^2$
$3d^8$	${}^{3}F$	${}^{3}A_{2}$	$(t_{2g}^{\uparrow})^3 \ (e_{g}^{\uparrow})^2 \ (t_{2g}^{\downarrow})^3$
$3d^9$	^{2}D	^{2}E	$(t_{2g}^{\uparrow})^3 \ (e_{g}^{\uparrow})^2 \ (t_{2g}^{\downarrow})^3 \ (e_{g}^{\downarrow})^1$
$3d^{10}$	^{1}S	${}^{1}A_{1}$	$(t_{2g}^{\uparrow})^3 \ (e_{g}^{\uparrow})^2 \ (t_{2g}^{\downarrow})^3 \ (e_{g}^{\downarrow})^2$
low spin			
$3d^4$	${}^{3}(P,H)$	$^{3}T_{1}$	$(t_{2g}^{\uparrow})^3 \ (t_{2g}^{\downarrow})^1$
$3d^5$	$^{2}(I)$	$^{2}T_{2}$	$(t_{2\sigma}^{\uparrow})^3 (t_{2\sigma}^{\downarrow})^2$
$3d^6$	$^{1}(G, I)$	${}^{1}A_{1}$	$(t_{2g}^{\uparrow})^3 \ (t_{2g}^{\downarrow})^3$
$3d^7$	$^{2}(G)$	^{2}E	$(t_{2g}^{\uparrow})^3 \ (t_{2g}^{\downarrow})^3 \ (e_{g}^{\uparrow})^1$

For a d^n configurations with n = 1, ..., 10 one obtains the free ion terms ${}^{2S+1}L$ listed in Table 7.7. The energetic order of the various free ion terms for a given d^n configuration is determined by diagonalizing the Hamiltonian $\sim 1/r_{ij}$ describing the interactions between the *d* electrons, using methods developed by Slater [225, 227]. The Slater integrals⁸ F^k and G^k denote the Coulomb and exchange terms, respectively, and the expectation value of the Hamiltonian is given by the sum

$$E(SL) = \sum_{k} a_k F^k + b_k G^k = a_1 A + a_2 B + a_3 C , \qquad (7.32)$$

where the coefficients a_k, b_k are angular momentum dependent quantities. In our case of *n* equivalent *d* orbitals (d^n) we have $F^k \equiv G^k$ and the term splitting can be written in terms of the Slater integrals F^k , only. The quantities *A*, *B*, and *C* are the so-called *Racah parameters* which combine certain Slater integrals. Tables of the term energies in terms of the Racah parameters are found in text books [181, 228, 253].

⁸Note that there is a difference between the Slater parameters, written F^k and G^k , and the Condon–Shortley [224] parameters F_k and G_k [181,253].

For a given d^n configuration the lowest of all possible free ion terms ${}^{2S+1}L$ [181, 183, 253], is that of maximum S and L according to Hund's rule discussed in Sect. 6.5. For a weak LF interaction, i.e., the high spin case, one only needs to determine the lowest-energy free ion term and then consider its splitting into IRs of the LF symmetry. The lowest IRs for the case of octahedral symmetry are listed in Table 7.7. The so-determined multielectron ground state can also be written in terms of the spin dependent occupation of the one-electron orbitals, $(t_{2g}^{\uparrow})^i (e_g^{\uparrow})^j (t_{2g}^{\downarrow})^k (e_g^{\downarrow})^m$ with i + j + k + m = n, as shown on the right in the Table. Note that Sugano et al. [253] use the notation $d\epsilon$ for t_{2g} and $d\gamma$ for e_g .

The behavior of the electronic states for the various d^n configurations as a function of the ligand field strength is usually pictured in a Tanabe–Sugano diagram [260], which is shown for d^5 in Fig. 7.14. The diagram is a plot of the

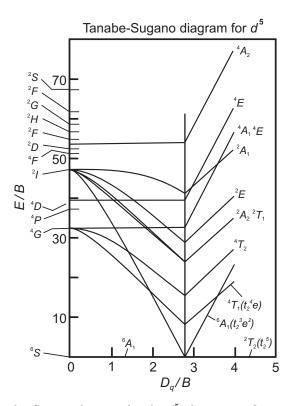


Fig. 7.14. Tanabe–Sugano diagram for the d^5 electron configuration in an octahedral (O_h) ligand field. Shown are the LF energies E, normalized to the Racah parameter B, plotted as a function of the cubic splitting parameter D_q , again normalized to B. On the left the free ion multiplets ${}^{2S+1}L$ are shown. As a function of D_q/B the multiplets split into the irreducible representations of the O_h group. Near $D_q/B \simeq 2.75$ the LF splitting relative to the Coulomb energy B becomes so large that the high-spin case switches to the low-spin case, as indicated by a break in the curves. The respective ground states for the two cases are those listed in Table 7.7

level splitting as a function of the cubic LF strength D_q divided by the Racah parameter B. The complete set of diagrams for all d^n configurations has been reproduced in many texts, e.g., [140, 183, 228, 253].

As the ligand field strength increases we have seen above that the high spin turns into a low spin configuration for the cases d^4 , d^5 , d^6 , and d^7 . The transition from high to low spin occurs when the value of D_q/B is in the range 2–3 and at this point the Tanabe–Sugano diagrams for $d^4 - d^7$ show a break. In the low spin state the LF ground state IR originates from one or more ^{2S+1}L terms, which for the free ion lie higher in energy. The relevant states for the low spin cases are also listed in Table 7.7.

The correspondence between the multiplet LF model and the independent electron LF model is illustrated for the case of a d^2 configuration in Fig. 7.15.

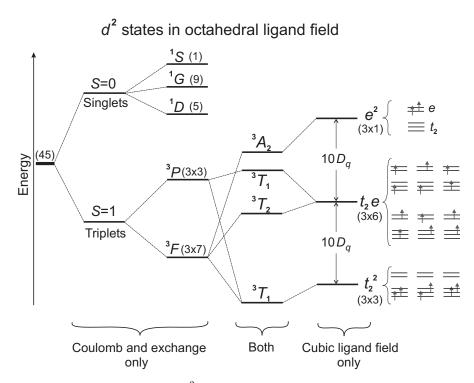


Fig. 7.15. Energy levels for a d^2 electron configuration for three important cases. On the left we show the effect of the Coulomb and exchange interactions resulting in multiplets ${}^{2S+1}L$ of the free ion. In the middle we show how the two triplet multiplets split under the action of an octahedral O_h ligand field, which is assumed to increase in strength from left to right. The levels are labelled by the irreducible representations of the O_h group. All states are *gerade*, and the *g* subscript has been omitted. On the right we show the strong LF field limit where the Coulomb and exchange interactions are neglected. The excited states t_2e and e^2 lie above the ground state by 10Dq and 20Dq, respectively. For all levels the total degeneracy is given in brackets

As the LF strength is increased it mixes the free ion ground state ${}^{3}F$ with the excited state ${}^{3}P$. In the strong field limit, shown on the right, the LF ground state is the $(t_{2}^{\uparrow})^{2}$ configuration, expected from the independent electron LF model. The excited states correspond to the spin-preserving excitation of, first, one electron to the state $(t_{2}^{\uparrow})^{1} (e^{\uparrow})^{1}$ which is higher by $10D_{q}$ and then both electrons to a state $(e^{\uparrow})^{2}$ which lies $20D_{q}$ above the ground state. On the right of the figure we have shown the various filling possibilities that determine the orbital degeneracy of the respective configurations. The spin degeneracy in all cases is 2S + 1 = 3. Figure 7.15 demonstrates a very important general point. We see that the multielectron LF states are mixtures of different L values so that L is no longer a good quantum number. We shall see later in Sect. 7.9 that this complicates things when we consider the effect of the spin–orbit interaction. We therefore need to remember this point.

For a multielectron system the LF mixes states of different L and therefore L ceases to be a good quantum number.

For the high spin case, the splitting of the free ion d^n configurations in the LF exhibits a certain symmetry as shown in Fig. 7.16. There are two important systematics in Fig. 7.16. First, we find the same splitting patterns for d^n and d^{n+5} . This arises because for the high spin case we fill the orbitals according to Hund's rule, and therefore repeat the filling process with opposite spin after five electrons. Second, we see that the patterns for d^n and d^{10-n} are just inverted. This comes about because of the equivalence of electrons and holes in the *d*-shell, except for their sign. For example, the LF splitting of eight electrons corresponds to that of two holes, except that the sign of the LF interaction changes sign and the level diagram is turned upside down. We can summarize as follows.

In the absence of spin orbit coupling, the LF diagram for a high spin d^n electron configuration in cubic symmetry is the same as that of the d^{n+5} configuration.

The d^n LF diagram for n electrons, when turned upside down, is that for n holes.

7.6 The Importance of Electron Correlation and Excited States

In this section we will use elements of band theory and ligand field theory discussed earlier in conjunction with new concepts regarding excited electronic states to understand the electronic structure of transition metal oxides. As

Lowest energy states for *d*ⁿ configurations in octahedral ligand field

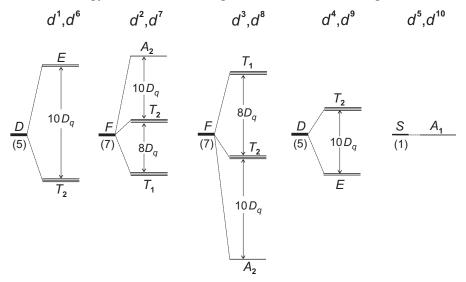


Fig. 7.16. Lowest energy LF energy levels for all d^n electron configurations assuming octahedral symmetry and high spin. Shown are the orbital multiplet ground states L for the d^n configurations with their degeneracy 2L + 1 indicated in brackets. We have ignored the spin-orbit coupling so that the ligand field acts only on the orbital degrees of freedom. The spin multiplicities for all d^n configurations are given in Table 7.1. All LF states are labelled by their irreducible representations and their degeneracies are shown. The magnitude of the cubic LF parameter D_q differs for different ions. The scale of the diagrams roughly correspond to the splitting observed for the 3d ions in aqueous solutions where the most complete data exists [140]. For reference, the total splitting for d^1 (Ti³⁺) has a value $10D_q \sim 2.5 \,\mathrm{eV}$

briefly mentioned in Sect. 7.3, it became clear in the late 1930s that the insulating nature of many of the transition metal oxides could not be explained by theories that were based on the independent electron model. We will now show that the key to the insulating behavior lies in two basic coupled concepts, electron correlation and the importance of excited states.

7.6.1 Why are Oxides often Insulators?

Based on the success of band theory to explain many of the important properties of the 3d transition metals, one may be inclined to use the same theory for the description of transition metal oxides, as well. In a simple model one would start with the atomic binding energies of the metal (M) and oxygen (O) valence electrons and form bands by bringing the atoms together as schematically shown in Fig. 7.17 for the metals and their oxides. From these simple arguments one would expect the oxides to be conductors because the Fermi

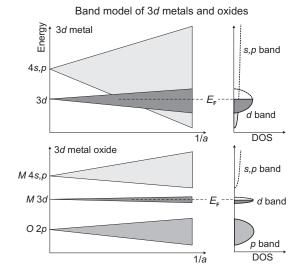


Fig. 7.17. Expected electronic structure for 3d transition metals and their oxides in the band model. We have plotted how the atomic valence orbitals, which are located at different binding energies, are expected to split under the influence of bonding interaction between the orbitals. We have assumed the atoms to be separated by a distance a, so that the bonding increases with 1/a. The lack of direct d-orbital overlap for the oxides leads to a reduced band width and to their correlated nature

level falls into the partially filled d band. Even when the various interactions in transition metal oxides are considered in great detail in modern band calculations, the basic picture remains similar to that shown in Fig. 7.17. While small band gaps may be obtained by state-of-the-art band calculations due to splittings of the 3d states, e.g., by inclusion of antiferromagnetic order, a main problem remains. It is the experimental fact that many oxides are insulators with large band gaps of several eV [234, 268].

Before we resolve the band gap problem we need to briefly mention the electronic configurations encountered in typical transition metal ions. The number of d electrons of the often encountered di- and tripositive ions of the first series of transition metals are listed in Table 7.8. In their lowest energy states none of the transition metal ions has any electrons in the 4s and 4p orbitals since they have been transferred to the electronegative ligands.⁹ Also, the oxygen 2p states are full and lie below the 3d states as schematically illustrated in Fig. 7.17. To first order one can therefore concentrate on the energetic structure and splitting of the 3d states which is

⁹The hybridization of the Ni 4s, p states and the ligand 2p orbitals was not specifically shown in Fig. 7.12, but we note that the resulting bonding and antibonding molecular orbitals are important for the formation of a covalent bond [204].

Table 7.8. Number of 3d electrons in the di- and tri-positive ions of the first series of transition metals. In their lowest energy states none of the ions has any electrons in the 4s and 4p orbitals

	\mathbf{Sc}	Ti	V	\mathbf{Cr}	Mn	Fe	Co	Ni	$\mathbf{C}\mathbf{u}$	Zn
M^{2+}	1	2	3	4	5	6	7	8	9	10
M^{3+}	0	1	2	3	4	5	6	7	8	9

determined by considering the relative size of the intra- and extra-atomic interactions of a 3d ion that is surrounded by oxygen ligands, as illustrated in Fig. 7.5.

7.6.2 Correlation Effects in Rare Earths and Transition Metal Oxides

Historically the understanding of electron correlation and verification of the associated theoretical concepts was based on the interpretation of the macroscopic properties like transport, susceptibility, specific heat etc. While in principle it was clear for some time that electron spectroscopies in the form of photoemission, inverse photoemission, core level photoemission, and X-ray absorption must contain valuable information on correlation effects, it was not recognized until the mid 1980s that the spectroscopic data contained definite systematics that could be cast into a tractable theoretical model. The seminal work was the analysis of the spectra of Ce intermetallics by Gunnarsson and Schönhammer in 1983 [269,270], which showed that the excitation and resulting correlation effects could be explained in a single underlying model which provides a criterion whether a material is "correlated" or not. Below we present the experimental basis for the Gunnarsson–Schönhammer model.

Gunnarsson-Schönhammer Model: Rare Earths

In a band-like picture one would expect the photoemission spectrum of the half filled Gd 4f shell, corresponding to a $4f^7$ ground state configuration, to consist of a narrow band at the Fermi level $E_{\rm F}$. Similarly, if the unfilled half of the 4f shell is measured in inverse photoemission one would expect to see it on the other side of the Fermi level. The measured spectra look very different from this expectation. One observes a band well below and one well above $E_{\rm F}$, as shown in Fig. 7.18 for Gd metal.

The band-like picture therefore gives the incorrect result. Let us therefore consider the multiplet LF model which accounts for intra-atomic correlations. When a photoelectron is removed from the 4f shell the excited Gd atom is left in a $4f^6$ configuration, which has as the lowest states the multiplets ${}^7F_{0,1,2,3,4,5,6}$. The splitting between the spin-orbit states $J = 0, \ldots, 6$ is expected to be of order 1 eV or less, so that the photoemission spectrum should consist of a broad peak, composed of these unresolved components.

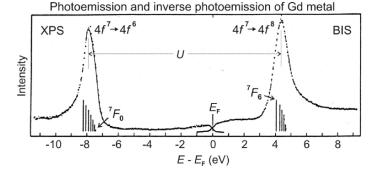


Fig. 7.18. X-ray photoemission spectrum (XPS) (*left*) and Bremsstrahlung isochromat spectrum (BIS) (*right*) for Gd metal [271], which has a $4f^7$ ground state configuration. The spectra are aligned at the experimentally determined Fermi level (E_F). Vertical bars indicate the positions and intensities of the lowest energy $^{2S+1}L_J$ multiplet manifolds of the final state configurations $4f^6$ and $4f^8$. The lowest energy multiplets according to Hund's rules, 7F_0 of the XPS final states, and 7F_6 for the BIS final states are specifically marked (see Table 7.1)

The average peak position is determined by the average difference of the final state multiplet energies $\varepsilon(4f^6, {}^7F_{0,1,2,3,4,5,6})$ relative to the ground state energy $\varepsilon(4f^7, {}^8S_{7/2})$, as illustrated in Fig. 7.19.

If we reference both these energies to the Fermi energy $E_{\rm F}$, the measured photoemission peak should fall at an electron kinetic energy (which is naturally measured relative to the vacuum level $E_{\rm V}$) that is determined by the energy balance equation (see Fig. 7.19)

$$E_{\rm kin} = h\nu - \Phi_{\rm W} - \underbrace{\left[\varepsilon(4f^6, {}^7\!F_{0,1,2,3,4,5,6}) - \varepsilon(4f^7, {}^8\!S_{7/2})\right]}_{\Delta\varepsilon_{\rm XPS}},\tag{7.33}$$

where $\Phi_{\rm W} = E_{\rm V} - E_{\rm F} > 0$ is the work function and $E_{\rm B} = -\Delta \varepsilon_{\rm XPS} < 0$ is called the XPS binding energy relative to the Fermi level. By choosing it to be a negative number we follow the intuitive notion that the photoemission peak will lie at a negative energy below the Fermi level which is typically chosen as the zero of energy.

The inverse XPS photoemission spectrum, called Bremsstrahlung isochromat spectrum (BIS), is recorded by adding a high energy (of order 1 keV) electron to the sample and measuring the X-ray emission spectrum of the electron dropping down into the 4f shell [272, 273]. Similarly, when low electron energies are employed one has the inverse ultraviolet photoemission (UPS) process and we shall refer to this case simply as inverse photoemission spectroscopy or IPES [274, 275]. The BIS or IPES final state consists of a Gd atom with a $4f^8$ configuration. Because of the equivalence of f^n and f^{14-n} (electrons and holes) the XPS ($4f^6$) and BIS ($4f^8$) final states both consist of lowest-energy ${}^7\!F_{0,1,2,3,4,5,6}$ multiplets. If the incoming electron has an energy $E_{\rm kin}$ relative to the vacuum level, and we reference the initial and final state

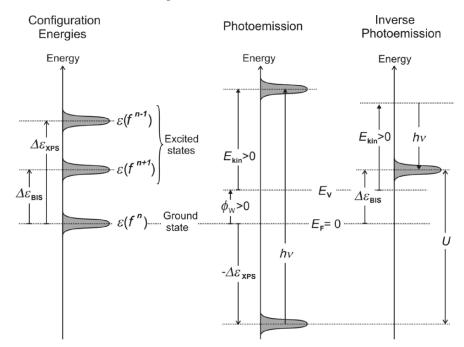


Fig. 7.19. Definition of energies associated with different electronic configurations (ground and excited states) and their differences, which are measured in photoemission and inverse photoemission spectroscopies as $\Delta \varepsilon_{\rm XPS}$ and $\Delta \varepsilon_{\rm BIS}$. The work function is defined as $\Phi_{\rm W} = E_{\rm V} - E_{\rm F} > 0$ and we define $E_B = -\Delta \varepsilon_{\rm XPS} < 0$ as the PES binding energy relative to the Fermi level. The sum of the energies measured in photoemission and inverse photoemission gives the Hubbard U as $U = \Delta \varepsilon_{\rm XPS} + \Delta \varepsilon_{\rm BIS}$

multiplet energies $\varepsilon(4f^7, {}^8S_{7/2})$ and $\varepsilon(4f^8, {}^7F_{0,1,2,3,4,5,6})$ to the Fermi level, we observe a peak at the photon energy

$$h\nu = E_{\rm kin} + \Phi_{\rm W} - \underbrace{\left[\varepsilon(4f^8, {}^7\!F_{0,1,2,3,4,5,6}) - \varepsilon(4f^7, {}^8\!S_{7/2})\right]}_{\Delta\varepsilon_{\rm BIS}} , \qquad (7.34)$$

where $\Delta \varepsilon_{\text{BIS}} > 0$ may be called the IPES binding energy. When the measured spectra are aligned relative to the Fermi level, where all intensity drops to zero, we obtain Fig. 7.18. We see that by combining both spectra one can determine $U = U_{ff}$ as the difference between the peak positions measured in XPS and BIS. We have the following important result.

The onsite Coulomb energy U is the energy it costs to create a positive and a negative ion from two neutral atoms on sites i and j, according to,

$$\varepsilon(f_i^n) + \varepsilon(f_j^n) + U = \varepsilon(f_i^{n-1}) + \varepsilon(f_j^{n+1}).$$
(7.35)

We note that despite the large energetic splitting of the filled and empty 4f bands which are located well away from $E_{\rm F}$, Gd is still a metal due to the presence of the 5d and 6s, p valence electrons which form a band across the Fermi level, as seen in Fig. 7.18.

Zaanen-Sawatzky-Allen Model: Transition Metal Oxides

Gunnarsson and Schönhammer's work on 4f systems was extended in 1984/85 to the transition metal oxides by three groups, Fujimori et al. [257, 258], Hüfner [276–278], and Zaanen, Sawatzky, and Allen [261]. Today, this work constitutes the basis for dividing the behavior of transition metal oxides into two main categories: *Mott-Hubbard compounds* and *charge transfer compounds* [234, 268], and the associated model is often referred to as the *Zaanen-Sawatzky-Allen model*. In the following, we shall touch upon these general concepts not only because of their great importance in modern condensed matter physics but also because we shall use them later in the treatment of indirect exchange.

Electron excitation processes in oxides are governed by two fundamental energies, the Coulomb energy U and the charge transfer energy Δ_c , which are defined as follows:

- The *intra-atomic Coulomb energy* $U = U_{ll}$ for a shell l of a given atom is defined in (7.35) as the energy required to remove an electron from shell l in one atom and add it to the shell l in a second atom.
- The charge transfer energy Δ_c is defined in (7.31) as the energy required to excite an electron from the ligand-like (O 2p) states to the metal-like (M 3d) states. The excitation occurs within the same electronic configuration and does not involve any change in Coulomb energy.

With these definitions we can classify transition metal oxides as follows:

Mott-Hubbard compounds are defined by $\Delta_{\rm c} > U$, so that the insulating gap is determined by U.

Charge transfer compounds are defined by $U > \Delta_{\rm c}$ and the insulating gap is determined by $\Delta_{\rm c}$.

In Mott-Hubbard compounds the separation Δ_c between the metal-like states and oxygen-like states (see Fig. 7.13) is larger than the Coulomb energy U. This situation is illustrated in Fig. 7.20. For $\Delta_c > U$ the lowest energy excitations correspond to transfer of an electron from one metal atom to another, as illustrated on the left of Fig. 7.20, assuming an antiferromagnetic ground state. An electron of a given spin is transferred to another metal site which contains an opposite spin electron. This costs an energy U. In the excited state one of the metal atoms has an electron less and the other an electron more than in the ground state. The corresponding diagram of the

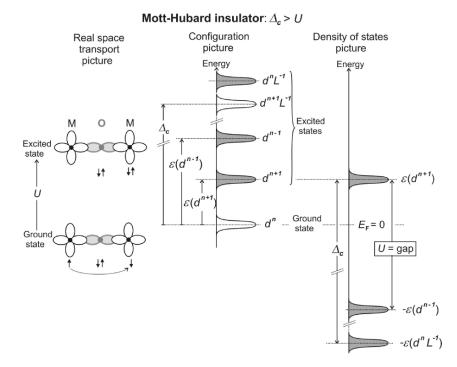


Fig. 7.20. Illustration of the concepts underlying Mott–Hubbard insulators, assuming a transition metal oxide. On the left we show a molecular orbital diagram of a local metal-oxygen-metal cluster and the spin structure corresponding to an antiferromagnetic ground state, with opposite spins on each metal atom. Electron transport is envisioned by moving an electron from one to another metal atom, costing an energy U. In the middle we picture the energy of the d^n ground state configuration and various excited configurations. The lowest-energy excited configurations are assumed to be ionic, d^{n+1} and d^{n-1} , similar to Fig. 7.19. Other excited state configurations involving the charge transfer energy Δ_c (see Fig. 7.21 below) are assumed to be higher in energy. On the right we show the energies of the excited ionic configurations when plotted relative to the Fermi level $E_{\rm F} = 0$. These configurations are measured in photoemission and inverse photoemission. Note that the charge neutral configurations shown in white shading d^n and $d^{n+1}L^{-1}$ are not observed experimentally. The system is seen to be an insulator with a gap energy U

configurational energies associated with the d^n ground state and the d^{n+1} and d^{n-1} excited state configurations is shown in the center of Fig. 7.20.

In our labeling of the configurations we have used the shorthand notation d^n instead of the full label $d^n L$, where L denotes that no electron has been removed from the ligand-like bonding orbital. In the following we shall continue to do so, i.e., $d^i \equiv d^i L$. Because the separation Δ_c between the two charge neutral configurations $d^n \equiv d^n L$ and $d^{n+1}L^{-1}$, shown in white shad-

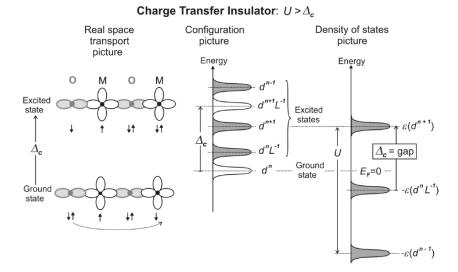


Fig. 7.21. Illustration of the concepts underlying charge transfer insulators, assuming a transition metal oxide. On the left we show a molecular orbital diagram of a local oxygen-metal-oxygen-metal cluster and the spin structure corresponding to an antiferromagnetic ground state, with opposite spins on each metal atom. Electron transport corresponds to moving an electron from an oxygen atom to a distant metal atom, costing an energy Δ_c . In the center we picture the energy of the $d^n \equiv d^n L$ ground state configuration and various excited configurations. The lowest-energy excited configuration is assumed to be $d^n L^{-1}$, with higher energy configurations $d^{n+1} \equiv d^{n+1}L$, $d^{n+1}L^{-1}$, and $d^{n-1} \equiv d^{n-1}L$. In particular, the excitation $d^n L \to d^{n+1}L^{-1}$ is the ligand to metal charge transfer excitation, in accordance with Fig. 7.13. On the right we show the energies of the excited configurations when plotted relative to the Fermi level $E_{\rm F} = 0$, measured in photoemission and inverse photoemission. Note that the charge neutral configurations shown in white shading, $d^n L$ and $d^{n+1}L^{-1}$ are not observed experimentally. The system is seen to be an insulator with a gap energy Δ_c

ing, is assumed larger than U, the ionic configurations d^{n+1} and d^{n-1} are the lowest-energy excited configurations, similar to the case in Fig. 7.19. In a binding energy picture one obtains a band gap U as shown on the right in Fig. 7.20.

The case $U > \Delta_c$ of a charge transfer insulator is shown in Fig. 7.21. Now the excitation process consists of transfer of an electron from oxygen to a distant metal atom. Because the process corresponds to an intraconfigurational excitation from the bonding to the antibonding states, as shown in Fig. 7.13, it involves no Coulomb energy. In the configuration-energy picture the lowest excited configuration is now the ionic state $d^n L^{-1}$, where one electron has been removed from the ligand-like bonding orbital L. The configuration $d^n L^{-1}$ lies $U - \Delta$ higher in energy than d^{n-1} and by Δ below d^{n+1} . This is shown on the right side where we have plotted a binding energy diagram, corresponding to

photoemission and inverse photoemission. Now the charge neutral configurations shown in white shading, $d^n L$ and $d^{n+1}L^{-1}$ are not observed. Now the band gap is given by Δ_c .

As an example of a charge transfer insulator we discuss NiO. From a band-like model one would expect NiO to be a metal or have a small band gap, as discussed in Sect. 7.6.1 and illustrated in Fig. 7.17. In contrast to this picture and in accord with its insulating nature, the photoemission and inverse photoemission spectra reveal a gap at the Fermi level, as shown in Fig. 7.22. In the figure we show photoemission and inverse photoemission spectra recorded at high and low energies, as discussed in the caption, in order to emphasize the oxygen 2p versus the metal 3d states. The selective sensitivity to the p

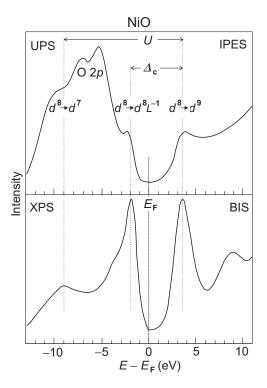


Fig. 7.22. Photoemission and inverse photoemission spectra of NiO, recorded for different photon energies, taken from Hüfner [237]. The "UPS" and "IPES" spectra were taken at low photon energies (21.2 eV (UPS) and 9.7 eV (IPES)) which enhance the oxygen 2p states over the metal 3d states, while the "XPS" and "BIS" spectra were recorded at high photon energies (1254 eV) and emphasize the metal d states. The electron configurations responsible for the peaks are indicated. The charge transfer energy Δ_c and the Coulomb energy $U = U_{dd}$ are also indicated

and d valence orbitals arises from the energy dependence of the BIS transition matrix element [273].

The NiO ground state consists of the configuration $3d^8 = 3d^8L$, and similar to the 4f case shown in Fig. 7.18, we observe a peak corresponding to $3d^7$ in photoemission and $3d^9$ in inverse photoemission, as indicated in the figure. Their peak-to-peak separation is $U = U_{dd} = \Delta \varepsilon_{\text{XPS}} + \Delta \varepsilon_{\text{BIS}} = \epsilon(d^7) + \epsilon(d^9) \simeq$ 12.5 eV.

We also see a third peak in the XPS spectrum located around 2 eV below $E_{\rm F}$. It is due to metal–oxygen interactions and corresponds to an excitation from the $3d^8L$ ground state to a screened excited state $(3d^7L)^*$. The screening process involves a charge transfer from the oxygen-like (L) to the metal-like (3d) bands and the state $(3d^7L)^*$ state may be written as $3d^7 + d + L^{-1} = 3d^8L^{-1}$. Calculations show that it interacts with the unscreened excited state $3d^7 = 3d^7L$ [258]. As expected the screened state $3d^8L^{-1}$ is lower in energy (closer to the Fermi level) than the unscreened state $3d^7L$. The importance of the $3d^8L^{-1}$ peak position is that its separation from the d^9 peak, which is < 5.5 eV, determines the transport properties of NiO, which is therefore found to be a charge-transfer insulator.

In summary, we have seen that the intra-atomic correlation effects within the 3d or 4f shell are of great importance for the electronic properties of a material and that the degree of correlation are nicely revealed by a combination of photoemission and inverse photoemission spectra. The correlated nature of the 4f electrons in the rare earths is due to their shielded location within the atom and their small involvement in bonding, as discussed further in Sect. 12.3. For the transition metal oxides, the 3d states are also found to be strongly correlated as indicated by their splitting. In agreement with their correlated nature, the 3d peaks show no band-like dispersion as a function of wavevector. The origin of the 3d localization is the lack of direct overlap of the 3d orbitals on different metal atoms. In contrast, the oxygen derived bands (see Fig. 7.22) are found to exhibit considerable dispersion, leading to a band width of about $5 \, \text{eV}$ [237,268]. In contrast to the d bands they are well described by band theory. The different correlation within the oxygen 2p and the metal 3d shells is partly due to centrifugal barrier effects as discussed in Sect. 7.2.

7.6.3 From Delocalized to Localized Behavior: Hubbard and LDA+U Models

The question arises whether the shortcomings of band theory in the DFT-LSDA approximation for the description of correlated electron systems can be remedied. This is indeed so and we shall now briefly discuss how this is done in practice.

We have seen above that density functional theory and the local spin density approximation simplify the many-body problem by approximating it by a system of noninteracting fictitious particles with a certain average (spin)

density. When the electron or spin density has a strong spatial dependence this approximation breaks down. It therefore cannot treat cases where locally intra-atomic correlation effects are strong. The band description will get worse the more the magnetic moments are localized as in the rare earth metals where 4f localized and 5d, 6s, and 6p delocalized shells need to be treated on an equal footing.

The difficulty in describing band behavior on one side and localized behavior on the other has led to the suggestion of a simplified model Hamiltonian that with the minimum number of features yields band-like and localized behavior in suitable limits. As discussed in Sect. 6.3.4 the Hubbard model has these features. Here we come back to this model to see how it can give rise to ferromagnetism and as an introduction for the L(S)DA+U model which attempts to combine band and atomic behavior in an efficient calculational scheme [279,280]. We will see later in Sect. 12.3 that the LSDA+U model gives state-of-the-art results for the description of ferromagnetic Gd metal.

The Hamiltonian in the Hubbard model takes the electronic states of individual ions in a solid and lumps them into single localized orbitals, with a single orbital or two spin–orbitals per each site. It contains two terms, one representing band-behavior the other localized behavior. One may write in simplified form,

$$\mathcal{H} = \sum_{i,j} f(t_{ij}) + \sum_{i} g(U_i).$$
(7.36)

The band behavior is described by the first term. It casts the band behavior into the language of electron hopping between neighboring sites (without change of spin), expressed as a function of a hopping parameter t_{ij} . In a tight binding model the hopping parameter corresponds to the overlap integrals and is proportional to the band width $t_{ij} \sim W$. Hence, if U = 0, the Hubbard model yields the band structure in the tight binding limit.

The localized behavior is given by the second term. It describes the Coulomb repulsion of electrons with opposite spin on the same site as a function of the famous Hubbard U parameter. When U is large the electrons do not move independently but feel their pairwise repulsion. This suppresses the probability that two electrons are on the same site (necessarily aligned antiparallel because of the Pauli principle), and therefore favors the formation of local moments on the individual atoms. In general, when both terms are present, the Hubbard model can only be solved in special cases. Its various solutions are still an active field of research and over the years this research has provided valuable insight [194, 214].

A particular instructive example is the case for a half filled valence shell, shown in Fig. 7.23. In contrast to the case of Gd metal, shown in Fig. 7.18, we have assumed in Fig. 7.23 that the valence electrons are either of the 4f or 3d type and that not both types are present.

For $U \gg W$ localized behavior dominates and in the absence of other valence states (such as s, p, d states in Gd) the material is an insulator because

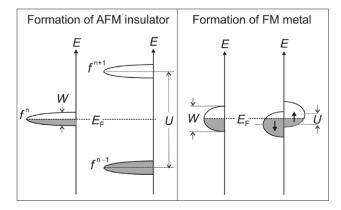


Fig. 7.23. Splitting of a half-filled energy band of width W under the influence of an onsite Coulomb repulsion U in the Hubbard model. The left side shows the case of $U \gg W$ and the case of a localized f^n shell, resulting in an antiferromagnetic insulator with a splitting U between the configurations f^{n+1} and f^{n-1} . For U < W shown on the right we obtain a ferromagnetic metal. This case resembles the Stoner model for the 3d metals shown in Fig. 7.6

the Fermi level falls in a gap of electronic states. In fact, one can show that the ground state is antiferromagnetic, as for the simplest case of the hydrogen molecule.¹⁰

The other case, U < W, may be treated in the Hartree-Fock approximation given by (6.75). Within this approximation the Hubbard model and the Stoner model become equivalent [281]. The localized states split into a spin-up and spin-down level with a separation proportional to U and one may obtain a ferromagnetic metal, as shown in Fig. 7.23. In the cross-over region $U \sim W$ there will be a metal-insulator transition.

Materials with $U \gg W$ are considered "correlated", those with $U \ll W$ are considered "uncorrelated". The band model reliably describes the low temperature properties of uncorrelated materials.

The concept of the Hubbard model can be combined with first principles LDA-L(S)DF theory in a computational scheme called LDA+U, developed by Anisimov, Aryasetiawan, and Lichtenstein [280]. In this model all

¹⁰ The case of the H₂ molecule discussed in Sect. 6.3.4 is the simplest case of a half filled "band". In this case (7.35) would correspond to the difference in energy between the two states with one electron per atom, $|R, R\rangle$ and $|R', R'\rangle$, and the two states with no electron on one and two electrons on the other atom, $|0, RR'\rangle$ and $|RR', 0\rangle$ (see (6.71). Hopping is allowed between these states as seen from the matrix in Table 6.3 and the energy difference between the two pairs of states is U.

states are divided into two subspaces. The delocalized states are treated by conventional LDA while all localized orbitals, are treated by inclusion of a Hubbard-like term in the Hamiltonian. In particular, the Hubbard-like term is treated within the atomic spheres by use of Slater-type integrals for both the Coulomb, U, and exchange, J, parameter. The new Hamiltonian consists of the conventional LDA part and a "localized" part that is orbital dependent and embedded in the delocalized part. We shall discuss the results for the LDA+U method in Sect. 12.3 for the specific case of ferromagnetic Gd, the fourth elementary ferromagnet besides Fe, Co, and Ni.

The great success of band theory in describing the electronic ground state (at zero temperature) of the ferromagnetic 3d transition metals, is often taken as evidence for the preferential itinerant character of the 3d electrons. However, this does not mean that correlation effects are negligible for the transition metals. Because this is such a complicated topic we have devoted the whole Chap. 12 to it.

7.7 Magnetism in Transition Metal Oxides

In Chap. 6 we have only discussed a certain type of exchange, namely that arising from the direct interaction of electrons within an atom or on adjacent atoms without an intermediary. Such "direct exchange" is due to direct wavefunction overlap. It is easy to imagine that exchange can also proceed if the wavefunction on one magnetic atom overlaps with an intermediary wavefunction which in turn overlaps with a wavefunction on another magnetic atom. This situation is referred to as "indirect exchange" and it comes in three prominent forms, superexchange, double exchange, and RKKY exchange. The first two types are particularly important in transition metal oxides and we shall discuss them now.

7.7.1 Superexchange

The first type of indirect exchange is called *superexchange*, owing to the fact that it extends the normally very short-range exchange interaction to a longer range. The idea that exchange can indeed proceed by means of an intermediate nonmagnetic atom was first pointed out by Kramers in 1934 [282] and the theory was more formally developed by Anderson in 1950 [283]. The superexchange is of importance in ionic solids such as the transition metal oxides and fluorides, where the bonding orbitals are formed by the 3*d* electrons in the magnetic transition metal atoms and the 2p valence electrons in the diamagnetic oxygen or fluorine atoms, as illustrated in the upper part of Fig. 7.24.

To understand the origin and spin coupling we assume that the metal atoms are magnetic and hence have at least one unpaired electron and that the oxygen atoms have a tendency to attract two electrons (to attain the filled shell structure of Ne). In the simplest such case there are four electrons involved in

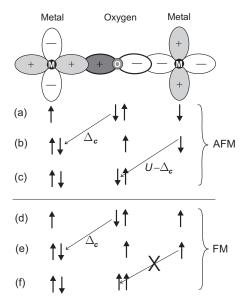
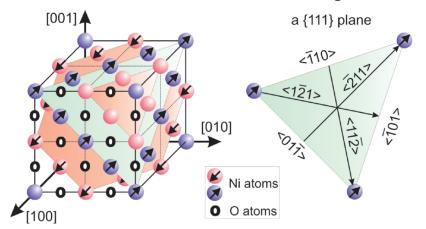


Fig. 7.24. Illustration of the superexchange interaction in a magnetic oxide. The metal atoms are assumed to have a single unpaired electron and there are a total of four electrons involved in bonding. The bonding involves symmetry adapted metal 3d and oxygen 2p orbitals. In (**a**) we show the spin configurations for an antiferromagnetic (AFM) ground state and in (**b**) for a ferromagnetic (FM) ground state. For the AFM ground state the excited state (**c**) is the lowest energy excited state, as discussed in the text. For the FM ground state (**d**) no comparable low energy excited state (**f**) exists because it is forbidden by the Pauli principle and spin flips are not allowed

the bonding between the oxygen and the metal atoms. The bonding involves symmetry adapted metal 3d and oxygen 2p orbitals as shown in Fig. 7.24 for bonding along the x direction of a coordinate system. The bonding orbitals are pictured as usual by means of the 2p and 3d orbital charge densities (wavefunctions squared), where light (minus) and dark (plus) colors indicate the sign of the wavefunctions. Bonding requires overlap of wavefunctions of the same sign.

We can locate and orient the four spin polarized electrons in different ways on the three atoms. As discussed in Sect. 6.3.8 for the H_2 molecule, the kinetic exchange energy will be minimized if we distribute the four electrons across the whole molecule with adjacent electrons being antiparallel. The superexchange interaction therefore leads to antiferromagnetic coupling of the metal atoms with the oxygen atom remaining nonmagnetic. We will derive this result below in a simple Hubbard model. The size of the superexchange depends on the magnitude of the magnetic moments on the metal atoms, the metal–oxygen (M–O) orbital overlap and the M–O–M bond angle.



Atomic moment orientation in antiferromagnetic NiO

Fig. 7.25. Antiferromagnetic structure in NiO with the NaCl fcc crystal structure. Ni atoms with one spin direction are shown pink those with the opposite spin directions are in blue. The front (100) plane also shows the positions of the oxygen atoms. The superexchange interaction is along the cubic < 100 > directions. All spins lie in the {111} planes and within this plane point along $<\bar{2}11>$, as explicitly shown on the left for two selected planes, and in more detail on the right. The equivalence of the four <111> bulk directions leads to four T domains, that of the three $<\bar{2}11>$ directions in the {111} planes to three S domains

An example of antiferromagnetic structure due to superexchange is NiO, whose magnetic structure is shown in Fig. 7.25 [284,285]. We shall come back to NiO in conjunction with the topic of exchange bias in Sect. 13.4.3.

Hubbard Model of Superexchange

In order to prove that the antiferromagnetic state is in fact the ground state, we again need to invoke the influence of excited states. The recognition of their importance for magnetism goes back to Kramers [282]. He pointed out that if a system has a finite probability to be in several states, the true ground state wavefunction should be a linear combination of the states. Hence in order to determine the true minimum energy state the total wavefunction has to be used. We shall now use this concept to see whether the AFM coupling of the 3d atoms is indeed lower in energy than the FM one, as claimed earlier.

The lowest energy AFM and FM states are shown in Fig. 7.24a, d, respectively, and we have also shown possible excited states and the excitation energies involved. Hence states (b) and (e) lie higher than the assumed antiferromagentic or ferromagnetic ground states by the charge transfer energy $\Delta_{\rm c}$, and the state (c) lies by U above the AFM ground state (a). For the FM case (d), the excited state (f) is forbidden by the Pauli principle. The determination whether the AFM state (a) or the FM state (d) has lower energy, can therefore not be decided on the basis of the excited states (b) and (e), which lie above the respective ground states by the same energy Δ_c , but the crucial differentiation comes from the next higher excited state (c).

By comparing the spin structure of the two possible ground states (a) and (d) with the excited state (c), we see that for all three states the oxygen atom is in the filled shell O^{2-} configuration. Thus we can ignore the full-shell oxygen configuration in our search for the lowest energy magnetic state.

We can then diagonalize the Hubbard Hamiltonian (6.66) using the three relevant states,

$$\begin{aligned} |a\rangle &= |R, R\rangle & |\uparrow, \downarrow\rangle \\ |c\rangle &= |RR', 0\rangle & |\uparrow\downarrow, 0\rangle \\ |d\rangle &= |R, R'\rangle & |\uparrow, \uparrow\rangle . \end{aligned}$$
(7.37)

Similar to the treatment of the H₂ molecule (compare (6.71)), we describe the three states by their spatial components, which in our case refer to the two metal atoms. On the right side of (7.37) we have explicitly indicated the spin parts of the functions in accordance with Fig. 7.24. As for the H₂ calculation the Hubbard Hamiltonian acts only on the spatial parts of the wavefunction and the symmetry of the spin eigenfunctions follows from the antisymmetrization principle. However, it is easier to keep track of the states by use of their spin configurations as shown in Fig. 7.24 and we shall simply write the interaction matrix of the Hubbard Hamiltonian (6.66) in terms of these states, as done in Table 7.9. For simplicity we define $U = U_{dd}$.

The eigenfunctions and eigenvalues in order of decreasing energy are,

$$E_{3} = U + \frac{t^{2}}{U} \qquad |\phi_{3}\rangle = |\uparrow\downarrow,0\rangle - \frac{t}{U}|\uparrow,\downarrow\rangle$$

$$E_{2} = 0 \qquad |\phi_{2}\rangle = |\uparrow,\uparrow\rangle$$

$$E_{1} = -\frac{t^{2}}{U} \qquad |\phi_{1}\rangle = |\uparrow,\downarrow\rangle + \frac{t}{U}|\uparrow\downarrow,0\rangle , \qquad (7.38)$$

and we see that the effect of the excited state (c) is to lower the energy of the lowest AFM eigenstate $|\phi_1\rangle$ below that of the FM eigenstate $|\phi_2\rangle$, and the superexchange interaction favors an antiferromagnetic alignment.

 Table 7.9. Matrix elements of the Hubbard Hamiltonian for the lowest energy FM

 and AFM states in transition metal oxides with equal charge on the metal atoms

	$ \uparrow,\downarrow angle$	$ \uparrow\downarrow,0 angle$	$ \uparrow,\uparrow angle$
$ \uparrow,\downarrow angle$	0	-t	0
$ \uparrow\downarrow,0 angle$	-t	U	0
$ \uparrow,\uparrow angle$	0	0	0

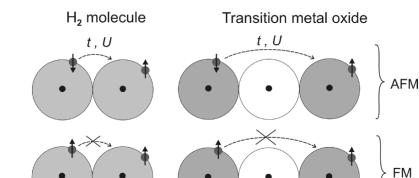


Fig. 7.26. Electron transfer in the H_2 molecule (compare Fig. 6.9) and for the case of a transition metal oxide (compare Fig. 7.24). In both cases we show the possible excited states where an electron is transferred between like atoms, hydrogen to hydrogen, and metal to metal, assuming either a antiferromagnetic (AFM) or ferromagnetic (FM) initial state. In the case of the transition metal oxide we assume that the spin configuration on O remains unchanged, owing to the fact that oxygen is electronegative and wants to assume a full shell (O²⁻ state). The picture shows that the transition metal oxide case can be treated in an equivalent fashion as the H₂ molecule, in both cases yielding a lowest energy state that is antiferromagnetic

While our quick calculation contains the important physics, the energies are not quite correct because we have only considered half of the possible states. When the states with interchanged \uparrow and \downarrow are added one gets a factor of 2 (see footnote 11). In fact, we have already done the proper calculation. It is that for the H₂ molecule. As shown in Fig. 7.26, one can picture the electron transfer in transition metal oxides the same way as in the H₂ molecule (compare Fig. 6.9). We see that there is a complete correspondence if we assume that the spin configuration on the oxygen atom remains unchanged.

The close correspondence between the two pictures means that the two cases can be treated in the same Hubbard formalism already used for H₂. In both cases the full interaction matrix is simply given by that in Table 6.3. It differs from that in Table 7.9 because the full set of basis states (6.71) is used. In Table 6.3, E_0 is some common energy, which does not enter in the determination of which state is lowest in energy.

For the case $U \gg t$ the ground state energy and wavefunction, given by (6.73), correspond to an antiferromagnetic (singlet) state,¹¹ which is lower in energy by $2|J_{12}| = 4|t^2/U|$ than the ferromagnetic (triplet) state, as illustrated in Fig. 6.8. Hence we may associate an exchange coupling constant of $J_{12} = -2t^2/U$, where U > 0, with the AFM superexchange coupling.

¹¹Note that the ground state energies and wavefunctions in (7.38) and (6.73) differ by the above mentioned factor of 2, i.e., $t \rightarrow 2t$.

7.7.2 Double Exchange

The indirect coupling of spins across a diamagnetic atoms can also be ferromagnetic. An example is the oldest known magnetic material, magnetite. The spinel magnetite, Fe_3O_4 , is overall ferrimagnetic but contains Fe atoms in two different valence states, Fe^{2+} ($3d^6$) and Fe^{3+} ($3d^5$) that are ferromagnetically coupled. Another famous example of a ferromagnetic oxide are the mananese oxides (manganites) $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ in the range (0.16 < x < 0.5) [286]. In these manganites with the perovskite-type structure, the metal atoms again have different valences. Perovskite blocks are stacks of corner sharing MnO₆ octahedra. The nominal 3+ valency of Mn can be gradually increased to an average valency of +(3+x) by replacing the trivalent rare earth ion La by the divalent alkali earth ion Sr. The Sr_x substitution therefore creates additional holes on the Mn sites through a procedure called *hole doping*. We can envision the structure to be composed of Mn³⁺ ($3d^4$) and Mn⁴⁺ ($3d^3$) ions.

The magnetic interaction in such oxides containing different valency metal ions is typically referred to as double exchange. The term was introduced in 1951 by Clarence Zener [287] to explain the magneto-conductive properties of mixed-valence solids, notably doped Mn perovskites. Zener proposed a mechanism for hopping of an electron from one Mn to another through an intervening O^{2-} . Because in O^{2-} the oxygen *p*-orbitals are fully occupied, the process has to proceed in two steps, by "double exchange", the movement of an electron from O to one Mn followed by a transfer of a second electron from the other Mn into the vacated O orbital. Let us discuss double exchange for the cases of Mn and Fe oxides in a ligand field model.

If the LF is relatively small we can fill up the different orbitals according to Hund's first rule with electrons of parallel spin, as shown in Fig. 7.10 for the cases of Fe³⁺ with a $3d^5$ configuration and Fe²⁺ with a $3d^6$ configuration. In general, two metal atoms which are bonded through O may have a valency that differs by one, as illustrated in Fig. 7.27 for the cases Mn³⁺ ($3d^4$) and Mn⁴⁺ ($3d^3$) in La_{1-x}Sr_xMnO₃ and for Fe²⁺ ($3d^6$) and Fe³⁺ ($3d^5$) in Fe₃O₄. In these materials electron conduction proceeds by double exchange as explained by Zener and one of the metal electrons therefore hops back and forth across the oxygen. The electron is thus delocalized over the entire M–O–M group and the metal atoms are said to be of mixed valency.

Since spin-flips are not allowed in the electron hopping process it is energetically more favorable if the magnetic structure of both metal atoms, apart from the extra electron, is identical. Therefore the moments on the metals atoms are aligned ferromagnetically. Today the case of double exchange is typically treated in a model originated by Zener [287] and further developed by Anderson and Hasegawa [288] and de Gennes [289]. The double exchange Hamiltonian is written in terms of a hopping term and a Heisenberg-like exchange term that takes care of Hund's rule coupling between the spins in the t_{2g} orbitals and the extra spin in the e_g orbital (see Fig. 7.27). We shall

Indirect ferromagnetic or double exchange

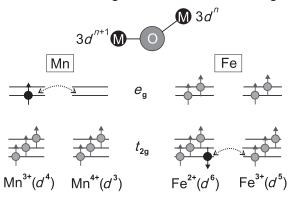


Fig. 7.27. Illustration of indirect ferromagnetic exchange coupling, called double exchange, for bonding of two 3d metal atoms M with different occupations $3d^{n+1}$ and $3d^n$ through an O atom. We have assumed an octahedral ligand field as in Fig. 7.10 and a filling according to Hund's rule. The cases for Mn and Fe atoms are shown

later use a Hubbard like approach to see that the ground state is indeed ferromagnetic.

Hubbard Model of Double Exchange

In order to see that the double-exchange ground state is ferromagnetic we set up the problem as shown in Fig. 7.28. Again we use the simple model where there is an electron on each metal atom, representing a magnetic configuration that in reality may consist of several electrons. We represent these configurations by black circles and indicate the net spin by a double arrow. In addition there is an extra electron on one of the metal atoms which we show in white. The lowest excited configurations will again consist of a closed shell O^{2-} atom, as discussed for the case of superexchange and we therefore show the O atom as passive.

As for the case of superexchange we find that there are three lowest energy configurations which we need to consider as basis states for our Hubbard diagonalization. Using again a spin rather than spatial notation for the basis states we can write,

$$|1\rangle = |\Uparrow\downarrow,\Uparrow\rangle$$
$$|2\rangle = |\Uparrow,\Uparrow\downarrow\rangle$$
$$|3\rangle = |\Uparrow\downarrow,\Downarrow\rangle.$$
(7.39)

Here we have indicated the magnetic configuration, corresponding to the black electron in Fig. 7.28, by a double arrow and the extra (white) electron by a

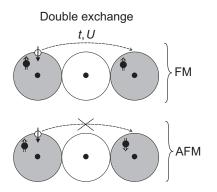


Fig. 7.28. Electron transfer in a transition metal oxide with an extra electron (shown in white) on one transition metal ion. We show a simplified scheme of Fig. 7.27 where the configurations without the extra electron are shown in black with a double arrow. They may consist of parallel (FM) and antiparallel (AFM) spin alignments on the two transition metal atoms. In accordance with Fig. 7.26 we assume a passive oxygen atom. By comparing the energies associated with electron transfer the lower energy state is found to be FM

Table 7.10. Matrix elements of the Hubbard Hamiltonian for the lowest energy FM and AFM states in transition metal oxides with unequal charge and spin on the two metal atoms

	$ \Uparrow\downarrow,\Uparrow angle$	$ \Uparrow,\Uparrow\downarrow, angle$	$ \Uparrow\downarrow,\Downarrow angle$
$ \uparrow\downarrow,\uparrow\rangle$	U	-t	0
$ \uparrow\uparrow,\uparrow\downarrow\rangle$	-t	U	0
$ \Uparrow\downarrow,\Downarrow angle$	0	0	U

single arrow. The interaction matrix of the Hubbard Hamiltonian (6.66) in terms of these states is given in Table 7.10.

The eigenfunctions and eigenvalues in order of decreasing energy are:

$$E_{3} = U + t \qquad |\phi_{3}\rangle = |\uparrow\downarrow\downarrow\uparrow\uparrow\rangle + |\uparrow\uparrow\uparrow\downarrow\rangle$$

$$E_{2} = U \qquad |\phi_{2}\rangle = |\uparrow\downarrow\downarrow\downarrow\downarrow\rangle$$

$$E_{1} = U - t \qquad |\phi_{1}\rangle = |\uparrow\downarrow\downarrow\uparrow\uparrow\rangle - |\uparrow\uparrow\uparrow\uparrow\downarrow\rangle.$$
(7.40)

Because we have worked for convenience with a spin rather than the (proper) spatial notation of the states, care has to exercised in interpreting the symmetry of the eigenstates. The sign of the linear combinations actually reflects the spatial parts so that the lowest energy state is not a singlet-type state as indicated by the minus sign but in fact a triplet-type state. With this in mind we see that the effect of the excited FM basis state is to yield a lowest energy FM eigenstate, and the double exchange interaction favors a ferromagnetic alignment.

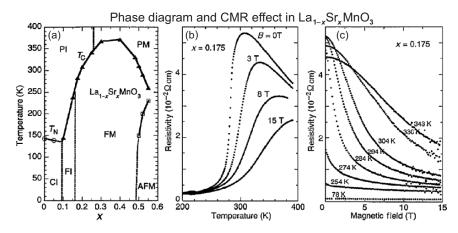


Fig. 7.29. (a) Phase diagram of $La_{1-x}Sr_xMnO_3$ [286]. The acronyms stand for spincanted insulating (CI), paramagnetic insulating (PI), paramagnetic metallic (PM), ferromagnetic insulating (FI), ferromagnetic metallic (FM), and antiferromagnetic (AFM). (b) and (c) Dependence of the resistivity for $La_{1-x}Sr_xMnO_3$ with x = 0.175on magnetic field and temperature [234]

7.7.3 Colossal Magnetoresistance

The double exchange mechanism is responsible for many of the interesting electric and magnetic properties of the perovskite-type manganites $R_{1-x}A_x$ MnO₃ and their wider family of compounds known as *Ruddlesden-Popper* phases [229]. Here R stands for trivalent rare earths such as La, Pr, Nd, Sm, Eu, Gd, Ho, Tb and the related Y, and A for divalent alkali earths ions such as Sr, Ca, and Ba (or for Pb²⁺) [234, 286, 290]. For example, $La_{1-x}Sr_xMnO_3$ exhibits a very complex phase diagram as a function of doping (x) and temperature, with phases such as paramagnetic metallic, paramagnetic insulating, spin-canted insulating, ferromagnetic insulating, ferromagnetic metallic, and antiferromagnetic metallic [286]. Indeed, entire books may be written on the properties of this family of compounds [234, 286, 290].

Within the magnetism community, $La_{1-x}Sr_xMnO_3$ and related compounds, e.g., $Nd_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$, are best known because they exhibit an effect called colossal magnetoresistance (CMR). For example, in the concentration range around x = 0.175, the phase diagram of $La_{1-x}Sr_xMnO_3$ exhibits a critical point near 250 K where three phases meet, the low-temperature ferromagnetic insulating and metal phases which at higher temperature both turn into a paramagnetic insulating phase, as shown in Fig. 7.29a. When a magnetic field of order of a few Tesla is applied in this critical x region the resistivity is found to change significantly in the temperature range 250–350 K as shown in Fig. 7.29b, c. For example for x = 0.175and T = 284 K the resistivity changes by about a factor of 5. The occurrence of the CMR effect in the tricritical region shows the close correlation between charge (insulator to metal) and spin (ferromagnetic to paramagnetic) ordering as the basis of the CMR effect. This points to the importance of the double exchange hopping mechanism. Theoretical studies show that in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ the double exchange interaction is indeed the primary source of the CMR effect and the temperature dependent resistivity in the critical region [234]. We do not present a more extended treatment of the CMR effect because the necessity of large fields and low temperature appear to be a barrier to its technological exploitation.

7.7.4 Magnetism of Magnetite

In this section we will put together what we have learned to discuss the properties of the oldest magnetic material, magnetite, Fe_3O_4 . Its electronic and magnetic structure is of fundamental importance from a historical, educational and contemporary point of view as reviewed by Tsuda et al. [291]. Here is a quick summary, why:

- Magnetite is the oldest magnetic material known.
- It has a first-order metal-insulator phase transition at $T_{\rm V} = 120$ K, called the *Verwey transition*, discovered in 1939 [292]. When the temperature is lowered through $T_{\rm V}$ the electrical resistivity increases by two orders of magnitude. The Verwey transition is a charge order-disorder transition,¹² the details of which are still debated [234].
- Its rather complicated magnetic structure, containing three inequivalent Fe atoms, was partly proposed by Verwey and Haayman in 1941 [294] and the total structure was proposed by Néel in 1948 [295]. It was confirmed three years later by neutron scattering [296].
- The metal-insulator transition was associated as early as 1941 [294,297] with an electron localization-delocalization transition. Such correlation phenomena are the essence of electron transport in most oxides, following a theoretical model developed by Mott starting in 1949 [233].
- The two indirect exchange mechanisms discussed earlier, super-exchange and double exchange, are simultaneously present in magnetite and give rise to a ferrimagnetic structure.
- Magnetite is a *half-metal* with the highest known Curie temperature (858 K). In a half-metal, conduction is due to one spin channel, only. The other spin channel exhibits a gap at the Fermi level.
- To this day, the localized versus delocalized nature of the 3d electrons in magnetite, and associated phenomena such as short and long range charge ordering, are actively debated in the context of the Verwey transition [234, 298–301].

¹²As proposed by Anderson [293] it is thought that the long-range order of the "extra" electrons on the B sublattice is lost above $T_{\rm V}$ while the short-range order is maintained across the transition.

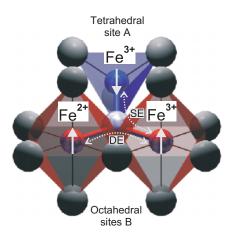


Fig. 7.30. Crystallographic and magnetic structure in magnetite, Fe_3O_4 , near tetrahedrally (site A) and octahedrally (site B) coordinated Fe atoms. The cages around the 3 shown iron atoms are formed by O atoms. The moment on a given Fe atom is coupled antiferromagnetically via superexchange (SE) to another Fe atom of the same valency and ferromagnetically via double exchange (DE) to a Fe atom of different valency. Both exchange interactions go via the same O atom which because of the DE interaction carries a magnetic moment

The key features of the crystallographic and magnetic structure of magnetic are illustrated in Fig. 7.30. We have highlighted the crystallographic environment and relative magnetic alignment of the three inequivalent Fe sites. Overall the comparatively large oxygen O^{2-} -ions form an fcc-lattice and the Fe atoms are located in interstitial sites. The formula can be written $(Fe^{3+})_{tet}(Fe^{2+}, Fe^{3+})_{oct}(O^{2-})_4$, where the subscripts mean tetrahedral (usually called A-sites) and octahedral (B) sites.

In the figure we have also shown the magnetic superexchange (SE) and double exchange (DE) coupling of one Fe atom to its two inequivalent neighbors. We see that both superexchange and double exchange proceed via the same oxygen atom. The octahedral Fe²⁺ and Fe³⁺ ions are ferromagnetically coupled through double exchange. In contrast, the two Fe³⁺ ions in tetrahedral and octahedral sites are antiferromagnetically coupled through superexchange and their moments of $\pm 5\mu_{\rm B}$ cancel each other out. What remains is the unpaired moment on the octahedral Fe²⁺ ions which, as expected from four uncompensated parallel spins has a value of $4\mu_{\rm B}$. Fe₃O₄ therefore possesses ferrimagnetic order and it has a high Curie temperature of 858 K.

Magnetite is an interesting system for which we can explore the band and ligand field concepts discussed in Sects. 7.4 and 7.5 earlier. To this day the debate continues whether it can be described by band theory [298, 300, 301] or whether the size of the correlation effects requires other methods, such as the LDA + U [300, 302] or even multiplet [299, 303] schemes.

The electronic structure of the 3*d* electrons on the three Fe sites can be pictured in the independent electron ligand field model, the band model and the multiplet ligand field model, as illustrated in Fig. 7.31. The energy states associated with the three atoms, Fe^{3+} in site A, Fe^{3+} in site B, and Fe^{2+} in site B, in the independent electron LF model are those already discussed in conjunction with Fig. 7.10. We have shown in (a) the high spin configuration because it is consistent with the band theory results, shown in panel (b).

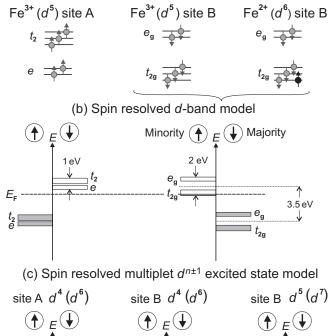
The band results, schematically shown in (b), represent the calculations of Zhang and Satpathy [298] and Antonov et al. [300], obtained in the local spin density calculation. They yield an exchange splitting ($\sim 3.5 \text{ eV}$) that is larger than the $e_{\rm g} - t_{2\rm g}$ splitting (< 2 eV). The calculations yield essentially flat 3*d* bands so that they directly reflect the LF splitting into $e_{\rm g}$ and $t_{2\rm g}$ components which according to Fig. 7.9 have opposite ordering for the tetrahedral A sites and octahedral B sites. The splitting for the B sites is larger, as shown, because of stronger covalent overlap with the 2*p* states of the O ligands. Note that we only show the DOS projection on one B-site, so that relative to the A-site the actual B-site density is twice as large as shown.

Band theory finds that magnetite is metallic because the Fermi level falls at the bottom of the minority spin band on site B which is of t_{2g} character. In contrast, the majority spin bands have a gap at the Fermi level. Hence magnetite is predicted to be a half-metal by band theory. Here we need to recall that DFT-LSDA band theory, in principle, is only reliable at zero temperature. However, at low temperature, below the Verwey transition of 120 K, magnetite is known to be an insulator, not the predicted metal. We therefore need to conclude that the band theoretical results cannot describe the electronic structure correctly, since they cannot account of the Verwey transition.

While band theory can describe the *intersite* Coulomb energy well, it is deficient in the treatment of the *intrasite* Coulomb energy which is the driving force for the Mott–Hubbard localization and can lead to charge ordering. At low temperature a proper theory should give a small gap in the minority spin channel, in addition to the large gap in the majority states. Such a gap of 0.14 eV has been observed in the low temperature optical conductivity spectrum [305]. A small 0.19 eV gap in the minority channel is indeed obtained, when the intra-atomic Coulomb energy is taken into account in an LDA + U scheme [300]. In conjunction with a trigonal symmetry component of the LF at the B sites, which splits the t_{2g} states into e'_{g} and a_{1g} components, the intra-atomic Coulomb interaction opens up the gap.

Rather than going into details of the LDA + U calculation, we explore in Fig. 7.31c the multiplet LF concept. The reason is that we want to elucidate the difference between the independent electron and strong correlation approach and develop a conceptual understanding of the origin of a band gap below the Verwey transition temperature. As discussed before, the transport properties are determined by excited states probed in photoemission and inverse photoemission. For this reason we consider in Fig. 7.31c, the excited states expected for the three Fe ions. For Fe³⁺ with a d^5 ground state config-

(a) Ligand field model with Hund's rule filling



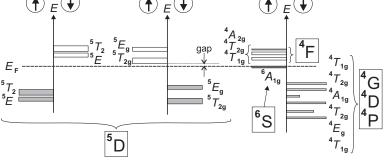


Fig. 7.31. (a) Energy levels and filling of the 3*d* ligand field states for the three Fe atoms in magnetite, Fe₃O₄, shown in Fig. 7.30, assuming an independent electron LF model and high spin configuration. (b) Schematic spin dependent densities of states (DOS) obtained with band theory in the local spin density approximation [298,300]. The areas of the bars, shaded dark for filled and light for empty states, indicate the number of states. The DOS shown for site B constitutes an average over the two sites. Note that there is no band gap for the minority spins. (c) Multiplet excited states for both electron removal (photoemission, below $E_{\rm F}$) and electron addition (inverse photoemission, above $E_{\rm F}$), corresponding to configurations $d^{n\pm 1}$ on each of the Fe atoms. We have indicated the multiplets (*boxed*) and their splitting into irreducible representations of the tetrahedral (A-site) and octahedral (B-site) LF. For the d^5 configuration (*bottom right*) we have used the results Alvarado et al. [304]. The states are schematically indicated by bars

uration, the photoemission final state is the d^4 configuration and the inverse photoemission final state the d^6 configuration. Similarly, for Fe²⁺ (d^6) the excited states are d^5 and d^7 . By inspection of Table 7.7 we can find the lowest energy multiplets ${}^{2S+1}L$ for the different high spin d^n configurations, and from Fig. 7.16 we find their LF splitting in octahedral symmetry. This allows us to construct the shown energy level diagrams in Fig. 7.31c.

In doing so we need to remember that when we reference the energy relative to $E_{\rm F}$, the negative binding energy of the filled states increases away from $E_{\rm F} = 0$ and the configurational energy level diagram (see Fig. 7.16) is turned upside down. For this reason, the multiplet LF diagrams for the d^4 and d^6 excited states consisting of the T_2 and E irreducible representations, when plotted in a binding energy diagram, give an identical level ordering as in the independent electron LF model in Fig. 7.10b, with the substitution $t_2 \leftrightarrow T_2$ and $e \leftrightarrow E$. The multiplet final state diagrams for d^5 and d^7 differ from those in an independent electron model. For the inverse photoemission d^7 configuration the lowest-energy multiplet is 4F which according to Fig. 7.16 splits into ${}^{4}T_{1g}$, ${}^{4}T_{2g}$, and ${}^{4}A_{2g}$ states in an octahedral LF. The d^{5} photoemission final state reached from the d^6 ground state may involve either excitation of a minority spin with a 6S , ${}^6A_{1g}$ high-spin singlet final state, or excitation of a majority spin yielding ${}^{4}G, {}^{4}D, {}^{4}P$ final states. These excited states are composed of several LF states as seen in Fig. 7.14 (also see Table 7.6). The level structure determined by Alvarado et al. [304] is schematically indicated in Fig. 7.31c.

The most important difference between the independent electron and multiplet diagrams in Figs. 7.31b, c lies in the states around $E_{\rm F}$. The multiplet diagram predicts a gap at the Fermi level in both spin channels. In particular, the minority spin gap which does not exist in the independent electron model lies between the filled ${}^{6}A_{1\rm g}$ and empty ${}^{5}T_{2\rm g}$ states on site B. This small gap is the all important feature that determines the transport properties in magnetite and is associated with the Verwey transition.

Experimental results for the valence states of magnetite are shown in Fig. 7.32. In part (a) we show photoemission, inverse photoemission (BIS), and X-ray absorption (XAS) data [299]. They reveal the occupied and unoccupied states close to the Fermi level $E_{\rm F} = 0$ and should correspond to the electron removal d^{n-1} and electron addition d^{n+1} states in the multiplet LF model shown in Fig. 7.31c. Therefore the photoemission state closest to the Fermi level has been denoted ${}^{6}A_{1g}$ and the lowest energy BIS and XAS state ${}^{5}T_{2g}$. Their separation gives rise to the gap as indicated in Fig. 7.31c. In Fig. 7.32b we show the results of spin polarized photoemission measurements for the states closest to the Fermi level, recorded at $h\nu = 21.2 \,\text{eV}$ by Dedkov et al. [301]. The photoemission intensity close to $E_{\rm F}$ is seen to be due to minority spins, only.

Finally, we show in Fig. 7.32c the photon energy dependence of the measured spin polarized electron yield, using newer data [304] than those shown in Fig. 1.8. The spin polarization of the photoelectrons at a photon energy

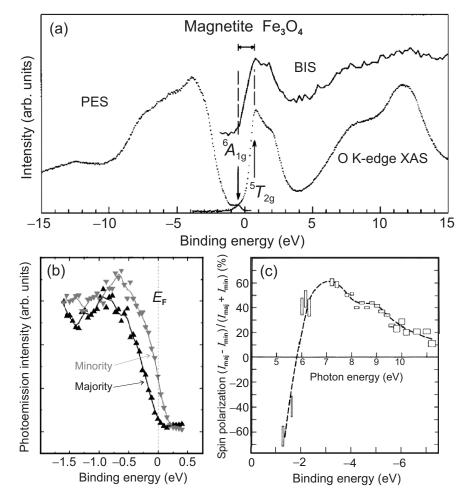


Fig. 7.32. (a) Valence band photoemission spectrum taken at $h\nu = 110 \text{ eV}$ and 130 K, and BIS and X-ray absorption (XAS, shifted by -529.1 eV) spectra, all aligned relative to the Fermi level [299]. The shown spectra represent the electronic density of states associated with electron-removal (photoemission) and electron-addition (BIS and XAS) final states. The indicated LF states ${}^{6}A_{1g}$ and ${}^{5}T_{2g}$ correspond to those shown in the multiplet diagram in Fig. 7.31c, forming the band gap in the minority channel. (b) Spin resolved photoemission spectra of the valence states just below $E_{\rm F}$, taken at $h\nu = 21.2 \text{ eV}$ and 300 K [301]. The spectra reveal a gap in the majority bands and metallic behavior of the minority band, in support of a half metal. (c) Spin polarized electron yield measured as a function of photon energy [304]. The negative spin polarization at threshold is due to the minority ${}^{6}A_{1}$ state, as shown at the bottom of Fig. 7.31. Photon energy and binding energy are related according to $E_{\rm B} = -h\nu + \phi_{\rm W}$, where $\phi_{\rm W} = 4 \text{ eV}$ is the work function of the sample

 $h\nu$ represents the number of spin-resolved states, integrated from $E_{\rm F}$ up to a binding energy $E_{\rm B} = -h\nu + \phi_{\rm W}$, where $\phi_{\rm W} = 4\,{\rm eV}$ is the work function. It is found to be negative at photoemission threshold, in accord with the measured spin polarization in Fig. 7.32b. The spin polarization changes sign and increases to a peak and then, except for a second weaker peak, decreases to a spin polarization value below +25% at the highest energies. From Fig. 7.31a one would expect that if all 3d states, but no other states, are involved in photoemission the spin polarization should have a value P = 4/16 or +25%, given by the difference in the number of majority and minority spins (+4), divided by the total number of electrons (16). We see that at the highest energies the observed spin polarization drops below this value, indicating the presence of unpolarized electrons from the oxygen 2p valence band. This is consistent with a higher binding energy of the O 2p states relative to the Fe 3d-states.

Historically, the spin-polarized photoemission studies played an important role. Until the mid 1970s, the electronic structure of the ferrites was a subject of speculation [64]. This was due to the ambiguities of the spectroscopies without spin analysis which cannot distinguish whether an optical transition involves the excitation of an oxygen 2p-electron or an Fe 3*d*-electron, nor on which of the two sublattices, identified as A and B in Fig. 7.30, the excitation occurred. The spin polarized results for magnetite provided early evidence that the O 2p states lie below the partially occupied Fe 3*d* states. The negative spin polarization at threshold furthermore indicated half-metallic behavior originating from minority spin transport, only.

While the basic nature of the spin dependent states near $E_{\rm F}$ has thus been answered by various spin polarized photoemission measurements, the question remains about the nature of the Verwey transition at $T_{\rm V}$. The temperature dependence of the band gap, responsible for the Verwey transition has been studied by spin-integrated photoemission by Park et al. [299] using high resolution $h\nu = 110 \,\text{eV}$ synchrotron radiation. These results, shown in Fig. 7.33, disagree in the placement of the Fermi level with the later spin resolved ones in Fig. 7.32b by Dedkov et al., in that they show no intensity at the Fermi level. As was pointed out by Park et al. the use of helium-lamp ($h\nu = 21.2$) excitation, by accident, produces spurious intensity near $E_{\rm F}$, so that the results of Dedkov et al. should only be used to illustrate the sign of the spin polarization near $E_{\rm F}$ but do not reflect the true band gap. Park et al. found that when the temperature is raised through $T_{\rm V}$, merely a small (50 meV) decrease of the gap is observed. The implied decrease in activation energy across the gap from 150 meV below to 100 meV above T_V was argued to be consistent with the two order of magnitude conductivity jump at $T_{\rm V}$ [299]. However, one has to also remember that the surface sensitive PE-techniques could respond to electronic and/or magnetic changes in the surface that are bound to be present as well.

The various experimental results support the basic model for the metalinsulator or Verwey-transition put forward by Mott in 1974 [64]. It is based on

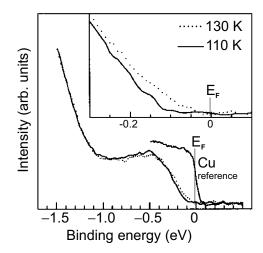


Fig. 7.33. High resolution (60 meV) valence band photoemission spectrum taken at $h\nu = 110 \text{ eV}$, below (110 eV) and above (130 K) the Verwey transition [299]. The energy scale was carefully calibrated relative to the Fermi level, revealed by the sharp Fermi edge of Cu metal. Both magnetite spectra do not show any appreciable intensity at the Fermi level, indicating insulator-like behavior, but above the Verwey transition the gap is reduced by about 50 meV

the assumption that the electrical conduction at $E_{\rm F}$ is generated by hopping of minority spins at the B-sites which at low temperature have to overcome the ${}^{6}A_{1} - {}^{5}T_{2}$ gap arising from the B-site Fe atoms. Above the metal-insulator transition the hopping is thermally activated. In addition they provide evidence that magnetite is a *half-metallic oxide* above $T_{\rm V}$, where thermally activated conduction occurs in only the minority spin channel.

7.8 RKKY Exchange

The different kinds of exchange (direct and indirect) discussed so far emphasize the relationship between magnetism and bonding, as exemplified by the HL calculation and by the directional superexchange and double-exchange interactions. We have seen that the requirement of wavefunction overlap leads to the short range of the exchange interaction.

In 1954, Ruderman and Kittel [306] first suggested that a local moment, in their case a nuclear spin, can induce a spin polarization in the surrounding conduction electron sea. A few years later Kasuya [307] and Yosida [308] used similar concepts to treat the coupling of localized rare earth 4f moments with the conduction electrons. These studies showed that the spin polarization of the conduction electrons oscillates in sign as a function of distance from the localized moment and that the spin information was carried over relatively large distances. In honor of the above scientists we today call this effect RKKY exchange.

The RKKY oscillatory effect is an example of a general phenomenon arising from the wave nature of the quasi "free" conduction electrons. When such "free" electrons are scattered by an atom, they will rearrange themselves in order to minimize the disturbance. This process is called *screening*. Screening can exist for either spin or charge scattering and results in oscillations of the charge or spin density around the scattering center. Indeed, the oscillations in the charge density around a point-charge impurity were first derived in 1958 by Friedel [309] and hence go by the name *Friedel oscillations*. They can be directly imaged today by means of scanning tunneling microscopy as first done by two IBM groups in 1993 [310, 311].

While in the transition metals there is direct overlap of the d electrons and the magnetic coupling is therefore determined by direct exchange, the case of the rare earths indeed resembles the early models of localized moments. Owing to the localization of the 4f shell which contains the magnetic electrons the direct exchange mechanism is ineffective. It therefore needs to involve an indirect mechanism. In the 4f metals the indirect mechanism involves the outer 5d electrons (see Fig. 12.5) which partly overlap with the 4f shell. In contrast to the case of superexchange, the indirect coupling between two atoms thus proceeds through the outer electronic states of the atoms themselves rather than through the electronic states of a third atom.

7.8.1 Point-like Spins in a Conduction Electron Sea

In the derivation of the RKKY interaction [222] one assumes a delta function like interaction of a point-like spin S with the spins s of the conduction electrons

$$\mathcal{H} = 2A\,\delta(\boldsymbol{r} - \boldsymbol{R})\,\boldsymbol{S}\cdot\boldsymbol{s}\;, \qquad (7.41)$$

where A describes the intra-atomic exchange parameter and the δ function limits the interaction to be of contact form. The RKKY interaction energy between two localized spins S_i and S_j , separated by a distance R can then be written in the Heisenberg form (6.59) with a distance dependent exchange constant J(R). It can be related to the free electron density N_V in-between the atoms. We can describe the free electrons as plane waves normalized to a volume V,

$$\psi(r) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} , \qquad (7.42)$$

where the electron momentum k is related to the electron kinetic energy by the free electron dispersion relation

$$E = \frac{\hbar^2 k^2}{2m_{\rm e}} \ . \tag{7.43}$$

The total density of states per unit energy (including two spins per energy) is obtained by counting the number of states in the volume V per unit energy and is given by

$$D(E) = \frac{V}{\pi^2 \hbar^2} m_{\rm e} k = \frac{V}{2\pi^2 \hbar^3} (2m_{\rm e})^{3/2} \sqrt{E}.$$
 (7.44)

If we denote the electron density per unit volume as $N_{\rm V}$, the total number of electrons in the volume V is $N_{\rm V}V$. By equating $N_{\rm V}V$ with the energy integral of (7.44) up to the Fermi energy we obtain

$$N_{\rm V} = \frac{1}{V} \int_0^{E_{\rm F}} D(E) \,\mathrm{d}E = \frac{(2m_{\rm e}E_{\rm F})^{3/2}}{3\pi^2 \,\hbar^3} = \frac{k_{\rm F}^3}{3\pi^2} \,, \tag{7.45}$$

where the Fermi energy $E_{\rm F}$ and Fermi wave vector $k_{\rm F}$ are related according to $E_{\rm F} = \hbar^2 k_{\rm F}^2 / 2m_{\rm e}$. The RKKY exchange coefficient J(R) is found to be oscillatory with distance R according to

$$J(R) = \frac{16 A^2 m_{\rm e} k_{\rm F}^4}{(2\pi)^3 \hbar^2} \left[\frac{\cos(2k_{\rm F}R)}{(2k_{\rm F}R)^3} - \frac{\sin(2k_{\rm F}R)}{(2k_{\rm F}R)^4} \right] .$$
(7.46)

It makes a damped oscillation with distance from positive to negative values, which at large R takes a simple form

$$J(R) = \frac{2 A^2 m_{\rm e} k_{\rm F}}{(2\pi)^3 \hbar^2} \left. \frac{\cos(2k_{\rm F}R)}{R^3} \right|.$$
(7.47)

Therefore, depending upon the separation between a pair of ions their magnetic coupling can be ferromagnetic or antiferromagnetic. It follows the polarization of the conduction electrons, as illustrated in Fig. 7.34a. The RKKY exchange couples localized moments over relatively large distances.

7.8.2 Metallic Multilayers

RKKY exchange around magnetic impurities is nondirectional. The same mechanism also applies when two magnetic layers are separated by a nonmagnetic spacer, for example, in a Co/Cu/Co sandwich. Now the oscillatory coupling is in the direction perpendicular to the layers. If the two magnetic layers L_1 and L_2 are separated by a nonmagnetic spacer layer of thickness d, one can define an interlayer exchange coupling constant J_{12} per unit interface area. It leads to an oscillatory magnetization in the spacer layer that decays with $1/z^2$, where z is the distance from one of the layers, chosen as the reference layer. The magnetization of the "nonmagnetic" spacer layer has been observed by photoemission [313,314] and X-ray magnetic dichroism [315,316]. In the limit of large distance z it has the simple form [222]

$$J_{12}(z) = J_0 \frac{d^2}{z^2} \sin(2k_{\rm F}z) . \qquad (7.48)$$

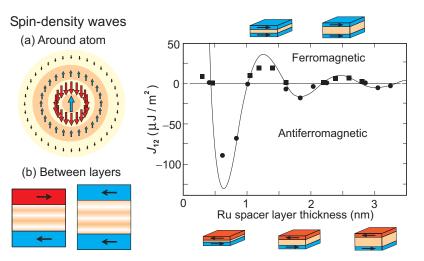


Fig. 7.34. (a) Spin polarization of the conduction electrons around a localized magnetic impurity, showing the characteristic RKKY oscillations given by (7.46). (b) Spin polarization of electrons between two magnetic layers. The relative magnetization alignment in the two layers depends of the distance between the layers, and is caused by induced spin polarization in the "nonmagnetic" spacer layer, the sign of which is distance-dependent. Right: Interlayer exchange coupling strength J_{12} between two ferromagnetic Ni₈₀Co₂₀ layers across a Ru spacer layer of variable thickness [312]. The experiment utilized a specially engineered multilayer structure. The interlayer exchange coupling constant J_{12} given by (7.48) has the dimension [energy/unit area] and is positive for ferromagnetic and negative for antiferromagnetic coupling

The induced *spin density wave* in the spacer layer serves as an indirect coupling mechanism between the magnetic layers, as illustrated in Fig. 7.34b, which change their coupling from ferromagnetic to antiferromagnetic alignments as a function of the spacer layer thickness d. This oscillation has been observed by magnetization measurements [312] for Ni₈₀Co₂₀ magnetic layers coupled through Ru as shown in Fig. 7.34, and can also be directly imaged [317] by use of a wedge structure as for the Cr spacer layer wedge between ferromagnetic Fe layers shown in Fig. 1.9.

The interlayer exchange coupling may also be explained by a standing spin density wave in the spacer layer caused by the quantum well set up by the parallel magnetic layers, first suggested by Ortega and Himpsel [318]. The RKKY and quantum well pictures are related but not identical, since in the quantum well the oscillation is caused by a coupled charge and spin density wave. The quantum well picture has been reviewed by Himpsel et al. [249,250] and will also be discussed in Sect. 13.4.5 later.

In the next section we take a look at the effect and importance of the small spin–orbit interactions. We shall see that despite its size it is of great importance since it determines the magnetocrystalline anisotropy.

7.9 Spin–Orbit Interaction: Origin of the Magnetocrystalline Anisotropy

The treatment of the spin-orbit interaction in atoms is straight forward as discussed in Sect. 6.4 and it can be viewed as simply coupling the atomic spin to the orbital momentum. For a single electron this results in the vector coupling relation $\mathbf{l} + \mathbf{s} = \mathbf{j}$. Similarly, for a multielectron system with L - S coupling we have $\mathbf{L} + \mathbf{S} = \mathbf{J}$ and the terms ${}^{2S+1}L$ are coupled into subgroups ${}^{2S+1}L_J$ with $L - S \leq J \leq L + S$. The general form of the Hamiltonian is a generalized form of (6.89) or

$$H_{\rm so} = \xi(r) \ \boldsymbol{L} \cdot \boldsymbol{S} \ . \tag{7.49}$$

In solids the situation is complicated by bonding. In the multiplet approximation the intra-atomic Coulomb and exchange interactions still create coupled terms ^{2S+1}L but these terms are modified by the LF which mixes different Lvalues, as discussed in Sect. 7.5.2. In the independent electron approximation we have seen in Sect. 7.5.1 that the LF wavefunction (7.30) contain a mixture of m_l values. Therefore in the respective models, L and m_l cease to be good quantum numbers. The Hamiltonian (7.49) is therefore no longer diagonal and needs to be diagonalized with the LF eigenfunctions. In this section we shall take a look how this is done and, as a consequence, we shall find an important effect, which is directly related to the anisotropy of bonding - the magnetocrystalline anisotropy, MCA.

In general, the magneto-crystalline anisotropy is defined as follows.

The magneto-crystalline anisotropy is the energy that it takes to rotate the magnetization from the "easy" direction into the "hard" direction, assuming a bulk sample where magnetostatic effects are absent. It is given by the anisotropy of the spin–orbit energy

 $\Delta E_{\rm so} = \langle H_{\rm so} \rangle_{\rm hard} - \langle H_{\rm so} \rangle_{\rm easy} = \zeta \left[\langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm hard} - \langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm easy} \right] > 0 \ , \ (7.50)$

so that it costs energy to rotate the magnetization into the hard direction.

The microscopic origin of magnetic anisotropy in transition metals has been debated ever since the early work by Van Vleck in 1937 [319]. Recently, interest in this problem has been revived in conjunction with artificially created transition-metal films and multilayers which exhibit perpendicular magnetic anisotropy [320, 321]. The microscopic origin of the MCA is nontrivial and therefore only general hand-waving arguments are often given [322, 323]. The difficulty in treating the spin–orbit interaction in transition metals and their compounds lies in its small size, as seen from Fig. 7.5. For this reason the MCA is typically also a small energy. For example, as discussed in Sect. 11.2.2, it has only recently been possible to correctly obtain the known

[111] anisotropy direction in bulk fcc Ni. Because of the high symmetry of the lattice, the magnetocrystalline anisotropy is only about $10^{-5} \text{ eV}/\text{atom}$, and it remains difficult to develop a conceptual understanding of the origin of the MCA, which arises from the subtleties of the band structure.

More generally, it is difficult to picture the origin of such anisotropy energies since our visualization of magnetism is closely related to magnetic moments. It would therefore be preferable to cast anisotropy concepts in terms of "moment anisotropies" and in this section we shall do so, following concepts due to Bruno [123, 324].

In particular, we shall here consider systems where symmetry breaking creates a large bonding anisotropy and MCA. For example, metallic multilayers like Co/Pd may exhibit MCAs that are enhanced by orders of magnitude, up to about 1 meV/atom [123, 325]. It is in such systems that we can hope to directly link bonding anisotropy and MCA. The goal of this section is to establish this link, both conceptually and through a model calculation. We shall start by presenting a simple model based on bonding and the orbital magnetic moment.

7.9.1 The Bruno Model

Bruno [123,324] has shown theoretically¹³ that under certain assumptions the anisotropy of the *spin-orbit energy* is directly related to the anisotropy of the *orbital moment* according to

$$\Delta E_{\rm so} = \zeta \left[\langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm hard} - \langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle_{\rm easy} \right] = \frac{\zeta}{4\mu_{\rm B}} (m_{\rm o}^{\rm easy} - m_{\rm o}^{\rm hard}) > 0 \ . \tag{7.51}$$

This equation predicts that the easy magnetization direction has a larger orbital moment than the hard magnetization direction. Let us remember this result.

The *Bruno model* states that the *orbital moment* is larger along the easy magnetization direction, and that the difference between the orbital moments along the easy and hard directions is proportional to the magneto-crystalline anisotropy.

Bruno's model leads to a particularly simple and beautiful picture for the origin of the MCA based on the anisotropy of the orbital moment illustrated in Fig. 7.35. We will later see that this concept has been experimentally verified

¹³Bruno's work followed careful high field measurements of the anisotropy of the total (spin plus orbital) magnetic moment by Aubert, Rebouillat, Escudier, and Pauthenet [326]. The relationship between the orbital moment and the magnetic anisotropy was also discussed in an early paper by Ducastelle and Cyrot-Lackmann [327].

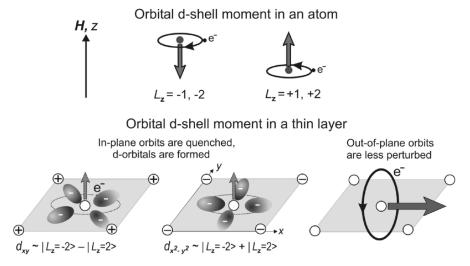


Fig. 7.35. Directional quenching of the orbital momentum of an atom by ligand field effects in a thin film, as discussed in the text

by Weller et al. [328] by means of angle dependent XMCD measurements of a Co/Au/Co wedge.

In the independent electron ligand field model the microscopic origin of the MCA may be envisioned to come about as illustrated in Fig. 7.35, using concepts by Smit [329]. Consider a *d* electron in a free atom whose spin is oriented by an external magnetic field. The orbital momentum of the *d* electron circling about the spin direction can then take on values $-2 \leq \langle L_z \rangle \leq +2$, as depicted in Fig. 7.35. For an external magnetic field \boldsymbol{H} along +z, the lowest energy state will be the $L_z = -2$ state, which is aligned in the opposite direction to \boldsymbol{H} .

Let us now assume that, instead, the atom is bonded in a planar geometry to four other atoms with a negative or positive charge as shown in Fig. 7.35. Now the orbiting electron will experience a Coulomb repulsion where the negative neighbor ions are located and a Coulomb attraction where the positive atoms are located. The orbiting electron will form a standing wave by superposition of two oppositely traveling waves with $\pm L_z$, with characteristic charge maxima as shown. One may say that the in-plane orbit of the electron is broken up through the formation of molecular orbitals (e.g., a $d_{x^2-y^2}$ orbital or a d_{xy} , as shown in the figure). Therefore the corresponding orbital momentum along the normal of the bonding plane, will be quenched. We shall later show that the individual real *d*-orbitals indeed have zero orbital moment.

On the other hand, the orbital motion perpendicular to the bonding plane will be less disturbed owing to the lack of neighbor ions and the corresponding in-plane orbital momentum remains largely unquenched. The simple model pictured in Fig. 7.35 therefore relates the anisotropy of the orbital moment of an atom to the anisotropy of the bonding environment. For a *free monolayer* the orbital momentum \boldsymbol{L} (or moment $\boldsymbol{m}_{\rm orb} = -\mu_{\rm B}\boldsymbol{L}/\hbar$) is predicted to be larger in the bonding plane than perpendicular to it. For the opposite case of stronger out-of-plane bonding, which may occur in a multilayer, the orbital moment would be larger in the out-of-plane direction.

The total magnetic moment of atoms has two contributions arising from the spin and the orbital moment, according to $m_{tot} = m_s + m_o$. As discussed in Sect. 12.2.2, for the ferromagnetic metals Fe, Co, and Ni, the spin moment is about ten times larger than the orbital moment. The large spin moment is intrinsically isotropic because the exchange interaction is isotropic. We then have the interesting situation that the small orbital moment is "locked" into a favorite direction by the bonding anisotropy of the lattice and it directs the spin moment into its favorable lattice direction through the spin–orbit coupling. The latter keeps the orbital and spin moments parallel to each other according to Hund's rules discussed in Sect. 6.4.¹⁴

The above simple atomic moment based model has the following key ingredients:

- The existence of an (isotropic) spin moment on the central atom through the exchange interaction.
- The symmetry and strength of the LF around the central atom.
- The creation of an anisotropic orbital moment on the central atom by the spin–orbit coupling.

We shall now look at the theoretical underpinning of this model. We do not need to elaborate on the spin moment but simply assume its existence. Instead, we concentrate on points two and three, the LF and spin-orbit interaction. To facilitate things we shall use the independent electron LF model where we can visualize bonding by means of the real *d*-orbitals.

7.9.2 Description of Anisotropic Bonding

In order to quantitatively link bonding anisotropy with MCA, we use the *d*orbitals for the description of the bonding. Their energetic positions and splitting is described by the independent electron LF theory discussed in Sect. 7.5.1 or the band structure effects treated in Sect. 7.4.3. We picture a central transition metal atom that is located in three different types of environments, as illustrated in Fig. 7.36: (a) a bulk fcc crystal composed of identical atoms, (b) a free standing (001) monolayer of identical atoms, and (c) an interface layer

¹⁴It has been suggested by electronic structure calculations [330] that ligand field effects which traditionally are only known to quench the orbital moment may, for certain materials, invert the sign of the orbital moment thereby violating Hund's third rule.

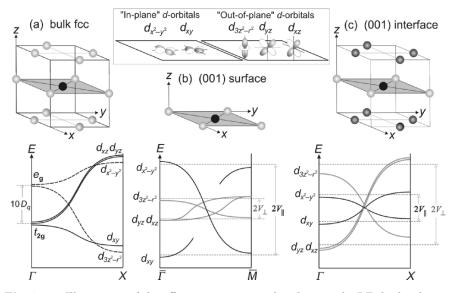


Fig. 7.36. Illustration of the effect on anisotropic bonding on the LF *d* orbitals in a simple band picture. In the inset we illustrate that in many cases, e.g., surfaces and thin films, one may distinguish in-plane (x, y) and out-of-plane (z) d orbitals. In (a) we show the case of a bulk fcc lattice. At the center of the Brillouin zone, Γ , both the t_2 and *e* manifolds are isotropic because they contain in-plane as well as out-of-plane *d* orbitals. Even band dispersion does not affect the in-plane/out-of plane equivalence as shown for the canonical *d* band behavior in the $\Gamma - X$ direction [222]. In contrast, in tetragonal symmetry the in-plane/out-of-plane equivalence is broken, as shown for two cases. (b) illustrates the case of a free (001) monolayer, where the in-plane orbitals, V_{\parallel} , is larger than that of the out-of-plane orbitals, V_{\perp} . (c) illustrates the opposite case where the out-of-plane interaction for a sandwiched layer is assumed to be stronger. Now the out-of-plane *d* orbitals split more than the in-plane ones, so that $V_{\perp} > V_{\parallel}$

of the same structure that is sandwiched between layers composed of different atoms, with stronger out-of-plane than in-plane bonding.¹⁵

In order to picture anisotropic bonding we divide the *d*-orbitals into inplane and out-of-plane orbitals as shown in the inset of Fig. 7.36. If we now look at the bonding of a central atom, shown in black, in an fcc lattice its *d*-orbitals are split into t_{2g} and e_g states due to the octahedral environment as shown in (a). Both t_{2g} and e_g states are isotropic since they contain both in-

¹⁵Harrison [331] has tabulated interaction strengths between different elements. This concept has been used by Wang et al. [332] to discuss bonding in multilayers. For example, if the in-plane Co–Co bonding strength for a sandwiched Co monolayer is normalized to 1.00, then the corresponding out-of-plane Co–X bonding strength is 1.53, 1.60, 1.38, 0.83 for X = Au, Pt, Pd, and Cu, respectively.

plane and out-of-plane orbitals. In a band picture, the orbital splitting changes as a function of wavevector, as shown for the $\Gamma - X$ direction [222], but on average the states maintain their in-plane/out-of-plane equivalence. Hence in cubic symmetry the bonding is isotropic, and for this reason the MCA enters only in higher order and is very weak.

The situation is quite different if we isolate a single (001) layer out of the bulk fcc lattice, as shown in Fig. 7.36b. Now the reduced (tetragonal) symmetry leads to a pattern similar to that shown in Fig. 7.9 with a larger in-plane than out-of-plane splitting. Which in-plane or out-of-plane state is lowest and highest depends on where we are in the Brillouin zone. As an example, we show the bands as calculated by Wang et al. [332] for a Co (001) monolayer along the $\bar{\Gamma} - \bar{M}$ direction in the surface Brillouin zone. In order to account for the different in-plane and out-of-plane behavior we can therefore define splitting energies V_{\parallel} (in-plane) and V_{\perp} (out-of-plane) that reflect an average over prominent points (flat bands) in the Brillouin zone. This concept therefore lets us avoid the consideration of the detailed **k**-dependent band structure and leads to a significant simplification.

Finally, we show in Fig. 7.36c the case where the (001) monolayer has been sandwiched between two layers of different atoms on fcc lattice positions. We shall assume that the in-plane bonding between like atoms is weaker than the out-of-plane bonding between different atoms (see footnote 15). This situation is indeed encountered, for example, for a Co layer that is sandwiched between Pt or Au layers [332, 333]. Now the splitting between out-of-plane orbitals, V_{\perp} , is larger than that, V_{\parallel} , between in-plane orbitals.

The task before us in the next section is to link the bonding asymmetry described by V_{\parallel} and V_{\perp} to the anisotropy of the orbital magnetic moment.

7.9.3 Bonding, Orbital Moment, and Magnetocrystalline Anisotropy

The molecular orbitals formed through bonding, in our case the *d* orbitals, have zero orbital momentum. This is easily seen by writing the *d* orbitals in terms of spherical harmonics $Y_{L,M} = |L, M\rangle = |L, L_z\rangle$, as done in Table 7.4, and then calculating the expectation values $\langle d_i | L_\alpha | d_i \rangle$ ($\alpha = x, y, z$). Let's take the $d_{x^2-y^2}$ orbital, for example. It is given by $|d_{x^2-y^2}\rangle = (1/\sqrt{2}) \{|L=2, M=2\rangle + |L=2, M=-2\rangle\}$ and therefore $\langle d_{x^2-y^2} | \mathbf{L}_z | d_{x^2-y^2} \rangle = 0$. This result can also be derived from the matrix elements listed in Table 7.11, which readily allow the calculation of the orbital momentum along the *x* and *y* directions.

The case of the real d orbitals is only one example of an important general theorem which needs to be framed and remembered.

Table 7.11. Angular momentum operators L_{α} ($\alpha = x, y, \text{ or } z$) acting on *d*-orbitals, taken from Ballhausen [236]. Because all matrix elements between orbitals o_i are purely imaginary we have $\langle o_i | L_{\alpha} | o_n \rangle = -\langle o_i | L_{\alpha} | o_n \rangle^* = -\langle o_n | L_{\alpha}^{\dagger} | o_i \rangle = -\langle o_n | L_{\alpha} | o_i \rangle$. Eigenvalues are in units of \hbar

$L_x d_{xz}$	=	$-i d_{xy}$	$L_y d_{xz}$		$id_{x^2-y^2}$	$L_z d_{xz}$	$= i d_{yz}$
					$-i\sqrt{3}d_{3z^2-r^2}$		
$L_x d_{yz}$	=	$i\sqrt{3}d_{3z^2-r^2}$	$L_y d_{yz}$	=	$i d_{xy}$	$L_z d_{yz}$	$= -i d_{xz}$
		$+ id_{x^2-y^2}$					
$L_x d_{xy}$	=	$i d_{xz}$	$L_y d_{xy}$	=	$-id_{yz}$	$L_z d_{xy}$	$= -i 2 d_{x^2 - y^2}$
$L_x d_{x^2 - y^2}$	=	$-id_{yz}$	$L_y d_{x^2 - y^2}$	=	$-i d_{xz}$	$L_z d_{x^2 - y^2}$	$= i 2 d_{xy}$
$L_x d_{3z^2 - r^2}$	=	$-i\sqrt{3}d_{yz}$	$L_y d_{3z^2 - r^2}$	=	$i\sqrt{3} d_{xz}$	$L_z d_{3z^2 - r^2}$	= 0

States that carry an *angular momentum* are always described by a *complex* wavefunction. If a wavefunction is *real* the corresponding state has zero angular momentum.

The zero angular momentum value for all d orbitals arises from a perfect balance of substates with quantum numbers +M and -M. This balance is broken when two or more of the orbitals are mixed by the spin-orbit interaction and the new orbitals can then have a finite angular momentum. Let us see how this happens.

Calculation of the Spin–Orbit Interaction

The spin–orbit (SO) interaction, derived in Sect. 6.4, is given by

$$H_{\rm so} = \xi(r) \mathbf{L} \cdot \mathbf{S} = \xi(r) (L_x S_x + L_y S_y + L_z S_z) , \qquad (7.52)$$

where the relevant spin-orbit coupling constant (units [energy]) for the d shell is given by

$$\zeta = \langle \xi(r) \rangle = \int_0^\infty R_{3d}(r) \,\xi(r) \,R_{3d}^*(r) \,r^2 \,\mathrm{d}r.$$
(7.53)

The SO interaction couples the electronic ligand field orbitals that are "locked in" by the lattice to the spin which is created by the exchange interaction and is intrinsically isotropic. Without the SO interaction charge and spin are decoupled, the orbital moment is zero and the spin cannot "talk" to the lattice. For example, angular momentum cannot be transferred from the spin system to the lattice.

As shown in Fig. 7.5, for the 3d transition metals the SO interaction is more than an order of magnitude smaller that the exchange interaction and the LF splitting (band width). One can therefore treat it to a good approximation by perturbation theory [123, 324]. As usual in quantum theory this requires the evaluation of matrix elements of the perturbative Hamiltonian, i.e., the SO Hamiltonian, formed with the "zero-order" wavefunctions created by the ligand field and the exchange interactions.

By defining average splittings as done in Fig. 7.36 between in- and out-ofplane *d*-orbitals we can eliminate the complicated \mathbf{k} dependence and describe the bonding in a simple LF formalism, with the *d* orbitals as the LF eigenfunctions. The "zero-order" electronic wavefunctions for our perturbation calculation are simple products of the radial and angular *d* functions created by the LF and the spin-up and spin-down functions created by the exchange interaction.

At first sight the perturbative SO Hamiltonian (7.52) looks quite simple. However, we need to remember that the reference frame x, y, z for the d orbitals is given by the lattice and the quantization axis \tilde{z} for the spin is in general different from the z axis of the lattice. The spin quantization axis is chosen to lie along the magnetic field $\boldsymbol{H}_{\text{ext}}$. This complicates things and we need to rewrite the SO Hamiltonian to account for the two different frames.

In the following we shall assume that the \tilde{z} axis is specified by spherical angles $\tilde{\theta}$ and $\tilde{\phi}$ in the x, y, z frame of the lattice, as shown in Fig. 7.37. Since we want to calculate the magnetic anisotropy we assume that we can magnetically align the sample by an external magnetic field along any direction in the x, y, z frame. The magnetic anisotropy is then given by the energy difference between spin alignments along the easy and hard magnetization direction of the sample.

The components S_x, S_y , and S_z in (7.52) of the spin in the sample frame are related to the operators $S_{\tilde{x}}, S_{\tilde{y}}$, and $S_{\tilde{z}}$ in the spin frame according to,

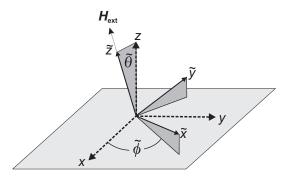


Fig. 7.37. Relationship of the coordinate system of the sample (x, y, z) relative to a rotated spin quantization frame, $\tilde{x}, \tilde{y}, \tilde{z}$. The spin quantization frame is naturally chosen so that the \tilde{z} axis lies along the magnetic field $\boldsymbol{H}_{\text{ext}}$. Its orientation is specified by spherical angles $\tilde{\theta}$ and $\tilde{\phi}$ in the x, y, z frame

$$S_{x} = S_{\tilde{x}} \cos \tilde{\phi} \cos \tilde{\theta} - S_{\tilde{y}} \sin \tilde{\phi} + S_{\tilde{z}} \cos \tilde{\phi} \sin \tilde{\theta}$$

$$S_{y} = S_{\tilde{x}} \sin \tilde{\phi} \cos \tilde{\theta} + S_{\tilde{y}} \cos \tilde{\phi} + S_{\tilde{z}} \sin \tilde{\phi} \sin \tilde{\theta}$$

$$S_{z} = -S_{\tilde{x}} \sin \tilde{\theta} + S_{\tilde{z}} \cos \tilde{\theta} , \qquad (7.54)$$

and we obtain the general equation for the SO Hamiltonian,

$$H_{\rm so} = \xi(r) \left(L_x \{ S_{\tilde{x}} \cos \tilde{\phi} \cos \tilde{\theta} - S_{\tilde{y}} \sin \tilde{\phi} + S_{\tilde{z}} \cos \tilde{\phi} \sin \tilde{\theta} \} \right. \\ \left. + L_y \{ S_{\tilde{x}} \sin \tilde{\phi} \cos \tilde{\theta} + S_{\tilde{y}} \cos \tilde{\phi} + S_{\tilde{z}} \sin \tilde{\phi} \sin \tilde{\theta} \} \right. \\ \left. + L_z \{ -S_{\tilde{x}} \sin \tilde{\theta} + S_{\tilde{z}} \cos \tilde{\theta} \} \right) .$$
(7.55)

This gives the following expressions for $\boldsymbol{H}_{ext}, \tilde{z} \parallel x, y$, or z

$$\boldsymbol{H}_{\text{ext}} \parallel \boldsymbol{x}: \qquad \boldsymbol{H}_{\text{so}}^{\boldsymbol{x}} = \xi(\boldsymbol{r}) \left(\boldsymbol{L}_{\boldsymbol{x}} \boldsymbol{S}_{\tilde{\boldsymbol{z}}} + \boldsymbol{L}_{\boldsymbol{y}} \boldsymbol{S}_{\tilde{\boldsymbol{y}}} - \boldsymbol{L}_{\boldsymbol{z}} \boldsymbol{S}_{\tilde{\boldsymbol{x}}} \right)$$
(7.56)

$$\boldsymbol{H}_{\text{ext}} \parallel y: \qquad H_{\text{so}}^{y} = \xi(r) \left(-L_{x} S_{\tilde{y}} + L_{y} S_{\tilde{z}} - L_{z} S_{\tilde{x}} \right)$$
(7.57)

$$\boldsymbol{H}_{\text{ext}} \parallel z : \qquad H_{\text{so}}^{z} = \xi(r) \left(L_{x} S_{\tilde{x}} + L_{y} S_{\tilde{y}} + L_{z} S_{\tilde{z}} \right). \tag{7.58}$$

Without the radial part $R_{3d}(r)$, the ten *d* electron spin orbitals which constitute the zero order states of our perturbation treatment have the general short form

$$\phi_n^+ = |d_n, S_{\tilde{z}}\rangle = |d_n, +\rangle , \qquad (7.59)$$

for spin-up states, and

$$\phi_l^- = |d_l, -S_{\tilde{z}}\rangle = |d_l, -\rangle , \qquad (7.60)$$

for spin-down states. In the following we shall only use the above angular parts of the spin orbitals, since all matrix element of the SO Hamiltonian with the radial parts $R_{3d}(r)$ simply give a factor ζ , according to (7.53). For simplicity, we shall indicate the orientation of \tilde{z} in the x, y, z frame by a single index α that incorporates the spherical angles $\tilde{\theta}$ and ϕ . For alignment of $\tilde{z} \parallel x$, for example, we simply write $\alpha = x$. The index α explicitly indicates that the wavefunctions depend on the magnetization (external field) direction. A resulting perturbed spin-up LF state arising from the spin–orbit interaction is then obtained by the first order perturbation expression

$$\Psi_i^{\alpha} = \phi_i^+ + \sum_m b_{m,i}^{\alpha} \, \phi_m^+ + \sum_k c_{k,i}^{\alpha} \, \phi_k^- \, . \tag{7.61}$$

Similarly a perturbed spin-down LF state is given by the first-order state,

$$\Psi_j^{\alpha} = \phi_j^- + \sum_m d_{m,j}^{\alpha} \phi_m^- + \sum_k e_{k,j}^{\alpha} \phi_k^+ .$$
 (7.62)

The anisotropic correction terms b^{α} and d^{α} reflect mixing of LF states of the same spin by the SO interaction, which for $\alpha = x, y, z$ is given by the expressions (7.56)–(7.58). The spin-up and spin-down terms are given by

7.9 Spin–Orbit Interaction: Origin of the Magnetocrystalline Anisotropy 303

$$b_{m,i}^{\alpha} = \frac{\langle \phi_m^+ | H_{\rm so}^{\alpha} | \phi_i^+ \rangle}{\Delta_{im}} \qquad d_{m,j}^{\alpha} = \frac{\langle \phi_m^- | H_{\rm so}^{\alpha} | \phi_j^- \rangle}{\Delta_{jm}} \tag{7.63}$$

and the terms c^{α} and e^{α} reflect mixing of band states of opposite spin and are given by

$$c_{k,i}^{\alpha} = \frac{\langle \phi_k^- | H_{\rm so}^{\alpha} | \phi_i^+ \rangle}{\Delta_{ik}} \qquad e_{k,j}^{\alpha} = \frac{\langle \phi_k^+ | H_{\rm so}^{\alpha} | \phi_j^- \rangle}{\Delta_{jk}}.$$
 (7.64)

Here we have defined the energy differences of the zero-order states with energies E_l and E_n according to the convention $\Delta_{ln} = E_l - E_n$.

The mixing terms will have approximate magnitudes $b^{\alpha}, d^{\alpha} \approx \zeta/\Delta_{\rm LF} \approx 0.1$, where $\Delta_{\rm LF}$ is the LF energy splitting, and $c^{\alpha}, e^{\alpha} \approx \zeta/\Delta_{\rm ex} \approx 0.1$, where $\Delta_{\rm ex}$ is the exchange splitting.

Spin and Orbital Moments and Spin–Orbit Energy

By use of the wavefunctions in (7.61) and (7.62) the spin and orbital moments and their anisotropy may now be calculated. The matrix elements of the angular momentum operator L_{α} with the orbital parts of the wavefunctions are obtained from Table 7.11, the matrix elements of the spin operator S_{α} and the spin functions are given in Table 7.12.

The spin moment is created by the exchange interaction which leads to an unequal population of spin-up and spin-down states. It is defined as the expectation value of $S_{\tilde{z}}$. If for brevity we define the expectation values of the spin and angular momentum operators as unitless numbers so that we can ignore the factors of \hbar , we have

$$m_{s}^{\alpha} = -2\mu_{\rm B} \left\langle S_{\bar{z}} \right\rangle = -2\mu_{\rm B} \sum_{n} \left\langle \Psi_{n}^{\alpha} | S_{\bar{z}} | \Psi_{n}^{\alpha} \right\rangle$$
(7.65)

where the sum extends over *filled states*. We shall assume that there are N^+ filled spin-up states and N^- filled spin-down states. We obtain,

Table 7.12. Spin operators S_{α} ($\alpha = x, y, \text{ or } z$) acting on spin-states $\chi^{\pm} = \pm$, where we have assumed the quantization axis $\tilde{z} = z$. Eigenvalues are in units of \hbar

$S_x +\rangle = \frac{1}{2} -\rangle$	$S_y +\rangle =$	$\frac{i}{2}\left -\right\rangle$	$ S_z +\rangle =$	$\frac{1}{2}\left +\right\rangle$
$S_x - angle = \frac{1}{2} + angle$	$ S_y -\rangle = -$	$-\frac{i}{2}\left +\right\rangle$	$ S_z -\rangle =$	$-rac{1}{2}\left - ight angle$

$$m_{s}^{\alpha} = -2\mu_{\rm B} \left[\sum_{i}^{N^{+}} \langle \phi_{i}^{+} | S_{\bar{z}} | \phi_{i}^{+} \rangle + \sum_{i}^{N^{-}} \langle \phi_{i}^{-} | S_{\bar{z}} | \phi_{i}^{-} \rangle + \cdots \right]$$

$$= -2\mu_{\rm B} \left[\sum_{i}^{N^{+}} \langle + | S_{\bar{z}} | + \rangle + \sum_{i}^{N^{-}} \langle - | S_{\bar{z}} | - \rangle + \cdots \right]$$

$$\simeq \mu_{\rm B} \left[N^{-} - N^{+} \right] + O \left[(\zeta / \Delta_{\rm CF})^{2}, (\zeta / \Delta_{\rm ex})^{2} \right] .$$
(7.66)

This shows the expected result that the magnetic moment in first-order is given by the difference in spin-down and spin-up electrons. The second order terms enter through the spin-orbit coupling. The size of these contributions resulting from mixing of states of the same spins are of order $(b^{\alpha})^2 \simeq (d^{\alpha})^2 \simeq$ $(\zeta/\Delta_{\rm CF})^2$ and the mixed spin contributions $(c^{\alpha})^2$ and $(e^{\alpha})^2$ are of magnitude $(\zeta/\Delta_{\rm ex})^2$. Both are of the order of 1% and hence the spin moment remains isotropic to a good approximation. We shall see in Sect. 12.5.3 later that the higher order anisotropy in the spin moment is indeed very important in the context of anisotropic magnetoresistance.

We now calculate the angle dependent orbital moment m_o^{α} of the *d* shell along the principal Cartesian axes $\alpha = x, y$, or *z*. It is given by

$$\boxed{m_o^{\alpha} = -\mu_{\rm B} \left\langle L_{\alpha} \right\rangle = -\mu_{\rm B} \left\langle \sum_n \left\langle \Psi_n^{\alpha} | L_{\alpha} | \Psi_n^{\alpha} \right\rangle \right]}.$$
(7.67)

An orbital moment exists if there is a net orbital current from the d electron motion around the nucleus. This requires time reversal symmetry to be broken so that the motion of the orbiting electron, on average, is larger in one direction than the opposite direction. In magnetic materials the symmetry breaking is caused by the SO coupling. The d electron orbits may be anisotropic by bonding alone (e.g., the orbits may be confined to the x-y plane) but without SO coupling they will possess time reversal symmetry (e.g., an in-plane current giving rise to an orbital moment along +z will be cancelled by the opposite current, giving rise to a moment in the -z direction). We see from these considerations and (7.67) that the size of the orbital moment in different directions depends on two ingredients: the d electron bonding (i.e., the LF symmetry) contained in the wavefunctions Ψ_n^{α} and the size of the SO coupling given by the parameter ζ .

By use of the functions in (7.61) and (7.62) and the notation $\chi^{\pm} = \pm$ of Table 7.12 we can evaluate (7.67) to first-order

$$\langle L_{\alpha} \rangle = 2 \zeta \sum_{n,m,j} \langle \chi^{j} | S_{\tilde{z}} | \chi^{j} \rangle \frac{|\langle \phi_{n}^{j} | L_{\alpha} | \phi_{m}^{j} \rangle|^{2}}{\Delta_{nm}}$$

$$= \zeta \sum_{n,m} \frac{|\langle \phi_{n}^{+} | L_{\alpha} | \phi_{m}^{+} \rangle|^{2}}{\Delta_{nm}} - \frac{|\langle \phi_{n}^{-} | L_{\alpha} | \phi_{m}^{-} \rangle|^{2}}{\Delta_{nm}} = \langle L_{\alpha}^{+} \rangle - \langle L_{\alpha}^{-} \rangle , \quad (7.68)$$

where the sum extends over filled states n and empty states m within the spin-up and spin-down manifolds (index j). Note that the coupling between pairs of filled (and empty) states does not need to be considered since the spin-orbit induced terms cancel each other for any pair. Also, to first order m_o^{α} does not depend on c^{α} , i.e., the mixing of spin-up and spin-down states by the SO interaction, since the relevant matrix elements $\langle d_n \chi^+ | L_{\alpha} | d_m \chi^- \rangle = 0$. According to (7.68) the orbital momentum is the sum of contributions from all filled states in the spin-up and spin-down sub-bands. If a sub-band is filled its contribution vanishes because of the perfect balance of contributions from states with +M and -M.

The angular momenta expectation values $\langle L_x \rangle, \langle L_y \rangle$, and $\langle L_z \rangle$ vanish for an empty or filled electronic shell with angular momentum quantum number L.

We note, that conventional electronic structure calculations underestimate the size of the orbital moment unless an orbital polarization term is included [334]. For a more (less) than half filled d shell m_s and m_o have the same (opposite) sign, i.e., are parallel (antiparallel) according to Hund's rule.

Similarly, we can derive from the general forms of the spin–orbit Hamiltonian given by (7.55) the angle-dependent spin–orbit energy. It is given by

$$\langle H_{\rm so}^{\alpha} \rangle = \frac{\zeta^2}{4} \sum_{n,m,j} \frac{|\langle \phi_n^j | L_{\alpha} | \phi_m^j \rangle|^2}{\Delta_{nm}} + \sum_{n,l,j,j'} \frac{|\langle \phi_n^j | H_{\rm so}^{\alpha} | \phi_l^{j'} \rangle|^2}{\Delta_{nl}} = E_{jj}^{\alpha} + E_{jj'}^{\alpha} , \quad (7.69)$$

where the terms E_{jj}^{α} and $E_{jj'}^{\alpha}$ represent the contributions from states of the same and opposite spin, respectively, and the sums extend over filled states (n, j) and empty states (m, j) and (l, j'). For $E_{jj'}^{\alpha} = 0$ we obtain

$$\langle H_{\rm so}^{\alpha} \rangle = E_{jj}^{\alpha} = \frac{\zeta}{4} \left(\langle L_{\alpha}^{+} \rangle + \langle L_{\alpha}^{-} \rangle \right) , \qquad (7.70)$$

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showing the direct correlation between the orbital moments of the spin-up and spin-down manifolds and the spin-orbit energy. Note that the contributions of the spin-down states, $\langle L_{\alpha}^{-} \rangle$, enter with opposite signs in the expressions for the orbital moment (7.68) and the spin-orbit energy (7.70). In general, we therefore obtain a direct proportionality between the orbital moment and the spin-orbit energy only if $\langle L_{\alpha}^{-} \rangle = 0$, i.e., if the spin-down band is full. In the limit of a vanishing exchange splitting the orbital moment vanishes $(\langle L_{\alpha}^{+} \rangle = \langle L_{\alpha}^{-} \rangle)$, and so does the spin-orbit energy $(E_{jj}^{\alpha} = -E_{jj'}^{\alpha})$.

Origin of Orbital Moment Anisotropy

The origin of the orbital magnetic moment and its anisotropy is illustrated in Fig. 7.38 by means of a perturbation picture [333]. In 3d transition metals the

d shell is split by bonding effects into d-orbitals with a large energy separation (\approx 1eV at high symmetry points in the BZ). Let us for simplicity assume that the magnetic exchange splitting is large and all spin-down states are full so that we only need to consider the partially filled spin-up shell [332]. The pure d orbitals shown (e.g., at a high symmetry point in the BZ) possess no orbital moment (which is said to be "quenched") since the d orbitals have a perfect balance of $\pm M$ states (or have M = 0). The effect of the smaller spin-orbit interaction ($\zeta \approx 0.05 \,\mathrm{eV}$), which can be treated by perturbation theory, is a mixing of the pure or zero-order d orbitals, creating new first-order states which have anisotropic orbital momenta as shown.

The small *spin-orbit interaction* recreates the orbital momentum that was destroyed by the LF.

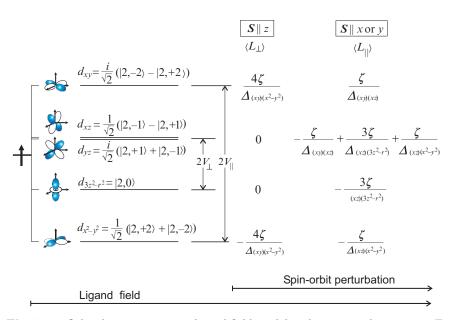


Fig. 7.38. Orbital momentum in a ligand field model with tetragonal symmetry. For simplicity we assume that the magnetic exchange splitting is large and we consider only states of one spin. Band structure or ligand field effects result in d orbitals which are linear combinations of functions $|L, M\rangle$ ($-2 \leq M \leq +2$). The inclusion of the spin–orbit interaction in lowest order perturbation theory results in new states which have anisotropic orbital momenta (units \hbar) as shown, where ζ ($\sim 0.05 \text{ eV}$ for the 3d transition metals) is the spin–orbit coupling constant and $\Delta_{(i)(j)} \approx 1 \text{ eV}$ is the energy separation (taken positive) between a higher energy state i and a lower state j. The indicated orbital momenta for spin alignment $\mathbf{S}||z$ and $\mathbf{S}||x$ or y result from mixing of the spin-up states, only. Note that the total orbital momentum (sum) vanishes if all states are empty or full

The orbital momentum of a state $|n\rangle$ is given by the first-order perturbation expression (7.68) which takes the form

$$\langle L_{\alpha}^{n} \rangle = \zeta \sum_{m} \frac{|\langle d_{n}^{+} | L_{\alpha} | d_{m}^{+} \rangle|^{2}}{\Delta_{nm}} , \qquad (7.71)$$

where the sum is over all other zero-order spin-up states d_m^+ and $\Delta_{nm} = E_n - E_m$ is the energy separation of two states. The matrix elements of the angular momentum operators L_{α} can be calculated by use of Table 7.11. The size of the orbital momenta is of order $\zeta/\Delta_{nm} \approx 0.1$, or about 5–10% of the size of the spin moment.

We see from Fig. 7.38 that for each orbital the orbital moment is anisotropic. This anisotropy as well as the orbital moment for each direction vanishes if a sum is performed over all states, as discussed earlier. In transition metals the *d* shell is only partly filled and the total orbital momentum is given by the sum over all *filled* states $|n\rangle$. This explains why in practice, a finite orbital moment with a finite anisotropy is obtained for Fe, Co, and Ni.

Let us explore the above model for the case of a Co monolayer which has approximately 7.5 d electrons [333, 335]. The majority band is full and we therefore only need to consider the half filled minority band (2.5 electrons). It may be separated into contributions from in-plane and out-of-plane d states, as shown in Fig. 7.39a. For the free layer the in-plane band width is larger because of the preferential in-plane bonds between the Co atoms and the empty and filled states have an average separation $2V_{\parallel}$. The narrower band of the out-of-plane d orbitals has an average separation between the empty and filled states of $2V_{\perp}$. In accordance with Fig. 7.36 the band picture may be represented by a ligand field model where the in-plane and out-of-plane dorbitals are separated by $2V_{\parallel}$ and $2V_{\perp}$, respectively. In order to account for the fact that in the Brillouin zone the orbital scheme can also be turned upside down as illustrated in Fig. 7.36, we need to average over two cases, indicated by wavevectors (\mathbf{k}_1 and \mathbf{k}_2) in Fig. 7.39a, where the empty and filled d orbitals are exchanged.

The anisotropies for the orbital moment m_o^{α} ($\alpha = \perp, \parallel$) are plotted in Fig. 7.39b. We see the preference for an in-plane easy axis for $V_{\parallel} > V_{\perp}$, revealed by the fact $m_o^{\parallel} > m_o^{\perp}$, and for an out-of-plane easy axis for $V_{\perp} > V_{\parallel}$. Our results confirm the expectations based on the simple model shown in Fig. 7.35. The in-plane easy axis predicted for a free Co layer is in good accord with the results of a first principles calculations [335]. The preferred out-of-plane orbital moment direction also supports experimental results and first principles theory [336] for a Au/Co/Au sandwich. More details may be found in reference [333].

In summary, we have seen that the origin of the magnetocrystalline anisotropy is somewhat tricky and involves an interplay between the exchange interaction, the ligand field and the spin–orbit interaction. Given the exchange and ligand field interactions, the spin–orbit interaction can be regarded as the origin of the magnetocrystalline anisotropy. This may be stated in short as follows.

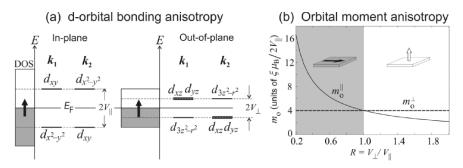


Fig. 7.39. (a) Schematic model for the density of minority spin states for a free Co monolayer. The majority band is full and the minority band, responsible for the orbital moment, is half filled. As in Fig. 7.36 the band picture may be represented by a ligand field model where the in-plane and out-of-plane d orbitals are separated by $2V_{\parallel}$ and $2V_{\perp}$, respectively. The average over the Brillouin zone is done by averaging over two points, $(\mathbf{k}_1 \text{ and } \mathbf{k}_2)$, where the empty and filled d orbitals are exchanged. (b) Calculated in-plane (m_o^{-}) and out-of-plane (m_o^{-}) orbital moments as a function of $R = V_{\perp}/V_{\parallel}$. The easy magnetization direction lies in-plane for R < 1 (shaded region), as indicated by the icons in the plot and out-of-plane for R > 1. Results taken from reference [333]

In magnetic materials the *exchange interaction* creates the spin moment and the *ligand field* creates anisotropic d orbitals. The spin–orbit coupling forms the link between the spin system and the orbital system by creating an orbital moment that is locked into a particular lattice direction.

Experimental Verification of the Model

Experimental support for our simple model of the microscopic origin of the magnetocrystalline anisotropy is presented in Fig. 7.40 for a Co wedge grown between Au layers [328, 333]. As shown in (a), the wedge sample consisted of ten Co terraces of 2 mm length and 10 mm width and a thickness ranging from 3 to 12 atomic Co layers. The Co was grown on a thick Au (111) buffer layer that was deposited on a float-glass substrate, and was capped for protection with a Au layer of about 9 atomic layers thickness. The wedge was characterized by means of magnetooptical Kerr effect measurements [333] which showed an out-of-plane easy axis at the thin end and an in-plane easy axis at the thick end of the wedge.

Figure 7.40b shows the anisotropy of the orbital moment m_o determined by means of angle dependent XMCD measurements. The circularly polarized X-ray beam (spot size <1 mm) with a fixed helicity was positioned on a Co terrace and on each terrace two measurements were made. First both the Xray helicity (angular momentum) and the external magnetic field that was

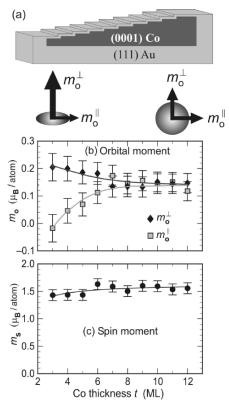


Fig. 7.40. (a) Schematic of the investigated Au/Co-staircase/Au sample with a Co thickness ranging from 3 to 12 monolayers (ML). The sample showed a perpendicular easy axis at small Co thickness and an out-of-plane easy axis for thick Co layers. The easy axis is determined by the preferred direction of the anisotropic orbital moment as illustrated schematically later. This anisotropy was directly determined by XMCD as shown underneath. (b) Orbital moments m_o^{\perp} and m_o^{\parallel} determined by XMCD as a function of Co thickness. (c) The spin moment m_s determined by angle-averaged XMCD. The net spin moment decreases with decreasing Co thickness, due to a drop in Curie temperature. Taken from [328, 333]

used to saturate the sample, were oriented perpendicular to the surface. In a second measurement both were oriented nearly parallel to the surface. The respective orbital moments m_o^{\perp} and m_o^{\parallel} derived from the data are plotted in Fig. 7.40b. When the Co layer is thin there is a large anisotropy in the orbital moment with $m_o^{\perp} > m_o^{\parallel}$. It vanishes when the Co thickness exceeds about 8 monolayers. In contrast, the spin moment is nearly constant. Since the measurements were done at room temperature the slight drop at the smallest

Co thickness is most likely due to a reduced Curie temperature (finite size effect).

Above the experimental results we illustrate schematically how the magnetic anisotropy of the sample can be understood by means of the orbital moment anisotropy. At the thick end of the wedge the orbital magnetic moment is nearly isotropic. Here, the overall in-plane anisotropy of the sample is simply due to the macroscopic shape anisotropy, which will be discussed in more detail in Sect. 11.2.1. Because it is due to the dipolar coupling of atomic moments and because the size of the total atomic moment is dominated by the spin moment, one may regard the shape anisotropy as a macroscopic spin-spin dipolar anisotropy. With decreasing sample thickness, the average symmetry of the Co atoms becomes increasingly anisotropic. At the thin end of the wedge the anisotropy of the orbital moment has become so large that it has a strong preference for a perpendicular orientation. Now there are two opposing forces acting on the spin moment. The dipolar field wants to rotate it in-plane and the spin–orbit coupling wants to rotate it parallel to the out-of-plane orbital moment (Hund's third rule). The easy axis is determined by which of the two forces is stronger, i.e., whether the dipolar energy is smaller or larger than the anisotropy of the spin-orbit energy. Clearly, at the thin edge of the wedge the anisotropy energy associated with the spin-orbit interaction exceeds the value of the shape anisotropy and we have the interesting situation that the small orbital moment redirects the larger spin moment into a perpendicular alignment.

It is important to note that the magnetocrystalline anisotropy energy values derived from the measurement of the anisotropy of the orbital moment by XMCD are significantly larger than the energies measured with conventional methods. The origin for these discrepancies are not understood [333].

Polarized Electrons and Magnetism

8.1 Introduction

The central cornerstone of magnetism is the quantum theoretical concept of the spin. It first revealed itself in the Stern–Gerlach experiment discussed in Sect. 3.5.1 and in atomic emission spectra, as discussed in Sect. 6.3.1. We have also discussed in Chap. 7 the fundamental role the electron spin has played in the magnetic structure of matter. Today one of the most prominent research topics in magnetism deals with the generation of spin polarized electrons and their transmission or transport through matter. Such studies cover a broad range of topics such as the creation of spin-modulated electron beams in vacuum and their transmission and reflection by magnetic materials, the excitation and switching of the magnetization in metals by "spin torques" associated with injected spin polarized currents, the optical excitation and orientation of spin polarized electrons in semiconductors, the spin-dependent transport from metals to semiconductors, the tunneling of spin-polarized electrons through insulators, all the way to finding ways of encoding information in quantized spin states for the futuristic concept of quantum computing.

This chapter specifically addresses the creation of free spin-polarized electron beams with kinetic energies of several eV above the Fermi level, so called ballistic electrons, and their interactions with a magnetic material. Over the years such studies have provided a wealth of information. For simplicity we shall discuss here transmission experiments through a thin magnetic foil. Such experiments are important for three reasons. First, they have a resemblance to those performed with light, namely Faraday and Kerr effect measurements. Second, they contain specific information on the *energy and angular momentum transfer* between the polarized electrons and the sample, which is of great importance in the switching dynamics of magnetic bits, as discussed in Chap. 15. Third, the concepts underlying "beam" studies are closely related to those underlying spin transport through matter involving spin-polarized electrons with kinetic energies near the Fermi energy, as discussed later in Chap. 14.

8

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Possibly the most important result that has emerged from spin-polarized beam studies is the fact that they jointly with spin-dependent transport measurements support the so-called *two current model*, a cornerstone of modern spintronics. This shows that this model is valid for kinetic energies ranging from the diffusion (Fermi level) to the ballistic regime (several eV above $E_{\rm F}$). The model, reviewed in detail in Sect. 12.5.2, states that electrons with spin parallel and antiparallel to the magnetization direction form two distinct channels that carry the current in parallel yet are subject to different resistivities.

It is this concept that leads to dramatic effects when the magnetization changes abruptly at the interface between two different materials, as discussed in Chap. 14. Prominent examples are the giant magnetoresistance (GMR) effect [79–81], the tunneling magnetoresistance effect [337], the spin torque effect during spin injection [84, 85], and the spin transport across metal– semiconductor interfaces [78]. Through the technological use of the GMR effect in magnetic recording today, the direction quantization of the electron spin has thus moved from its discovery by Stern and Gerlach and a theoretical physics concept to a cornerstone of modern technology, allowing the efficient reading of magnetic memories with ever increasing capacity.

In this chapter we will develop the tools for a quantum mechanical description of spin-polarized electron beams and their interaction with matter. Such experiments became possible by the invention of the laser in the late 1950s [47] and the invention of the spin-polarized electron gun in the mid 1970s [73]. After reviewing the generation of spin-polarized electron beams, we will show how nonrelativistic polarized electrons are described by the Pauli spinor formalism. Key to the understanding of polarized electron beams is the counter-intuitive quantum mechanical concept of *self-interference*. It is based on the description of one single electron by a superposition of two phasecoherent partial wave functions, one for "spin up" and one for "spin down," as already discussed in conjunction with the Stern–Gerlach experiment in Sect. 3.5.1. The coherent superposition of the partial wave functions then affects the transmission of spin-polarized electrons through matter, based on preferential scattering of electrons in one of the two channels.

In the process we shall encounter that the same partial wave formalism can also be used for the description of polarized X-rays. In the case of photons, this leads to the well-known magneto-optical Faraday and Kerr effects. In particular, the precession of the electron spin about the magnetization axis of a ferromagnet and its relaxation into the axis will be shown to be formally analogous to the magneto-optical effects with photons.

8.2 Generation of Spin-Polarized Electron Beams

8.2.1 Separation of the Two Spin States

In order to study the interaction of spin-polarized electrons with a magnetic material, one must have a suitable source of spin-polarized electrons, that is a source of electrons whose spins point preferentially into a predetermined direction in space. A detector for the spin polarization is required as well. Both tools, source and detector of spin polarization, involve spatially separating the two spin states. A device that can produce spin polarization is, at least in principle, also suitable to detect it, in close analogy to polarized light optics.

In the famous Stern–Gerlach experiment discussed in Sect. 3.5.1, the two spin states of the unpaired valence electron of the *charge-neutral* Ag-atom were separated in an inhomogeneous magnetic field. However, there is no classical method to spatially separate the two spin states of the *free* electron in macroscopic fields due to the overwhelming effect of the Lorentz force acting on the charge of the moving electron as discussed in detail by Kessler [131]. Yet a large variety of approaches based on quantum mechanics may be used to produce and detect spin-polarized electrons.

Natural sources of polarized electrons are the ferromagnets from which polarized electrons may be extracted in photoemission or with some caution also in tunneling. But the ferromagnetic sources have the disadvantage that in order to switch the spin direction, the magnetization of the cathode must be inverted. This disturbs, if only slightly, the emerging electron beam due to residual stray magnetic fields present at ferromagnetic cathodes. A comparison and review of different spin-polarized electron sources has been given by Pierce [338]. The ferromagnets may also be used for detecting electron spin polarization through the spin-dependence of the transmission or reflection process [339]. Classical reviews or books on polarized electrons reflecting the fast historical development are due to Tolhoek [133], Farago [340], Kessler [131], Pierce and Celotta [341], Siegmann, Meier, Erbudak, and Landolt [342], Feder [343], Kirschner [344], and Makdisi, Luccio, and MacKay [345].

Today, most polarized electron sources are based on photoemission of electrons from GaAs-type semiconductors. GaAs is a nonmagnetic semiconductor, but one can extract large currents of spin-polarized electrons from it with the help of circularly polarized infrared radiation. This source is based on *optical spin orientation* which is not limited to semiconductors or insulators but may be applied equally well to metals as described in detail by Meier and Zakharchenya [346]. Optical pumping and related phenomena are also key to the emerging field of spin electronics [78, 115]. Below we shall discuss the principle of the GaAs source.

8.2.2 The GaAs Spin-Polarized Electron Source

GaAs is isoelectronic with Ge (Z = 32), that is, it has a direct band gap centered at the Γ -point in the Brillouin zone where the electronic wave vector vanishes (k = 0). This means that the electrons at the top of the fully occupied valence band are localized between the sites of the As atoms (Z = 33)and the electrons at the bottom of the conduction band are localized on the

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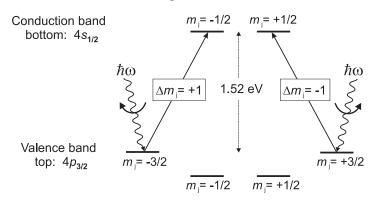


Fig. 8.1. Optical spin orientation induced by transitions across the band gap in GaAs-type semiconductors. The transitions shown occur with left $(\Delta m_j = -1)$ and right $(\Delta m_j = +1)$ circularly polarized light, at a photon energy close to the band gap. The crystal field of cubic GaAs is distorted by epitaxial growth on a mismatched substrate leading to the energy difference of ~0.1 eV between $m_j = \pm 3/2$ and $m_j = \pm 1/2$ sublevels

site of the Ga atoms (Z = 31). The electrons are then able to undergo direct vertical transitions from the top of the valence band to the bottom of the conduction band. The valence band is built from the atomic 4p-wave functions of As, which are split by the spin-orbit coupling into $4p_{1/2}$ and $4p_{3/2}$ states with an energy separation of ~0.34 eV. The bottom of the conduction band is composed of the atomic 4s-functions of Ga, giving rise to a $4s_{1/2}$ state. By choosing the photon energy close to the band gap energy of 1.5 eV, one can suppress the higher energy transitions $4p_{1/2} \rightarrow 4s_{1/2}$. The electronic transitions induced by a photon of energy close to the energy of the band-gap involve the energy levels shown in Fig. 8.1.

The $4p_{3/2}$ state is fourfold degenerate, consisting of substates with magnetic quantum numbers $m_j = -3/2, -1/2, +1/2, +3/2$. These levels are degenerate in energy in the electric field near the center of the Brillouin zone of a cubic crystal. The different angular momenta of linear polarized $(L_z = 0)$ photons and circularly polarized photons with positive (RCP, $L_z = +\hbar$) and negative (LCP, $L_z = -\hbar$) angular momentum allow only transitions between states with specific differences in magnetic quantum numbers. In particular, conservation of angular momentum in the absorption of circularly polarized light requires $\Delta m_j = \pm 1$. With LCP light, for instance, only transitions with $\Delta m_j = -1$ are allowed so that in cubic GaAs only the transitions $4p_{3/2}(m_j = +3/2) \rightarrow 4s_{1/2}(m_j = +1/2)$ and $4p_{3/2}(m_j = +1/2) \rightarrow 4s_{1/2}(m_j = -1/2)$ can occur. Therefore, both spin states will be present in the conduction band. But the transition probability for the sublevel $m_j = 3/2$ is three times larger compared to the transition probability for the sublevel $m_j = 1/2$ because its component along the photon angular momentum is three times larger (also see

Fig. 9.15). Therefore, with undisturbed cubic GaAs, one obtains the degree of spin polarization P = (3 - 1)/(3 + 1) = 0.5. The preferred direction of the spin is parallel or antiparallel to the direction of the circularly polarized light beam.

But almost completely spin-polarized electrons can also be obtained. The case of P = 1 is illustrated in Fig. 8.1. By distorting the cubic crystal field in GaAs through epitaxial growth on a lattice mismatched substrate one can destroy the spherical symmetry of the crystal field and the energy of the states with $m_j = \pm 3/2$ increases compared to those with $m_j = \pm 1/2$ by $\sim 0.1 \text{ eV} [347]$.¹ By tuning the photon energy to the very edge of the band gap, one can now produce fully polarized spin-up or spin-down electrons in the conduction band by simply switching between RCP and LCP light. One additional important feature of the GaAs-source is that the surface can be made with negative electron affinity by a delicate treatment with cesium and oxygen. Negative electron affinity means that the electrons at the bottom of the conduction band can escape into vacuum without further supply of energy.

Besides enabling important applications in magnetism to be discussed later, the invention of the spin-polarized electron source has been of great interest in high energy physics. With a spin modulated electron beam from a GaAs-type of electron source it is possible to detect even very tiny spin dependent effects in electron interactions. It has thus been possible to measure the spin asymmetry of 10^{-5} in the scattering of 20 GeV polarized electrons on deuterium due to the parity violation in the electroweak interaction [75, 76]. In later developments at the Stanford Linear Accelerator Center (SLAC) a stressed GaAs photocathode has delivered electron beams with a spin polarization of |P| = 0.85 at an intensity of 1,000 A. With this source, spin dependent effects can be determined at the 10^{-8} level, an almost incredible achievement of great value for the study of mirror asymmetry or parity violation in high energy interactions [348]. Recently, this has been used to determine the parity violation in electron/electron scattering providing the first measurements of the weak charge of the electron [349]. At even higher, teravolt, electron energies polarized electrons are envisioned to collide head-on with positrons resulting in a complete spin asymmetry. Figure 1.11 in Chap. 1 shows the structure and performance of a strained superlattice cathode delivering almost completely polarized electrons of crucial importance for the realization of ILC.

¹The origin of the splitting can be understood with help of Fig. 9.21. In cubic symmetry the four states $m_j = -3/2, -1/2, +1/2, +3/2$ are degenerate and the sum of the orbital densities is spherically symmetric. In lower symmetry, the resulting states can no longer be spherically symmetric, so that we obtain a splitting between the $m_j = \pm 3/2$ and $m_j = \pm 1/2$ substates which have distinctly different orbital densities.

8.3 Spin-Polarized Electrons and Magnetic Materials: Overview of Experiments

The general principle of studies of magnetic materials with spin-polarized electrons is shown in Fig. 8.2. The electron beam from the GaAs-type source is spin modulated, that is it produces a spin polarization that switches its direction periodically from up to down as the polarization of the light is varied from right to left circularly polarized. This allows one to selectively detect the effects that depend on spin direction even on a large background of spin independent interactions. The spin modulated, monochromatic electron beam is incident on a sample that is magnetized in a particular direction, either in- or out-of-plane. The detected signal consists of the reflected or scattered electron current, the absorbed current or the transmitted current (assuming a thin film sample). The spin polarization of the detected signal may be analyzed as well. One method to measure the spin polarization, Mott-scattering, has already been discussed in Sect. 3.5.2. Other spin detection schemes will emerge when we discuss the transmission or reflection of electrons with magnetic materials in Sects. 12.6 and 13.3. For inverse photoemission experiments (IPE), an energy resolving photon detector with sensitivity in the ultraviolet range may be used.

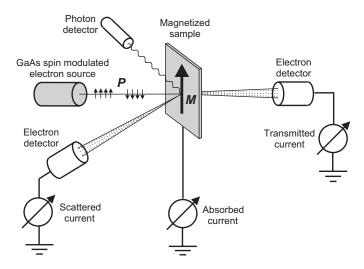


Fig. 8.2. Principle of experiments with spin-polarized electrons on magnetic materials. A monochromatic spin modulated electron beam emerges from the GaAs source and hits the magnetic sample. The spin polarization vector P can be parallel, antiparallel, or perpendicular to the magnetization M. With P parallel or antiparallel to M, one observes the spin asymmetries A of the transmitted, absorbed, and the reflected current. With $P \perp M$ one detects the motion of P relative to M. Inverse photoemission (IPE), based on the detection of the photons that are emitted when an injected excited electron makes a transition to the lower-energy unoccupied states near the Fermi-energy $E_{\rm F}$, detects the spin polarization of the unoccupied electron states

There are also a number of additional, equally important experiments not indicated in Fig. 8.2 where the incident electron or photon beam is *unpolarized* and spin-polarized photoelectrons, secondary electrons, or Auger-electrons are analyzed [350, 351]. Some of these will be discussed in detail in Sects. 12.6 and 13.3.

Experiments with spin-polarized beams have generated a wealth of new knowledge but their applications in magnetism have by no means been fully exploited. Opposite to high energy physicists, solid-state experimentalists have so far contented themselves with a spin sensitivity of 10^{-3} . The spin dependencies in magnetism are generally much larger compared to high energy physics interactions, approaching unity for instance in some transmission or reflection experiments [352]. This implies that only one spin state is transmitted through or reflected from a ferromagnet under certain conditions. In general, the interaction of polarized electrons with magnetic materials depends on the exchange interaction and on spin-orbit coupling. Luckily, it is possible to separate these two interactions due to their different symmetry.

8.4 Formal Description of Spin-Polarized Electrons

8.4.1 Quantum Behavior of the Spin

According to the fundamental postulate of quantum mechanics, a wave function Ψ is associated with any particle of linear momentum p and energy E. Ψ is a function of the position coordinates r and the time t according to

$$\psi(\boldsymbol{r},t) = C \,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\boldsymbol{r}-\omega t)},\tag{8.1}$$

where C is a constant. The frequency of the wave is given by the energy E according to $E = \hbar \omega$ and the wave vector \mathbf{k} by the linear momentum $\mathbf{p} = \hbar \mathbf{k}$. The *phase velocity* of the wave is given by ω/k .

Electrons never obey Newtonian mechanics. At low energies, they have to be treated with wave mechanics and at high energies where a trajectory can be defined because the de Broglie wavelength $\lambda = 2\pi/k$ is small, they are relativistic. Since we are dealing with solid-state physics, we limit the description of spin to nonrelativistic electrons. In that case, the spatial part given by (8.1) and the spin part of the wavefunction, χ , can be separated so that the total wave function is given by

$$\psi(\boldsymbol{r}, t, \boldsymbol{s}) = \chi \ C \ e^{i(\boldsymbol{k}\boldsymbol{r} - \omega t)}.$$
(8.2)

If a difference in energy exists between the two spin states of the electron due to a magnetic field or an effective magnetic field so that $\Delta E = E^{\uparrow} - E^{\downarrow} \neq 0$, the two spin states travel with a different phase velocity.

The essence of the following sections is the description of the quantum mechanical behavior of individual spin-polarized electrons and an ensemble

or beam of spin-polarized electrons, and the description of their interaction with magnetic materials. We have seen that the quantum behavior manifests itself in the concept of two distinct spin states, up and down relative to a quantization direction. This cannot be explained by classical vector concepts for the spin. Hence in the general description of spin-polarized electrons we have to allow for the possibility that each electron may have a finite probability in the up and down direction. The basis for this description was developed by Pauli, and we shall discuss it below.

When the individual electrons are assembled into a beam, we also need to use a quantum description for the beam which is based on that of the individual electrons. It turns out that this is conveniently done by introduction of a spin polarization vector \boldsymbol{P} for the beam. It is defined so that its components P_{ξ} ($\xi = x, y, \text{ or } z$) are determined by the number of up and down spins along the direction ξ , called the quantization axis. The vector \boldsymbol{P} and the number of electrons completely describe the beam.

The task of spin-polarized electron physics is then the description of how the spin polarization vector \boldsymbol{P} and the number of electrons change as the electrons traverse a magnetic thin film sample with well defined magnetization direction. In particular, we would like to understand the physics behind a simple question: If a beam of n electrons, described by a spin polarization \boldsymbol{P} traverses a sample with a magnetization \boldsymbol{M} oriented at an angle from \boldsymbol{P} , what will be the number of electrons n and the direction of \boldsymbol{P} when the electron beam emerges from the sample?²

8.4.2 Single Electron Polarization in the Pauli Spinor Formalism

We shall now explain how this problem can be treated by means of the Pauli spinor formalism. We note upfront that this formalism may also be used to describe magneto-optics as discussed in Sect. 8.7.2. The formalism uses the familiar Pauli *spinors* and *spin matrices* for the description of the spin of nonrelativistic electrons. We start with the case of a single electron.

The *spinor basis states* of a general spin wavefunction of a *single electron* are defined as follows,

$$\chi_{\rm up} = |\uparrow\rangle = |+\rangle = \begin{pmatrix} 1\\ 0 \end{pmatrix} \tag{8.3}$$

$$\chi_{\rm down} = |\downarrow\rangle = |-\rangle = \begin{pmatrix} 0\\1 \end{pmatrix} \tag{8.4}$$

²Note that for nonrelativistic electrons the motion due to the charge (Lorentz force) is decoupled from the motion of the spin. We therefore do not have to consider the actual path of the electrons but only what happens to the spins.

The two basis states represent the so-called *spinor field*. With this concept we may describe an electron with the spin in any direction in space by a linear combination of the two spin states according to (3.25) as

$$\chi = u_1 \begin{pmatrix} 1\\0 \end{pmatrix} + u_2 \begin{pmatrix} 0\\1 \end{pmatrix} = \begin{pmatrix} u_1\\u_2 \end{pmatrix} .$$
(8.5)

Per definition, $\chi^* = (u_1^*, u_2^*)$ and $\chi^* \chi = (u_1^*, u_2^*) {u_1 \choose u_2} = u_1^* u_1 + u_2^* u_2$. With the normalization condition $\chi^* \chi = 1$, there are still three free parameters in the choice of the complex numbers u_1 and u_2 . These free parameters can be used to define the direction of the spin in space. In the following we shall follow the convention of defining the z-axis of a Cartesian coordinate system as the quantization axis. The expectation values of the direction of the spin along the x, y, z axes are then given as the expectation values of the *Pauli spin matrices*

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
 $\boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. (8.6)

We obtain the following expectation values for the spin direction:

$$\begin{split} \langle \boldsymbol{\sigma}_x \rangle &= \langle 2 \boldsymbol{s}_x \rangle = (u_1^*, u_2^*) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = (u_1^*, u_2^*) \begin{pmatrix} u_2 \\ u_1 \end{pmatrix} = u_1^* u_2 + u_2^* u_1, \\ \langle \boldsymbol{\sigma}_y \rangle &= \langle 2 \boldsymbol{s}_y \rangle = (u_1^*, u_2^*) \begin{pmatrix} 0 & -\mathbf{i} \\ \mathbf{i} & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = (u_1^*, u_2^*) \begin{pmatrix} -\mathbf{i} u_2 \\ \mathbf{i} u_1 \end{pmatrix} = \mathbf{i} [u_2^* u_1 - u_1^* u_2], \\ \langle \boldsymbol{\sigma}_z \rangle &= \langle 2 \boldsymbol{s}_z \rangle = (u_1^*, u_2^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = (u_1^*, u_2^*) \begin{pmatrix} u_1 \\ -u_2 \end{pmatrix} = u_1^* u_1 - u_2^* u_2. \end{split}$$

These three expectation values can now be used to define a three-dimensional vector which is called the vector of spin polarization,

$$\boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \langle \boldsymbol{\sigma}_x \rangle \\ \langle \boldsymbol{\sigma}_y \rangle \\ \langle \boldsymbol{\sigma}_z \rangle \end{pmatrix}, \qquad (8.7)$$

whose components represent the expectation values of the spin direction along the x, y, and z axes.

The two-dimensional spinor wavefunction χ describes the quantum behavior of a single spin. The corresponding three-dimensional polarization vector \boldsymbol{P} , which defines the spin direction in real space is given

$$\chi = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \to \boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} u_1^* u_2 + u_2^* u_1 \\ i [u_2^* u_1 - u_1^* u_2] \\ u_1^* u_1 - u_2^* u_2 \end{pmatrix}$$
(8.8)

with $u_1^* u_1 + u_2^* u_2 = 1$.

In particular we have:

$$\chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\1 \end{pmatrix} \to \boldsymbol{P} = \begin{pmatrix} 1\\0\\0 \end{pmatrix} \qquad \chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\-1 \end{pmatrix} \to \boldsymbol{P} = \begin{pmatrix} -1\\0\\0 \end{pmatrix},$$
$$\chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\i \end{pmatrix} \to \boldsymbol{P} = \begin{pmatrix} 0\\1\\0 \end{pmatrix} \qquad \chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\-i \end{pmatrix} \to \boldsymbol{P} = \begin{pmatrix} 0\\-1\\0 \end{pmatrix}, \qquad (8.9)$$
$$\chi = \begin{pmatrix} 1\\0 \end{pmatrix} \qquad \to \boldsymbol{P} = \begin{pmatrix} 0\\0\\1 \end{pmatrix} \qquad \chi = \begin{pmatrix} 0\\1 \end{pmatrix} \qquad \to \boldsymbol{P} = \begin{pmatrix} 0\\0\\-1 \end{pmatrix}.$$

For a single electron, |P| = 1 and the direction of the vector P is the direction of the electron spin. For the above six cases, the spin is aligned long the directions $\pm x, \pm y, \pm z$ of a Cartesian coordinate system, as illustrated in Fig. 8.3.

For a given polarization direction P in space one may use (8.8) to derive the complex coefficients u_1 and u_2 and the relative spin-up, $|u_1|^2$, and spindown, $|u_2|^2$, probabilities, where $|u_1|^2 + |u_2|^2 = 1$. This is best done by writing the complex quantities in the form $u_1 = \cos \alpha \exp[i\beta]$ and $u_2 = \sin \alpha \exp[i\gamma]$ that preserves the normalization. Since only the phase difference $\beta - \gamma$ is important we can choose $\gamma = 0$ so that

$$u_1 = \cos \alpha \, e^{i\beta}$$
$$u_2 = \sin \alpha \tag{8.10}$$

and the solution is given by

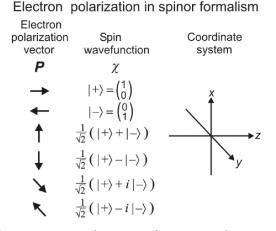


Fig. 8.3. Coordinate systems and spin wavefunctions in the spinor formalism. The picture is a graphical representation of the polarization states in (8.9). Note that for a nonrelativistic electron the electron position and electron spin functions are decoupled so that the spin is independent of the electron propagation direction

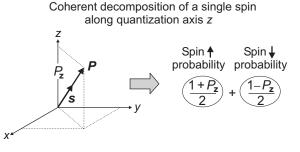


Fig. 8.4. Decomposition of a single spin with polarization vector $\mathbf{P}(|\mathbf{P}| = 2|\mathbf{s}| = 1)$ into two coherent components. By defining a quantization axis z, the spin wavefunction can be written in terms of two components, labelled spin-up (along +z) and spin-down (along -z), with probabilities $(1 + P_z)/2$ and $(1 - P_z)/2$, respectively

$$u_{1} = \sqrt{\frac{1+P_{z}}{2}} \exp\left[-i \arccos\left(\frac{P_{x}}{\sqrt{1-P_{z}^{2}}}\right)\right]$$
$$u_{2} = \sqrt{\frac{1-P_{z}}{2}}$$
(8.11)

with z being the quantization axis and $P_x^2 + P_y^2 + P_z^2 = 1$. We obtain the following result which is illustrated and summarized in Fig. 8.4.

For a single electron, the spin-up, $|u_1|^2$, and spin-down, $|u_2|^2$, probabilities along the quantization axis z can be expressed in terms of the projection P_z of the unit polarization vector **P** according to

$$|u_1|^2 = \frac{1+P_z}{2},$$

$$|u_2|^2 = \frac{1-P_z}{2}.$$
 (8.12)

For a nonrelativistic electron, \mathbf{P} can have any direction relative to the linear momentum \mathbf{p} . If \mathbf{P} is parallel to \mathbf{p} , we call the electron beam *longitudinally polarized*. If \mathbf{P} is perpendicular to \mathbf{p} , one speaks of a *transversely polarized* electron beam. One may rotate the spin by means of combined magnetic and electric deflections. For instance, if the electron beam is *longitudinally polarized* and deflected by an angle of 90° with an electric field, the spin polarization vector \mathbf{P} will keep its direction in space because of conservation of angular momentum and the resulting beam will be transversely polarized. If, however, the same longitudinally polarized beam is deflected by 90° with a magnetic field, the electron spin will precess about the perpendicular field direction by an angle very close to 90°, as well, and the beam will retain its state of

polarization. This is due to the fact that the Larmor frequency for the spin precession is almost equal to the electron cyclotron frequency according to (3.48).

8.4.3 Description of a Spin-Polarized Electron Beam

In practice, one does not deal with individual electrons but with a beam of spin-polarized electrons and the above formalism needs to be extended to many electrons which may have different spin directions. Classically one would define the spin polarization vector \boldsymbol{P} to be somehow proportional to the sum of the vectors of the individual spins $\sum_i \boldsymbol{s}_i$. This concept can also be used for a quantum mechanical ensemble of spins by proper definition of the proportionality factor. It is defined to give a special length for \boldsymbol{P} . If all individual electron spins point in the same direction and the beam is completely polarized, one defines $|\boldsymbol{P}| = 1$. The case where the individual spins point in different directions is described by $0 < |\boldsymbol{P}| < 1$ and such an ensemble is said to be in a *mixed spin state*. Because of this special normalization of \boldsymbol{P} a complete description of the beam also requires knowledge of the total number of electrons or spins in the beam. We can state as follows.

A spin-polarized electron beam is completely described by the number of electrons and the spin polarization vector \boldsymbol{P} . For a pure spin state $|\boldsymbol{P}| = 1$, for a mixed spin state $|\boldsymbol{P}| < 1$.

We now discuss how to determine P for a beam of spin-polarized electrons. As for a single electron, the spin polarization vector P is defined by its components according to

$$\boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix}.$$
(8.13)

The components may be obtained from the components u_1^i and u_2^i of the individual electrons *i* as follows. We label the quantization axis by the general index ξ , where ξ may be taken along either of the directions x, y, z of our Cartesian coordinate system. According to (8.4) and (8.5) each individual electron *i* may be described by a *coherent* superposition of two completely polarized electron states, a spin-up component $u_1^i \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ parallel to $+\xi$, and a spin-down component $u_2^i \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ parallel to $-\xi$. We can then describe the polarization of the entire electron beam along ξ by summing over the spin-up and spin-down *probabilities* of the individual electrons along the quantization axis ξ , given by (8.12) with P_z replaced by P_{ξ} . The sums of the respective spin-up and spin-down probabilities along the quantization axis are then given by

$$n^{\uparrow} = \sum_{i} |u_1^i|^2 \qquad n^{\downarrow} = \sum_{i} |u_2^i|^2.$$
 (8.14)

The sums therefore correspond to *incoherent* superpositions of the *coherent* polarization properties of the individual electrons and we can therefore describe a partially polarized ensemble of $N = n^{\uparrow} + n^{\downarrow}$ electrons by its *spin* polarization P_{ξ} along the quantization axis ξ , which is simply the sum of the spin up and down probabilities of the individual electrons according to

$$P_{\xi} = \frac{1}{N} \sum_{i}^{N} |u_1^i|^2 - |u_2^i|^2 . \qquad (8.15)$$

By use of the numbers of up n^{\uparrow} and down n^{\downarrow} (not necessarily integers) spins, where the total number of electrons is given by $n^{\uparrow} + n^{\downarrow}$ we have the following general result.

The degree of spin polarization of a beam of electrons relative to a quantization direction ξ is defined as

$$P_{\xi} = \frac{n^{\uparrow} - n^{\downarrow}}{n^{\uparrow} + n^{\downarrow}} , \qquad (8.16)$$

where \uparrow means in the direction of ξ (\downarrow along $-\xi$), so that $-1 \leq P_{\xi} \leq 1$ and $P_{-\xi} = -P_{\xi}$.

In practice, one does not define the *absolute* polarization direction of a beam but that *relative* to the magnetization direction \boldsymbol{M} of the sample. Since according to Sect. 7.4.2, \boldsymbol{M} always points into the direction of the *minority* spins, one uses the following definition for the spin polarization, defined in terms of the intensity $I^{\boldsymbol{P}\boldsymbol{M}}$, measured for parallel and antiparallel orientations of \boldsymbol{P} and \boldsymbol{M} . The intensity denoted $I^{\uparrow\uparrow} = I^{\downarrow\downarrow}$ is that for \boldsymbol{P} and \boldsymbol{M} pointing in the same direction, which we label I^{\min} . The intensity $I^{\uparrow\downarrow} = I^{\downarrow\uparrow}$ for \boldsymbol{P} and \boldsymbol{M} pointing in opposite directions is a measure of the beam polarization in the majority spin direction, labelled I^{\min} . Throughout this book we shall use the following convention for the discussion of experimental results.

In practice, the *spin polarization* of a beam is defined relative to the magnetization direction M of a sample, according to

$$P = \frac{I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}{I^{\uparrow\downarrow} + I^{\uparrow\uparrow}} = \frac{I^{\mathrm{maj}} - I^{\mathrm{min}}}{I^{\mathrm{maj}} + I^{\mathrm{min}}} .$$
(8.17)

P is *positive* if the beam is preferentially polarized in the *majority* direction, and P is *negative* if the polarization is mostly in the *minority* direction.

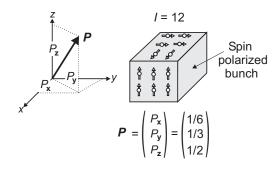


Fig. 8.5. Description of a spin-polarized electron beam by a polarization vector P. We assume 12 incident spin-polarized electrons, 6 polarized along z, 4 along y, and 2 along x, as shown. The components P_x , P_y , and P_z of the beam polarization vector P are calculated according to (8.16) with ξ along x, y, z

Example of a Spin-Polarized Beam

Let us use an example to familiarize ourselves with the concept of the polarization of a spin-polarized beam, according to (8.16). We assume an incident beam of 12 spin-polarized electrons as shown in Fig. 8.5 with 6 electrons polarized along z, 4 along y, and 2 along x. The components P_x, P_y , and P_z of the beam polarization vector \boldsymbol{P} are calculated according to (8.16) with ξ along x, y, z and we obtain the spin polarization vector shown in the figure, namely

$$\boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} 1/6 \\ 1/3 \\ 1/2 \end{pmatrix}.$$
(8.18)

We see that $|\mathbf{P}| \leq 1$ and the beam is therefore in a *mixed spin state*. This is expected, since the individual spins are not aligned in the same direction. In our Cartesian coordinate system x, y, z, the beam is completely described by its polarization vector \mathbf{P} and its intensity, given by the number of electrons.

For illustration purposes we have chosen in Fig. 8.5 a particularly simple example with the individual electron spin polarizations along the principal axes of our coordinate system, and we have chosen the number of electrons so that the number of electrons polarized along the principal axes comes out to be integer numbers. In general, the incident beam will contain spins of polarizations that are not parallel to the principal coordinate axes and one then needs to calculate the fractional spin-up and spin-down probabilities for each electron along the quantization axis ξ by means of (8.12) and (8.14).

A Related Formalism for the Description of P

An alternate way is to describe a polarized beam by a *polarization density* matrix given by [131, 133, 340]

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$$\hat{\boldsymbol{\varrho}} = \frac{1}{2} \begin{pmatrix} 1 + P_z & P_x - \mathrm{i}P_y \\ P_x + \mathrm{i}P_y & 1 - P_z \end{pmatrix}.$$
(8.19)

This formalism allows us to conveniently express the polarization vector P as the trace of the product of the Pauli spin matrices with the polarization density matrix as

$$\boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \operatorname{Tr}(\boldsymbol{\sigma}_x \hat{\boldsymbol{\varrho}}) \\ \operatorname{Tr}(\boldsymbol{\sigma}_y \hat{\boldsymbol{\varrho}}) \\ \operatorname{Tr}(\boldsymbol{\sigma}_z \hat{\boldsymbol{\varrho}}) \end{pmatrix}.$$
(8.20)

We shall use this formalism later.

8.5 Description of Spin Analyzers and Filters

8.5.1 Incident Beam Polarization: Spin Analyzer

To measure the polarization P of a beam one needs a spin analyzer. A spin analyzer consists of a spin filter and an electron detector, and one measures the preferential *transmission* of electrons polarized parallel ("spin-up") and antiparallel ("spin-down") to the maximum transmission direction of the spin filter. This direction then defines the quantization axis ξ .

A *spin analyzer* only measures intensities of "spin-up" and "spin-down" electrons relative to a quantization axis. It does not measure their phases.

In general, three parameters describe the properties of a spin analyzer.³

- A direction of maximum transmission, given by a unit vector \boldsymbol{e} in space.
- The transmission factor $T_R^{\max} \leq 1$ of electrons that are fully polarized (|P| = 1) along $e(P \parallel e)$.
- The transmission factor $T_R^{\min} \leq 1$ of electrons that are fully polarized (|P| = 1) along $-e (P \parallel -e)$.

In order to measure the polarization of the incident electron beam with an analyzer, one has to know the analyzer response. It is completely determined by the sum and the difference between the maximum and minimum transmission factors, defined as $T_R = 1/2 (T_R^{\max} + T_R^{\min})$ and $\Delta T_R = (T_R^{\max} - T_R^{\min})$. Choosing the ξ -axis parallel to e, the spin analyzer is described by the transmission filter matrix

$$\hat{\boldsymbol{F}} = T_R \begin{pmatrix} 1 + \frac{\Delta T_R}{2T_R} & 0\\ 0 & 1 - \frac{\Delta T_R}{2T_R} \end{pmatrix}.$$
(8.21)

³For a ferromagnetic spin filter we have defined e to point into the direction of the spin so that it is antiparallel to the magnetization M.

If we assume that T_R and ΔT_R are known, we can determine the polarization of the incident beam along ξ by two measurements. First, we measure the electron beam intensity, I, transmitted through the filter with $e \parallel \xi$, and second we remove the filter and measure the incident intensity, I_0 . If we denote the incident beam polarization density matrix by $\hat{\varrho}_0$ and write it in the coordinate system defined by the quantization axis ξ of the spin filter we have

$$\hat{\boldsymbol{\varrho}}_{0} = \frac{1}{2} \begin{pmatrix} 1 + P_{\xi}^{0} & P_{\eta}^{0} - iP_{\zeta}^{0} \\ P_{\eta}^{0} + iP_{\zeta}^{0} & 1 - P_{\xi}^{0} \end{pmatrix} .$$
(8.22)

where the axes η , ζ , and ξ form a right handed coordinate system. It turns out that we only have to know the projection P_{ξ}^{0} along the quantization axis, because the incident and transmitted intensities are determined by the relation,

$$\frac{I}{I_0} = \operatorname{Tr}(\hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}}) = T_R + \frac{P_{\xi}^0}{2} \Delta T_R . \qquad (8.23)$$

The polarization of the *incident beam* along $e \parallel \xi$ is given by

$$P_{\xi}^{0} = \left[\frac{I}{I_{0}} - T_{R}\right] \frac{2}{\Delta T_{R}} \qquad (8.24)$$

8.5.2 Transmitted Beam Polarization: Spin Filter

The transmitted beam also becomes polarized. If we describe the properties of the incident beam by the parameters $I_0, \hat{\varrho}_0, \mathbf{P}^0$ and use the labels $I, \hat{\varrho}, \mathbf{P}$ for the transmitted beam we have the following relation,

$$\hat{\boldsymbol{\varrho}} = \frac{\hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}}}{\mathrm{Tr}(\hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}})} = \frac{I_0}{I} \, \hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}}.$$
(8.25)

As an example, let us consider an incident *unpolarized* electron beam with $P^0 = 0$. It is described by the polarization density matrix

$$\hat{\boldsymbol{\varrho}}_0 = \frac{1}{2} \begin{pmatrix} 1 & 0\\ 0 & 1 \end{pmatrix}, \qquad (8.26)$$

so that we have $\hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}} = (1/2) \hat{\boldsymbol{F}}$. The transmitted intensity fraction is given by $I/I_0 = \frac{1}{2} \text{Tr}(\hat{\boldsymbol{F}}) = T_R$ and the transmitted polarization matrix and polarization vectors are

$$\hat{\boldsymbol{\varrho}} = \frac{1}{2} \begin{pmatrix} 1 + \frac{\Delta T_R}{2T_R} & 0\\ 0 & 1 - \frac{\Delta T_R}{2T_R} \end{pmatrix}, \qquad \boldsymbol{P} = \begin{pmatrix} 0\\ 0\\ \frac{\Delta T_R}{2T_R} \end{pmatrix}.$$
(8.27)

We see that the transmitted beam has acquired a polarization.

8.5.3 Determination of Analyzer Parameters

If one lets the electrons pass through the same spin filter twice, and starts with an unpolarized electron beam, one can calibrate the spin filter, that is one can determine T_{max} and T_{min} by experiment. This procedure has been used to calibrate the Mott polarization detector (Sect. 3.5.2) and is therefore referred to as the "double-scattering experiment" [131, 133]. Generally, the experimentally determined relative *P*-values may be quite accurate depending on the type of experiment and spin filter while the absolute *P*-values are often uncertain, typically within $\pm 5\%$.

8.6 Interactions of Polarized Electrons with Materials

8.6.1 Beam Transmission through a Spin Filter

In this Section we want to show by a simple example how a spin filter changes the polarization of a beam. For our example we use the special beam, illustrated in Fig. 8.5. In principle, we could just use the mathematical formalism developed in Sect. 8.5 to obtain the polarization and number of electrons of the transmitted beam through a chosen spin filter. We shall do so later after first taking a slightly different approach. It consists of using simple arguments to understand what happens to the beam as it traverses a perfect spin filter, which transmits all spins along the chosen spin filter direction ξ , and absorbs all spins polarized along $-\xi$.

We start by choosing ξ along the z-axis as shown in Fig. 8.6. The spin of each individual electron can now be decomposed into its two coherent components along the quantization axis z according to (8.12) or Fig. 8.4. The

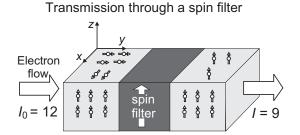


Fig. 8.6. Illustration of transmission of a spin-polarized beam through an ideal spin filter. We assume 12 incident spin-polarized electrons, as in Fig. 8.5. These electrons transverse an ideal spin filter with perfect transmission along +z and zero transmission along -z. The transmitted beam will be perfectly spin polarized along +z but its intensity will be reduced. While all electrons polarized along z are transmitted, only half of the electrons with spins aligned along x and y are transmitted according to the coherent decomposition (8.12) (also see Fig. 8.4)

6 spins along +z have probabilities $|u_1|^2 = 1$ (up-spin) and $|u_2|^2 = 0$ (downspin), those aligned along either x or y have probabilities $|u_1|^2 = 1/2$ and $|u_2|^2 = 1/2$. Hence for the shown spin filter direction the transmission is determined by the incoherent sum of the individual up-spin probabilities (see (8.14)) and we see that only 9 of the 12 electrons are transmitted. All transmitted electrons are perfectly polarized along +z, as shown.

If we turned the spin filter, so that it had perfect transmission along -z, only 3 of the 12 electrons would be transmitted and they would be spin-down. Similarly, if we aligned the spin filter along +y, we would obtain 8 electrons, spin polarized along y, after the filter, and so on.

Let us check our results by use of the formalism developed earlier. In our Cartesian coordinate system x, y, z, the incident beam of $I_0 = 12$ electrons is described by the polarization vector given by (8.18), i.e.,

$$\boldsymbol{P}^{0} = \begin{pmatrix} P_{x}^{0} \\ P_{y}^{0} \\ P_{z}^{0} \end{pmatrix} = \begin{pmatrix} 1/6 \\ 1/3 \\ 1/2 \end{pmatrix}.$$
(8.28)

The spin analyzer was assumed to have perfect transmission parallel to, and perfect blocking antiparallel to, the quantization axis ξ , which in general can lie along any direction in our Cartesian coordinate system x, y, z. Along the quantization axis ξ we have $\Delta T_R = 1/2$ and $T_R = 1$ and the transmission filter matrix is

$$\hat{\boldsymbol{F}} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad . \tag{8.29}$$

We now would like to calculate the transmitted intensity for alignment of our spin filter direction ξ along the various directions $\pm x, \pm y, \pm z$. It is given by (8.23) as

$$I = I_0 \operatorname{Tr}(\hat{\boldsymbol{\varrho}}_0 \hat{\boldsymbol{F}}) = I_0 \left(\frac{1}{2} + \frac{P_{\xi}^0}{2}\right) , \qquad (8.30)$$

where $I_0 = 12$ electrons. For $\xi = x$ we obtain with $P_x = 1/6$ the transmitted intensity I = 7, for $\xi = y$ and $P_y = 1/3$ we have I = 8 and for $\xi = z$ and $P_z = 1/2$ we get I = 9. Because for a perfect spin filter aligned along $+\xi$ the absorbed electrons would be transmitted if the filter was oriented along $-\xi$ we have the sum rule $I_{\xi} + I_{-\xi} = I_0$ and we therefore obtain the following numbers for ξ aligned along -x (I = 5), -y (I = 4), and -z (I = 3). These results agree with our earlier analysis.

A spin filter increases the spin polarization $|\mathbf{P}|$ at the expense of the transmitted number of electrons.

8.6.2 The Fundamental Interactions of a Spin-Polarized Beam with Matter

In the discussion above we have made things easy by assuming that a magic material exists that transmits all spin components along one direction, the spin filter quantization direction, and absorbs all spin components antiparallel to that direction. We have avoided looking at the detailed spin-dependent processes that actually happen when a spin-polarized beam traverses a magnetic material. We now want to explore these processes and come back to our basic question asked at the beginning of this chapter: What actually happens to the spin-polarization \boldsymbol{P} and the number of electrons $n = n^{\uparrow} + n^{\downarrow}$ as a spin-polarized electron beam traverses a material?

We know from experience that when a spin-polarized electron beam traverses a nonmagnetic noble metal such as Cu, the polarization of the beam is reduced. When it traverses an aligned ferromagnet the spin polarization is increased. It is often thought and colloquially said that these changes are due to "spin flips" in the sense of transitions from "up" to "down" spin or vice versa. It is of great importance to realize that a change in spin polarization can be caused by several mechanisms, and that, generally, "spin flips" are forbidden transitions unless an alternating magnetic field is present that oscillates with the frequency of the spin precession, or some other mechanism exists that can satisfy energy, linear, and angular momentum conservation in the spin transition. We shall see below that changes in the spin polarization of electrons are typically not due to "spin flips."

In this section we shall discuss the most important spin-dependent interaction processes and their consequences on the spin polarization \boldsymbol{P} . Four processes dominate and in our discussion below we shall refer to their illustration in Fig. 8.7. We shall assume that the incident beam has a polarization vector \boldsymbol{P}^0 aligned at some finite angle with respect to a reference field \boldsymbol{H} , which defines the quantization direction, chosen to be the z-axis of our coordinate system. For a ferromagnet, \boldsymbol{H} is the exchange field (parallel to the magnetization direction \boldsymbol{M}), and for a non-magnet, \boldsymbol{H} is an external field.

Spin Precession

We have already discussed the process of spin precession in Sects. 3.6 and 3.7, and seen that quantum mechanically the precession of the spin comes about through the development of a phase shift between the spin-up and spin-down components of the individual spins. The result is a precession of P about the quantization axis, without change of its magnitude, as illustrated in Fig. 8.7a. The spin precession time is given by the Larmor frequency $\omega_{\rm L}$, and depends on the strength of the effective field according to $\tau_{\rm L} = 1/\omega_{\rm L} = \hbar/(2\mu_{\rm B}H)$. In a typical external field of 1 T a full 360° precession takes 36 ps, while in the exchange field of a magnetic material which is of order 3×10^3 T according to Sect. 11.1.2, the precession time is only 10 fs.

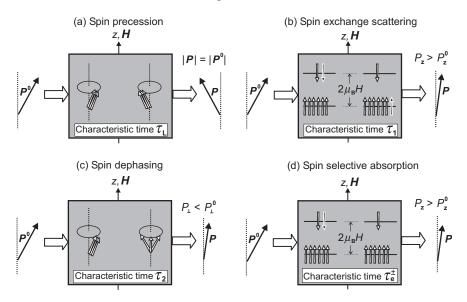


Fig. 8.7. Illustration of the main fundamental processes determining the change in the beam polarization P in the transmission of a spin-polarized electron beam through a material. We assume that an incident beam with polarization P^0 moves through the material, shown as a dark box. The quantization axis z is determined by the direction of the effective magnetic field H. If the material is a ferromagnet His the exchange field, for a nonmagnet H is an external magnetic field. (a) Larmor precession of P around the quantization axis, with a characteristic precession time $\tau_{\rm L} = 1/\omega_{\rm L} = \hbar/(2\mu_{\rm B}H)$. (b) Spin exchange scattering, corresponding to a "spin flip" transition of an electron with a characteristic longitudinal relaxation time τ_1 . The longitudinal component P_z along the quantization axis changes. In the case shown, where a minority electron makes a spin-flip transition, the beam polarization Protates toward the quantization axis. In the spin flip process, the magnitude of the spin polarization vector may be preserved $(|\mathbf{P}| = |\mathbf{P}_0|)$. (c) Spin de-phasing, corresponding to a loss of the precessional phase relationship between the individual electrons in the beam, as shown. The transverse component P_{\perp} decays to zero over a characteristic time τ_2 . The longitudinal component P_z may also change with a time constant that depends on the strength of the random de-phasing fields relative to the field H. In non-magnets, a complete randomization of the spin directions may occur, as discussed in the text. (d) Spin selective absorption, caused by preferential spin-conserving scattering in one of the spin channels, as in a spin filter. The shown loss of a minority electron corresponds to a rotation of P into the field direction and an increase in magnitude $|\mathbf{P}| \geq |\mathbf{P}_0|$

Spin Exchange Scattering

Transitions between opposite spin states have been studied in great detail in spin-1/2 systems by means of nuclear magnetic resonance (NMR) and electron spin resonance (ESR), as discussed for example by Abragam and Bleaney [140]. In the literature the "spin-flip" transition time is usually called the *longitudinal relaxation time* T_1 . In magnetic resonance experiments the necessary energy and angular momentum for spin flips is supplied by the applied radio-frequency field, as discussed in Sect. 3.6.3. Because the spin flip energy is determined by the applied static field according to $\Delta E = 2\mu_{\rm B}H$, it is rather small in ESR of order 100 µeV and the transition rate is of the order of 10 GHz.

Spin-1/2 systems are simple because they are two level systems, one for spin up and one for spin down as shown in Fig. 8.7b. If spin-polarized electrons traverse a *nonmagnetic* metal, such as Cu, transitions between opposite spin states may occur, most likely by *spin exchange collisions* with other electrons or via the hyperfine interaction with the atomic nuclei. If paramagnetic impurities are present, they might provide an additional effective sink for the angular momentum \hbar to be dissipated in a spin flip. The characteristic spin flip transition time is usually referred to as τ_1 .

The most important process leading to spin exchange in a *nonmagnetic* metal is electron-electron scattering. If for instance the incoming electron is in a spin-down state, and the target electron in a spin-up state, the indistinguishability of the electrons can lead to spin exchange, that is the outgoing electron may now be in a spin-up state and the target electron in a spin-down state. This very efficient process leads to a redistribution of the spin polarization over the available electron states in the metal. The scattering has to satisfy energy, linear momentum, and angular momentum conservation. Its theoretical understanding hinges on the ratio of the exchange scattering to the direct scattering amplitude, first explained for the case of the Coulomb interaction by Mott and Massey [134]. Yet in a metal, the Coulomb interaction is screened and it is difficult to predict the relevant cross sections theoretically. But we can say that the time scale is the one of electron–electron scattering, that is very fast, and it is connected with a sizeable energy loss of typically 1/2 of the incident primary electron energy. If electron-electron scattering is suppressed, for instance because no empty states are available as in a semiconductor near the band gap, spin exchange scattering is suppressed as well.

In a ferromagnetic metal the spin-up and spin-down states are separated by the exchange splitting of typically $\approx 1 \text{ eV}$. As discussed in detail in Sect. 12.6, spin exchange transitions are rare in ferromagnets relative to spin-conserving transitions (i.e., spin selective absorption discussed later). This important fact is the basis for the so-called *two current model* of spin transport, discussed in Sect. 12.5.2. One needs to realize, however, that transitions between the spin states nevertheless must occur since they are responsible for the establishment of the thermal equilibration of the spin-up and spin-down states. If the transitions involve the excitation of a spin wave, the energy scale is of the order of meV (see Sect. 11.1.5), that is $\tau_1 \approx 10^{-12}$ s, if the transitions involve the interaction with the crystal lattice (spin–lattice relaxation), the energy is of the order of μ eV, that is $\tau_1 \approx 10^{-10}$ s (see Sect. 15.2.2).

In order to see the effect of transitions to the other spin state on the polarization vector \boldsymbol{P} , we show in Fig.8.7b the case where one of the spin-down electrons in the incident beam undergoes a spin transition from the spin down to the spin-up state. The transmitted beam thus has an increased number of spin-up electrons. If we decompose the polarization vectors \boldsymbol{P}^0 of the incident beam and the vector \boldsymbol{P} of the transmitted beam into spin-up (along +z) and spin-down (along -z) components according to Sect. 8.4.3, we readily see that the change in occupation corresponds to a rotation of \boldsymbol{P} into the +z direction. For example, if \boldsymbol{P}^0 is initially perpendicular to \boldsymbol{H} it has an equal number of spin-up and spin-down components and if it becomes completely aligned along +z the spin-down component is zero.

If the length $|\mathbf{P}|$ is conserved, the component parallel to z, $P_{\parallel} = P_z$ will increase. Similarly, a transition from the up-spin to the down-spin state would lead to a rotation away from z and a decrease of P_{\parallel} . Hence in general the time τ_1 describes the change in the "longitudinal" component P_{\parallel} and, as in nuclear magnetic resonance, may be called the *longitudinal relaxation time*.

Spin Dephasing

Spin dephasing has also been extensively studied in magnetic resonance spectroscopy [140] and it is associated with a *transverse relaxation time* T_2 . We have seen in Section 3.6.3 that the times T_1 and T_2 are empirical parameters in the famous Bloch equations (3.41) used to describe the relaxation of spins into their equilibrium direction [140]. In electron spin resonance, the temporal evolution of transitions between the spin states is described by T_1 , and P_{\perp} is reduced while P_{\parallel} increases. Spin dephasing is described by T_2 , and P_{\perp} is reduced as well but P_{\parallel} remains constant.

Spin dephasing also exists in the transmission of a spin polarized electron beam through a material and we shall refer to its characteristic time as τ_2 . As the electrons traverse the sample they precess about the field direction $\boldsymbol{H} \parallel$ z. Initially their spins are aligned but their precession becomes increasingly out of phase with a characteristic time τ_2 . When the precessional motion is completely out of phase the polarization P_{\perp} is zero along any direction perpendicular to \boldsymbol{H} . In all cases, dephasing will lead to a component $P_{\perp} < P_{\perp}^0$, as shown in Fig. 8.7. The actual polarization of the de-phased beam depends on the strength of the random dephasing fields relative to the field \boldsymbol{H} and is different for non-magnets and magnets. In the following we shall discuss typical dephasing processes in non-magnets and magnets.

In non-magnets, spin dephasing is most likely to occur in the Coulomb scattering of the electrons on the atoms in the sample due to spin-orbit coupling. As the electrons traverse the sample they will experience scattering events on the atomic potentials. When the spin lies in the scattering plane, defined by the momenta of the incident and scattered electron, the scattering process may also affect the spin. The spin-dependent scattering is due to the gradients in the atomic potentials Φ which the electron encounters on

its way through the solid. According to (6.85) the scattering process may be viewed as a spin precession about an effective magnetic field $B^* \propto p \times \nabla \Phi$ perpendicular to the scattering plane, where p is the electron momentum. The field B^* is the same field responsible for spin-orbit coupling, and the change in electron spin upon scattering is taken up directly by the source of the field, that is by the atoms in the lattice, thus ensuring conservation of angular momentum. Because B^* is relatively strong, of order 0.1-1 T, in weak external fields H or in the absence of an external field, electrons with different scattering paths through the sample will experience B^* -fields with different orientations and after many scattering events, their spins will have precessed by different angles and point in random directions. In these cases, spin dephasing by means of spin-orbit scattering can actually lead to complete spin randomization ($|\mathbf{P}| = 0$) with an approximate time constant τ_2 . This situation is encountered in the diffusive transport of spin polarized electrons in non-magnets, discussed in Sects. 14.1.3 and 14.3, and in this context $\tau_2 = \tau_{se}$ is referred to as the *spin-equilibration time* or *spin-diffusion time*.

In magnets, the exchange field \boldsymbol{H} is much stronger than the spin-orbit field \boldsymbol{B}^* . Then the spin dephasing process resembles that shown in Fig. 8.7. Because of the dominance of \boldsymbol{H} , the precession is fast. The polarization component P_{\perp} will thus rapidly decay to zero and the polarization vector will rotate towards \boldsymbol{H} . In this case the component P_{\parallel} will change much slower. In general, the transmitted beam will have a spin-polarization which depends not only on the incident polarization \boldsymbol{P}^0 but also on the kinetic energy of the incident beam and the magnetic properties of the sample. For sample thicknesses t larger than the relaxation length $\lambda_2 = v\tau_2$, where v is the group velocity of the incident polarization and be solely determined by the kinetic energy and the magnetic properties of the sample.

In general, one expects spin dephasing to increase with the amount of Coulomb scattering and with the spin-orbit coupling in the valence states of the sample. Qualitatively, this picture is supported by an increase in τ_2 from about one picosecond in *d*-band metals such as Fe, Co and Ni, to tens of picoseconds in *s*-*p* band metals such as Al to tens of nanoseconds in semiconductors like GaAs with nearly pure *s*-like conduction bands (see Fig. 8.1).

Spin Selective Absorption

In transmission measurements through ferromagnets the unequal majority and minority density of states may also cause preferential scattering in one spin channel. As discussed in more detail in Sect. 12.5.2, it is the minority spins which are preferentially scattered, since they have more unfilled states to scatter into (see Fig. 7.6). Increased scattering leads to increased absorption as the spins traverse the sample.

The underlying process is illustrated in Fig. 8.7d, where we have assumed the preferential absorption of one minority electron. Note that no spin flips

occur but electrons in one spin channel are simply absorbed at a higher rate. If we decompose the polarization vectors \mathbf{P}^0 of the incident beam and the vector \mathbf{P} of the transmitted beam into spin-up (along +z) and spin-down (along -z) components we see that the loss of the spin-down (minority) component leads to a rotation of \mathbf{P} into the +z direction.

As will be discussed in Sects. 12.5.1 and 12.6.1, the characteristic spin selective absorption times are given by the spin dependent mean free paths $\lambda_{\rm e}^{\pm}$ according to $\tau_{\rm e}^{\pm} = \lambda_{\rm e}^{\pm}/v$. Here "+" indicates majority and "–" minority electrons, and $v = \sqrt{2E/m_{\rm e}}$ is the group velocity of the electrons, determined by their kinetic energy E. For beam energies of a few eV, the characteristic times $\tau_{\rm e}^{+} > \tau_{\rm e}^{-}$ are of the order of femtoseconds, as discussed in more detail in Sect. 12.6.

The spin conserving transitions that occur at femtosecond times and determine the electron mean free path are thus much more frequent than the spin-flip transitions involving spin-wave or phonon excitations which occur at picosecond or longer times, as discussed earlier. Since the importance of different transition channels is determined by their relative rates, the probability of spin-conserving transitions far exceeds spin-flip transitions.

We can summarize as follows.

The motion of the spin polarization vector P upon transmission through matter may be influenced by the following four fundamental processes.

- Spin precession is due to the development of a phase shift between the up and down spin partial wave functions. It leads to a precession of \boldsymbol{P} about the quantization axis, keeping $|\boldsymbol{P}|$ constant.
- Spin exchange scattering involves transitions from one to the other spin channel. It leads to rotation of \boldsymbol{P} relative to the quantization axis z with a change in the component $P_{\parallel} = P_z$.
- Spin dephasing is the development of an out-of-phase precession of the individual spins about the quantization axis. It leads to a decrease of the component P_{\perp} , perpendicular to the quantization axis. In non-magnets it may lead to complete spin randomization.
- Spin selective absorption arises from the preferential scattering (absorption) of spins in one spin channel. It causes a rotation of \boldsymbol{P} relative to the quantization axis and a change in magnitude $|\boldsymbol{P}| \neq |\boldsymbol{P}^0|$.

Relative Importance of the Four Interactions and Characteristic Times

The question arises as to the relative importance of the four processes discussed above in the transmission of a spin polarized beam through a magnetic material. It is clear that spin precession is an important process and it needs to be considered in the transmission of a spin polarized beam. It is difficult *a priori* to determine which of the other three processes dominates. It is only through experiments, discussed in Sects. 12.6.3 and 14.1.3, that we know of the dominant role of the *spin selective absorption* process. We can therefore make the following important statement, which is born out by experimental evidence.

The transmission of a spin-polarized electron beam through a material is dominated by the processes of spin precession and spin selective absorption.

For the description of the two dominant processes we can use the Landau– Lifshitz–Gilbert equation, (3.39), and this underscores its importance in describing spin dynamics. The two other processes, spin-flip scattering and dephasing are described by the Bloch equations (3.41) [139], discussed in Sect. 3.6.3. We did not extensively discuss the Bloch equations in this book because the dynamics of interest in modern spin physics is governed mostly by the LLG equations. For a thorough discussion of the Bloch equations, the interested reader is referred to books on magnetic resonance, e.g., the excellent book by Abragam and Bleaney [140].

We finish this section with another important point. In future chapters, especially Chaps. 12 and 14, we will learn that the spin-conserving absorption channel not only dominates over the spin-flip channel for the transmission of spin-polarized electron beams with kinetic energies of several eV above the Fermi energy, but also for the diffusive transport of spin polarized electrons in metals, that is for kinetic energies near the Fermi energy. Thus in all cases the rate of *spin-conserving* transitions $1/\tau_e$, which determines the electron mean free path, is considerably higher than the rate of *spin-flip* processes, $1/\tau_1$. Thus there are typically many spin-conserving scattering events for each spin-flip event.

8.6.3 Interaction of Polarized Electrons with Magnetic Materials: Poincaré's Sphere

The spinor formalism may also be conveniently used to describe the motion of the spin vector in elastic transmission and reflection of electrons from a magnetic material with uniform magnetization M and it can be conveniently visualized through a concept derived by Henri Poincaré around 1892. It is remarkable that the Poincaré formalism may be used quite generally to describe polarization changes of a "beam" due to the interaction with a magnetic material. It therefore can describe generalized versions of the magneto-optical Faraday (transmission) and Kerr (reflection) effects. In the present section we consider a "beam" of spin polarized electrons while a "beam" of polarized X-rays will be considered in Sect. 8.7.3. We can state as follows.

The *Poincaré formalism* describes polarization changes of a "beam" due to the interaction with a magnetic material, i.e., generalized versions of the Faraday (transmission) or Kerr (reflection) effects.

Let us assume that we deal with a *pure spin state*, i.e., a fully polarized beam with $|\mathbf{P}_0| = 1$, and for simplicity we consider a transmission experiment. For a fully polarized incident beam the polarization vector is then constant in magnitude, moving on the surface of a sphere with unit radius. This corresponds to the assumptions made when applying the *Landau–Lifshitz–Gilbert equation* (3.39). The changes in the direction of the polarization vector \mathbf{P} upon traversing a magnetic sample can then be described by the method of Poincaré illustrated in Fig. 8.8.

As shown in Fig. 8.8c, the endpoint of \boldsymbol{P} moves on a unit sphere, centered at the origin x = y = z = 0. The north-pole of the sphere lies on the positive z-axis. We assume that the magnetization direction of the sample lies along -z and that the spin polarization vector \boldsymbol{P}_0 of the incident beam is along the x-axis in the equatorial plane of the sphere. According to (8.9) the electron spin is described by the spinor $\chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and the initial spin state is a superposition of the two partial waves $\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \uparrow$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \downarrow$ with identical phases and amplitudes.

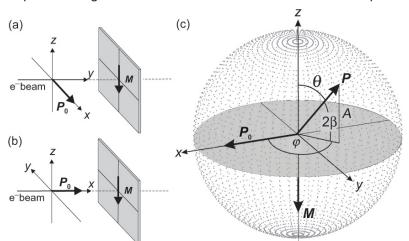
We describe the interaction of the electron spin with the ferromagnetic sample phenomenologically by a complex *interaction matrix* \hat{I}

$$\hat{\boldsymbol{I}} = \begin{pmatrix} \sqrt{1+A} e^{+i\varphi/2} & 0\\ 0 & \sqrt{1-A} e^{-i\varphi/2} \end{pmatrix},$$
(8.31)

where the constants A and φ account for the two dominant processes discussed in Sect. 8.6.2, the spin selective absorption and the spin precession, respectively.

In particular, the factor $\varphi = t\Delta E/\hbar$ is the phase difference that develops between the spin-up and spin-down states while they interact with the magnetic body, as discussed in Sect. 3.7. Thus φ increases *linearly* with time t or alternatively with the length $s = t v_{\rm G}$ of the pathway of the electrons within the sample, where $v_{\rm G}$ is the *electron group velocity*. Another factor contributing to φ is the spin dependent jump of the phase that may occur in reflection of the waves from magnetic surfaces.

The material constant A describes the relative transmission of the majority and minority components by a material and is called the *spin asymmetry parameter* A. It is defined for a material in terms of the *transmitted electron current* in analogy with our earlier definition of the *beam polarization* P in (8.17).



Experimental geometries Polarization vector on Poincaré sphere

Fig. 8.8. (a) Experimental geometries for a transmission experiment of spin polarized electrons through a magnetic thin film. The motion of the spin polarization vector P from its initial orientation along $P_0 \parallel x$ can be pictured as shown in (b) for both cases of a transversely or longitudinally polarized beam. (c) Motion of the polarization vector \boldsymbol{P} on the Poincaré sphere, with the magnetization direction \boldsymbol{M} chosen along the -z axis of the sample. The incident spin polarization P_0 is along x and the spin state is a coherent superposition of $\pm s_z$ states. If through interaction with a sample a phase difference φ develops between the two spin states the polarization vector rotates in the equatorial x-y plane. Note that the actual precession in the x-y plane follows the right hand rule about the direction M, as illustrated in Fig. 3.14. If there is preferential absorption of one of the spin states the polarization vector rotates out-of-plane by an angle $2\beta = 90^{\circ} - \theta$ toward one of the poles. For the shown geometry, it turns out (see Sects. 12.5.2, 12.6.3, and 12.6.4) that spins along -z (spin-down or minority spins) are absorbed stronger so that for the transmitted beam the polarization vector has a positive (spin-up or majority spins) z-axis projection, as shown. The component of P along z is the asymmetry parameter A, defined by (8.32)

The asymmetry parameter A describes the relative transmission of spins through a material, polarized parallel and antiparallel to the magnetization direction M, according to

$$A = \frac{I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}{I^{\uparrow\downarrow} + I^{\uparrow\uparrow}} = \frac{I^{\mathrm{maj}} - I^{\mathrm{min}}}{I^{\mathrm{maj}} + I^{\mathrm{min}}} .$$
(8.32)

A is *positive* if the *majority* intensity dominates and hence minority spins are preferentially absorbed, and vice versa.

In general we have $0 \leq |A| \leq 1$. When A = 0 the electron absorption (or reflection) does not depend on spin, while for $A = \pm 1$ only the majority or minority spin state is transmitted (or reflected). With increasing time spent by the electrons in the material the intensity of the electron beam decreases exponentially through absorption while the asymmetry A tends to ± 1 . We have not yet discussed the relative absorption of spin-up and spin-down electrons by a magnetic sample. This will be done in Sects. 12.5.2, 12.6.3, and 12.6.4. Here it suffices to say that the depicted directions of P_0 and M and the resultant motion of P in Fig. 8.8 indeed correspond to experimental observations.⁴

The zero off-diagonal matrix elements in \hat{I} indicate that the two spin partial waves do not get mixed up, that is, there are no transitions from up-spin to down-spin states or vice versa. In principle, such transitions are possible, as already mentioned in Sect. 8.6.2, but the experiments described in Sect. 12.6.3 show that spin transitions are sufficiently rare so that they can be neglected.

We also note that in contrast to the spin filter matrix \hat{F} given by (8.21), the interaction matrix \hat{I} depends on the phase shift φ between the two spin partial waves. Setting $I^{\uparrow} - I^{\downarrow} = \Delta T_R$ and $(I^{\uparrow} + I^{\downarrow}) = 2T_R$ in (8.32), one finds that $T_R(\hat{I} \cdot \hat{I}^*) = \hat{F}$. Hence by neglecting the phase, as appropriate for a partially polarized beam, we can describe the interaction with the ferromagnet by the spin filter matrix (8.21).

For the case of interest here, the incident fully polarized beam emerges from the magnetic body with the wave function $\chi' = \hat{I}\chi$ given by

$$\chi' = \hat{I} \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{1+A} e^{+i\varphi/2} \\ \sqrt{1-A} e^{-i\varphi/2} \end{pmatrix} .$$
(8.33)

As expected, a difference in phase and in amplitude has developed between the two partial waves. According to (8.8) the polarization vector of the transmitted beam is

$$\boldsymbol{P} = \begin{pmatrix} \sqrt{1 - A^2} \cos \varphi \\ \sqrt{1 - A^2} \sin \varphi \\ A \end{pmatrix}.$$
(8.34)

Since the polarization vector at incidence was $\mathbf{P}_0 = (1, 0, 0)$, we see that in the absence of spin dependent absorption, that is with A = 0, the vector \mathbf{P} moves azimuthally along the equator of the Poincaré sphere in Fig. 8.8. The

⁴ The incident beam is described as a superposition of up spins (along z) and down spins (along -z). If the magnetization vector M is along -z, the *minority* spins in the sample are also along -z (see Fig. 7.6), and hence incident down spins are preferentially absorbed by spin-conserving excitations within the minority band. This means that the transmitted beam will have a preferential up-spin polarization, as shown in Fig. 8.8.

angular frequency of this motion is $\omega = \Delta E/\hbar$, that is precisely the precession frequency of the spin derived in Sect. 3.6. On the other hand, if one sets $\varphi = 0$, \boldsymbol{P} rotates into the positive or negative z-axis depending on the sign of A. In the presence of both $A \neq 0$ and $\varphi \neq 0$, the polarization vector \boldsymbol{P} moves on a spiral into the north- or the south-pole of the Poincaré sphere. These two cases correspond to the motions of the magnetic moment with positive damping illustrated in Fig. 3.16 and negative damping in Fig. 3.17. We see from (8.34) that for the fully polarized incident beam considered above the beam remains completely polarized, i.e., $|\boldsymbol{P}| = |\boldsymbol{P}_0| = 1$.

We can also use the density matrix (8.19) to account for the interaction of a partially polarized incident beam $(|\mathbf{P}_0| < 1)$ with a sample. It is easy to show that after the interaction, \mathbf{P} is given by

$$\boldsymbol{P} = \begin{pmatrix} P_0 \sqrt{1 - A^2} \cos \varphi \\ P_0 \sqrt{1 - A^2} \sin \varphi \\ A \end{pmatrix}.$$
(8.35)

Now the transmitted beam has also changed the magnitude of the polarization vector, so that $|\mathbf{P}| \neq |\mathbf{P}_0|$. The polar angle θ enclosed between $-\mathbf{M}$ and \mathbf{P} is given by,

$$\theta = \arctan\left(\frac{P_0\sqrt{1-A^2}}{A}\right). \tag{8.36}$$

Both φ and θ can be directly measured. Such experiments are described in Sects. 12.6.4 and 13.3.2. The experiments show that the polarization vector \boldsymbol{P} indeed moves corresponding to (8.35). The difference of the motion of \boldsymbol{P} compared to the motion of the magnetic moment \boldsymbol{m} , discussed in Sect. 3.6.2, is that \boldsymbol{P} moves orders of magnitudes faster. The high angular velocity of precession is due to the high value of the exchange field. The fast rotation into the quantization axis is due to the very effective spin selective electron/electron scattering in a magnetic metal.

In summary, two separate phenomena act on the polarization vector \boldsymbol{P} .

- The precession in the equatorial plane of Poincaré's sphere is caused by the different phase velocities of spin-up and spin-down electrons. The phase shift φ that develops with time t is determined by the exchange energy ΔE according to $\varphi = t\Delta E/\hbar$. The phase shift φ increases linearly with the thickness of the sample.
- The spiralling into the north or south poles is caused by the asymmetric absorption of up and down spin electrons. The out-of-plane rotation angle 2β increases with absorption A according to $\tan 2\beta = A/\sqrt{1-A^2}$. The spin asymmetry A of the absorption increases with the thickness of the sample.

8.7 Link Between Electron Polarization and Photon Polarization

Classically the electromagnetic field is a vector field, where the electric and magnetic field vectors are described by three independent components in a Cartesian coordinate system, e.g., $\boldsymbol{E} = (E_x, E_y, E_z)$, as discussed in Chap. 5. Quantum mechanically photons are Bosons with angular momentum quantum number⁵ L = 1 and three possible values of $\langle L_z \rangle = -1, 0, +1$ in units of \hbar along the propagation direction z. Hence these three polarization states, two circular and one linear, span the three-dimensional vector field.

At first sight it seems therefore odd that the spinor field concept which is based on only *two basis* states appropriate for an s = 1/2 Fermion particle can also be used to describe the polarization states of a photon. That this can indeed be done is due to two facts,

- The transverse nature of EM waves imposes the restriction that E is always in a plane perpendicular to the propagation direction k.
- The state $\langle L_z \rangle = 0$ can be written as a linear combination of the states $\langle L_z \rangle = \pm 1$.

We can state as follows.⁶

For a given photon propagation direction k, the polarization properties of an EM wave can be completely described by either the conventional 3D vector formalism or the 2D spinor formalism.

Examples for the convenient use of the spinor formalism are transmission experiments of polarized light through a magnetized sample as performed for example in the measurement of the Faraday rotation. In the following we shall establish the correspondence between the vector field and spinor field descriptions and then describe the Faraday effect in the spinor formulation.

⁵Modern optics allows one to create photon states with unusual polarizations [184] and wave topographies. For example, an *optical vortex* state is characterized by a helical or corkscrew-like trajectory of the Poynting vector around the propagation direction \mathbf{k} and exhibit zero field amplitude at the beam center. The creation of such beams has led to a distinction in the literature between the "angular momentum" of such light beams from that of conventional circularly polarized beams, referred to as "spin" [187]. We do not consider such exotic states here.

⁶A complete experiment probes the properties of an anisotropic sample (either charge or spin) in three dimensions. It therefore consists of three orthogonal measurements as discussed later in Chap. 10, by probing the sample with either k or E along the x, y, and z axes of the sample. For example, we shall see that it takes an average over *three* orthogonal polarization states to obtain powerful sum rules that link the X-ray absorption intensity with angle-independent materials properties such as the number of empty valence states and the spin and orbital momenta per atom. In these cases the vector field formalism offers advantages.

8.7.1 Photon Polarization in the Vector Field Representation

Let us assume the same geometry as shown in Fig. 8.3, where the z-axis is special in that it is both the photon propagation direction k and also the direction of the sample magnetization M.

We have learned in Sect. 5.4.5 that any polarization state can be written as a linear combination of two basis states, which are either linearly polarized

$$\boldsymbol{\epsilon}_x = \begin{pmatrix} 1\\0\\0 \end{pmatrix}, \qquad \boldsymbol{\epsilon}_y = \begin{pmatrix} 0\\1\\0 \end{pmatrix}, \qquad (8.37)$$

where the subscript refers to the direction of E, or circularly polarized ($\epsilon^{\mathcal{R}} = \epsilon^+$ and $\epsilon^{\mathcal{L}} = \epsilon^-$),

$$\boldsymbol{\epsilon}_{z}^{+} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1\\ -\mathrm{i}\\ 0 \end{pmatrix}, \qquad \boldsymbol{\epsilon}_{z}^{-} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ -\mathrm{i}\\ 0 \end{pmatrix}, \qquad (8.38)$$

where the subscript labels the direction of k. In particular, the circular polarization vectors can be used as the basis vectors of our polarization description as discussed in Sect. 5.4.5. The link between the three-dimensional vector and two-dimensional spinor descriptions therefore simply lies in the correspondence between the two circularly polarized photon states (8.38) and the spinor states (8.4).

Before we explore this concept further let us briefly show how the expectation value of the angular momentum along the z direction is calculated in the vector field formalism. Rather than the two-dimensional Pauli matrices one uses the corresponding three-dimensional operator matrices for a L = S = 1particle [147, 181, 197]. In particular, the matrix for the z component of the angular momentum operator is given by,

$$\boldsymbol{L}_{z} = \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \qquad (8.39)$$

and we obtain the following angular momenta projections (in units of \hbar) for the states ϵ^+ and ϵ^- ,

$$\langle \mathbf{L}_{z} \rangle = (\boldsymbol{\epsilon}^{+})^{*} \, \mathbf{L}_{z} \, \boldsymbol{\epsilon}^{+} = \frac{1}{2} (-1, \text{ i}, 0) \begin{pmatrix} 0 - \text{i} \ 0 \\ \text{i} \ 0 \ 0 \\ 0 \ 0 \ 0 \end{pmatrix} \begin{pmatrix} -1 \\ -\text{i} \\ 0 \end{pmatrix} = 1.$$
 (8.40)

and

$$\langle \mathbf{L}_z \rangle = (\boldsymbol{\epsilon}^-)^* \, \mathbf{L}_z \, \boldsymbol{\epsilon}^- = \frac{1}{2} (1, i, 0) \begin{pmatrix} 0 - i \ 0 \\ i \ 0 \ 0 \\ 0 \ 0 \ 0 \end{pmatrix} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} = -1.$$
 (8.41)

and for linearly polarized light with E along x or y we can easily show that

$$\langle \boldsymbol{L}_z \rangle = (\boldsymbol{\epsilon}_x)^* \, \boldsymbol{L}_z \, \boldsymbol{\epsilon}_x = (\boldsymbol{\epsilon}_y)^* \, \boldsymbol{L}_z \, \boldsymbol{\epsilon}_y = 0.$$
(8.42)

This confirms our labeling of the states in terms of angular momenta "+" $= +\hbar$ and "-" $= -\hbar$, respectively, and agrees with our earlier results in Sect. 5.4.3. Linearly polarized photons carry no net angular momentum along the propagation direction. Thus we can state as follows.

For propagation k in the z direction, quantum mechanically a photon has the intrinsic angular momentum quantum number L = 1 (i.e., photons are Bosons) with possible projections $L_z = +\hbar, -\hbar$, or 0.

Note that conservation of the intrinsic magnitude of the angular momentum in the X-ray absorption process leads to the familiar dipole selection rule $\Delta L = \pm 1$, independent of photon polarization.

8.7.2 Photon Polarization in the Spinor Representation

The description of the photon polarization in the spinor formalism is identical to that used for the electron in Sect. 8.4.2. We use the two spinor states $\binom{1}{0}$ for the photon angular momentum $L_z = +\hbar$ and $\binom{0}{1}$ for $L_z = -\hbar$. The two basis states represent the spinor field.

However, care has to be taken regarding the meaning of the "polarization vector" \boldsymbol{P} for photons. In the vector field representation, the photon polarization is defined as the direction of the \boldsymbol{E} -vector of the EM wave, and the \boldsymbol{E} -vector direction and motion leads to the name "linear" and "circular" polarization. In the spinor representation the emphasis is placed on the direction of angular momentum, not the \boldsymbol{E} -vector, in analogy to the electron spin angular momentum. Therefore, the polarization vector \boldsymbol{P} for photons is a vector in configurational space only. This important point needs to be remembered.

In the *spinor formalism*, the polarization vector \boldsymbol{P} is associated with the direction of angular momentum. For *electrons* it describes the real space orientation of the spin. For *photons* it represents both circularly and linearly polarized states so that, in general, \boldsymbol{P} cannot be associated with the direction of the electric field vector \boldsymbol{E} .

In the following we will illustrate the motion of the polarization vector for polarized photons by considering a simple transmission experiment through a magnetic sample. We shall follow the discussion of the electron case given in Sect. 8.4.

8.7.3 Transmission of Polarized Photons through Magnetic Materials: Poincaré Formalism

The formalism developed above can be used to describe the transmission and reflection of polarized light by a magnetic material. We will now show that when photons pass through magnetic matter, the endpoint of P moves on the surface of Poincaré's sphere in a characteristic way. We assume that the photon is incident on a sample with magnetization M pointing into the +z direction, in the direction of photon propagation k, as illustrated in Fig. 8.9.

We assume that we have an incident photon beam, described by a spinor $\chi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$. As we have seen in Sect. 8.7.2, the photon state consists of two circularly polarized partial waves $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ with identical phase and amplitude. The photon is propagating along the *z*-axis and possesses the polarization vector $\mathbf{P}_0 = (1, 0, 0)$ according to (8.9), and hence is linearly polarized along the *x*-axis ($\mathbf{E}_0 \parallel \mathbf{P}_0$).

We now proceed as in Sect. 8.4 and describe the interaction of the photons with the magnetic sample by the *interaction matrix* \hat{I} , given by (8.31). The asymmetry factor

$$A = \frac{T^+ - T^-}{T^+ + T^-} , \qquad (8.43)$$

describes the transmission through the sample for positive and negative helicity photons, caused by preferential absorption. For $T^+ = 1$ only $L_z = +\hbar$ photons are transmitted and A = +1, and for $T^- = 1$ only $L_z = -\hbar$ photons are transmitted and A = -1. In general we have $0 \le |A| \le 1$ and A = 0 means that the material possesses no absorptive circular dichroism. The asymmetry A will depend exponentially on the length of the light path in the material as discussed in Sect. 9.4.1. By comparison of (8.43) with the definition of the degree of circular polarization P_{circ} given by (5.52) we see that for photons we expect $|A| = P_{\text{circ}}$, where P_{circ} refers to the polarization of the *transmitted* photons. This is indeed confirmed by experiment as illustrated in Fig. 8.10.

The parameter φ in the *interaction matrix* \hat{I} (8.31) accounts for the different phase velocities with which the two types of circularly polarized partial waves travel in the magnetized body. For photons, the zero values of the offdiagonal matrix elements of \hat{I} indicate that the two partial waves do not get mixed up, that is, there are no transitions between the two circularly polarized photon states. Such transitions are highly forbidden. The magnetic body acts selectively on each type of partial wave.

As for electrons, the photon emerges from the magnetic body with the wave function $\chi' = \hat{I}\chi$ given by (8.33) and a difference in phase and in amplitude has developed between the two partial waves. Since the light vector at X-ray incidence was $P_0 = (1, 0, 0)$, we see that in the case A = 0 the vector Pprecesses along the equator of the sphere. This is illustrated in Fig. 8.9 by the first transmission step through sample 1, corresponding to the motion $P_0 \rightarrow P = P_1$. Here we have assumed that the sample absorbs the two

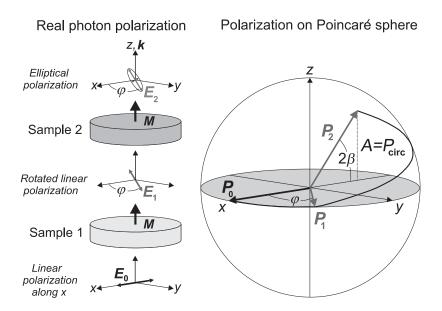


Fig. 8.9. Transmission of linearly polarized photons through two hypothetical magnetic samples. The corresponding photon polarizations are illustrated in real space on the left and on the Poincaré sphere on the right. Left: A photon beam, linearly polarized along x ($P_0 \parallel E_0 \parallel x$) is incident on the magnetic sample 1 with magnetization direction M pointing along the photon wavevector k and the z-axis of our coordinate system. Sample 1 is assumed to have different phase velocities for RCP $(L_z = +\hbar)$ and LCP $(L_z = -\hbar)$ photons but no or equal absorption of the two circular components. This results in a relative phase shift of the RCP and LCP partial waves that compose the incident linearly polarized light and leads to a rotation, the *Faraday rotation*, of the polarization vector by an angle φ . After sample 1 the photon beam is still linearly polarized but its E vector is rotated by φ in the x-y plane. The photon beam then traverses sample 2, which also has its magnetization M oriented along z. This sample is assumed to have different phase velocities and different transmission factors for RCP and LCP photons, with preferential absorption of LCP light. After the sample, the transmitted light is right elliptically polarized. Right: Illustration of the Poincaré sphere representation of the transmission experiment on the left. The polarization vector of the incident light is P_0 . After transmission through sample 1 the light vector is rotated along the equator on the Poincaré sphere according to $P_0 \rightarrow P_1$. Preferential absorption of LCP by sample 2 leads to an out-of-plane precession of P toward the north pole, illustrated as the path $P_1 \rightarrow P_2$. Now the light is right elliptically polarized. If the path continued to the north pole the light would be right circularly polarized (pure $L_z = +\hbar$). The component of **P** along z is the degree of circular polarization P_{circ} which is equal to the asymmetry parameter A. It is related to the Stokes angle 2β , by $\tan 2\beta = A/\sqrt{1-A^2}$

partial waves equally or not at all. The rotation angle φ of the polarization is called magneto-optic *Faraday rotation* in transmission and *Kerr rotation* when the light is reflected from the ferromagnet. It increases linearly with the length of the pathway of the light through the sample.

For finite A, the light vector moves out of the equatorial plane. This motion corresponds to the transmission through sample 2 in Fig. 8.9. Sample 2 is assumed to preferentially absorb negative spin or LCP light. The photon beam after the sample is now elliptically polarized and when \boldsymbol{P} reaches the north (south) pole we have pure right (left) circular polarization. With reference to the right side of Fig. 8.9 and defining two new angles $2\alpha = \varphi$ and $2\beta = 90-\theta = \arcsin A$ (see Fig. 8.8) for later reference, we can write the polarization vector as follows.

Poincaré's polarization vector \boldsymbol{P} is given by, $\boldsymbol{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \sqrt{1-A^2} \cos\varphi \\ \sqrt{1-A^2} \sin\varphi \\ A \end{pmatrix} = \begin{pmatrix} \cos 2\beta \cos 2\alpha \\ \cos 2\beta \sin 2\alpha \\ \sin 2\beta \end{pmatrix}.$ (8.44)

If the light is completely polarized we have P = 1, and P defines a point on the surface of the *Poincaré's sphere* with radius 1. For incompletely polarized photons P lies inside the sphere, and the point P = 0 defines natural or "unpolarized" light.

The spinor formalism mapped onto Poincaré's sphere describes the following polarization cases,

- Right circularly polarized light with $L_z = +\hbar$ corresponds to the north pole
- Left circularly polarized light with $L_z = -\hbar$ corresponds to the south pole
- Linearly polarized light corresponds to points on the equator
- In the positive half sphere $(90^{\circ} > 2\beta > 0)$ the polarization is right handed elliptical
- In the negative half sphere $(-90^{\circ} < 2\beta < 0)$ the polarization is left handed elliptical

As for spin-polarized electrons we can state as follows.

In magnetic materials two phenomena act on the light vector P:

- The precession angle φ in the equatorial plane is caused by the different *phase velocities* of right and left circularly polarized light, and φ increases *linearly* with the light path through the sample.
- The spiralling into the north and south poles is caused by the asymmetric *absorption* of right and left circularly polarized light. The absorption depends *exponentially* on the light path through the sample.

8.7.4 X-ray Faraday Effect and Poincaré Formalism

Similar to the visible range one can also measure the Faraday effect in the Xray range as first demonstrated by Kao et al. [99] in 1990. Later, quantitative measurements on Fe were carried out by Kortright and Kim [353] and on Fe, Co, and Ni by Gudat et al. [354] and Kuneš et al. [355]. A particularly large X-ray Faraday effect is observed for the rare earths, as measured by Prieto et al. [356]. While in the Faraday effect the magnetization is *parallel* to the propagation direction of the linearly polarized incident light, one may also measure the transmission of linearly polarized light that is incident perpendicular to the magnetization direction M of the sample, the so-called *Voiqt effect* [357]. In both cases the polarization state of the transmitted light is determined. This distinguishes the Voigt effect from the linear magnetic dichroism effect where only the transmitted intensities for E parallel and perpendicular to Mare measured and compared. Similar to the magneto-optical Kerr effect, Xray measurements can also be performed in a reflection geometry [358–360]. In this case care has to exercised in the analysis of the measured asymmetry, because the reflected intensity is dependent on the angle of incidence and the layered structure of the sample and it may reverse its sign [358, 361].

Fig. 8.10 gives an example of an X-ray Faraday effect measurement performed by Gudat et al. [354]. X-rays of variable polarization are incident on an in-plane magnetized film of permalloy $Fe_{0.5}Ni_{0.5}$ of thickness 50 nm, with the X-ray propagation direction at an angle of 30° with respect to M. By use of circular polarization one measures the transmission spectra, shown in the top panel, and from the transmitted intensities T^{\pm} one can determine the absorption asymmetry $A = |T^- - T^+|/(T^- + T^+)$, plotted in the bottom panel. By use of linearly polarized incident light and determination of the polarization of the transmitted beam one can determine both the Faraday rotation φ of the **E**-vector, shown in the middle panel of Fig. 8.10 and the degree of circular polarization $P_{\rm circ}$ (see Sect. 5.5.3), plotted in the bottom panel. The Faraday rotation exhibits a pronounced derivative-like structure near the L₃ resonance and a change of sign. This is what one expects on going through a resonance: The phase difference between the periodic exciting field and the harmonic oscillator changes sign on going through the resonance. The magnitude of the phase jump depends on the damping of the oscillator. As expected, the intensities at the L_3 and L_2 resonances behave in the opposite way. The bottom panel demonstrates the close correspondence of the asymmetry A determined from the transmitted *intensities* using circularly polarized light and the degree of circular polarization determined from the transmitted *polariza*tion for linear incident light. Note that $P_{\rm circ}$ corresponds to the z-component of the light vector P in Fig. 8.9. The results provide a nice example of how magneto-optics works and demonstrate the motion of the light vector on the sphere of Poincaré.

We see that X-rays are superior to visible light because the effects are enhanced and because the results can be interpreted more directly. We shall show

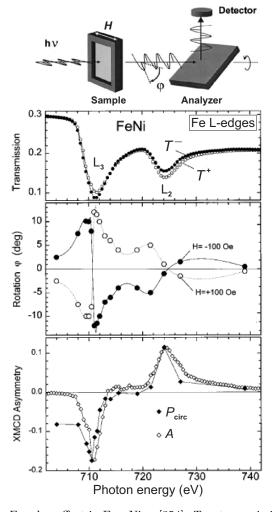


Fig. 8.10. X-ray Faraday effect in Fe_{0.5}Ni_{0.5} [354]. Top: transmission of right (T^+) and left (T^-) circularly polarized light versus photon energy around the Fe L-edge resonances. Center: Faraday rotation of the plane of polarization obtained with linearly polarized light for the two directions of M with respect to the photon light vector P. Bottom: Asymmetry A of the transmission and the degree of circular polarization $P_{\rm circ}$ of the emerging light

in Chap. 9 that polarization dependent X-ray measurements allow the determination of important quantities in magnetism such as the number of holes in the d-band, the spin and orbital magnetic moments and their anisotropy, and all that with elemental and chemical state specificity.

8.7.5 Poincaré and Stokes Formalism

Finally, we mention that Poincaré's description developed in 1892 is closely related to that developed earlier by George Stokes around 1852. Stokes' description of the properties of a light beam is based on four parameters that define the so-called *Stokes vector* according to

$$\boldsymbol{\mathcal{S}} = \begin{pmatrix} \mathcal{S}_0 \\ \mathcal{S}_1 \\ \mathcal{S}_2 \\ \mathcal{S}_3 \end{pmatrix} = \begin{pmatrix} T_{\max} + T_{\min} \\ \mathcal{S}_0 \cos 2\beta \cos 2\alpha \\ \mathcal{S}_0 \cos 2\beta \sin 2\alpha \\ \mathcal{S}_0 \sin 2\beta \end{pmatrix} .$$
(8.45)

The fact that one can establish a relationship between the Stokes vector \boldsymbol{S} and the Poincaré vector \boldsymbol{P} was in fact the reason why in (8.44) we introduced new angles 2α and 2β . There is a good reason for the factor of 2 in the angles occurring in (8.45). For photons the two linearly polarized basis states are orthogonal (90°), while for electrons the two basis states include an angle of 180°. Only three of the four Stokes parameters are independent. They are linked by the total beam intensity $S_0 = T_{\max} + T_{\min}$ and the fact that $S_0^2 = S_1^2 + S_2^2 + S_3^2$. The polarization information is contained in the three parameters S_1 , S_2 , and S_3 . When normalized by S_0 they define the three component Poincaré vector \boldsymbol{P} .

Interactions of Polarized Photons with Matter

9.1 Overview

This chapter discusses theoretical concepts underlying the description of the interactions of polarized photons with matter. Because of the long history of the subject in the optical wavelength regime we start with a brief summary of terminology associated with polarization dependent scattering and absorption effects of visible light in matter. This will allow us to clearly define a modern terminology that is most suitable for X-rays.

We start our theoretical treatment with *semiclassical concepts* (i.e., classical concepts with the addition of some quantum concepts) that conveniently build on those developed in Chap. 8. For example, the transmission of polarized photons through magnetic materials, the magneto-optical Faraday effect, can be understood semiclassically by assuming that polarized light is composed of right and left circular polarized components and that one circular component is preferentially phase shifted or absorbed upon transmission through a magnetic material. This explains the change in polarization state of the transmitted wave. Similarly, nonresonant scattering processes are readily understandable as a two step process where the EM wave jiggles the charge or the spin and the motion leads to re-radiation, i.e., scattering, of an EM wave.

Such semiclassical or phenomenological treatments, however, are unsatisfactory if one wants to understand the interaction of the EM wave with the material in detail or even quantitatively link measured intensities with magnetic parameters such as magnetic moments. A key problem with semiclassical treatments is that the processes with the largest cross-section, X-ray absorption or resonant scattering, are true quantum phenomena. This has historically been partially overcome by combining classical elements with the quantum mechanical concept of oscillator strength of an electronic transition. In analogy to the harmonic oscillator, a connection can then be established of resonant scattering and X-ray absorption intensities or cross-sections and such a treatment leads to the famous Kramers–Kronig relations [109,178,190,362].

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However, the Kramers–Kronig relations only allow one to connect an experimental absorption spectrum with the scattered intensity or vice versa but it does not provide a means to calculate either the absorption or scattered intensity from first principles. Such a *quantitative* treatment requires the operator and matrix element approach of modern quantum mechanics in conjunction with time-dependent perturbation theory. Only this approach allows the quantitative analysis of resonant X-ray scattering and X-ray absorption intensities in terms of atomic quantities such as magnetic moments and their anisotropies. For this reason we shall present the basic concepts of this approach.

In comparison to optical dichroism measurements, X-rays offer significant advantages. Because excitations are localized on atoms, X-rays offer specificity to individual elements and their chemical state. In contrast to the optical range, X-ray transition intensities represent an average over all valence states in the Brillouin zone, the same average that determines physical quantities like the valence shell occupation number and the spin and orbital magnetic moments. By use of powerful sum rules the spin and orbital moments can be separated and can be quantitatively determined from integrated peak intensities. Also, because of the short wavelength of X-rays, they offer higher spatial resolution, down to the size of the X-ray wavelength. In the era of nanoscience this provides another significant advantage over optical methods which are typically limited to a spatial resolution above 200 nm.

9.2 Terminology of Polarization Dependent Effects

In the past, optical effects were mainly described phenomenologically by means of a *refractive index*. In general, this index is dependent on the frequency and the polarization of the EM wave. For a given sample, the frequency dependence is particularly important around specific resonant frequencies and near such resonances the refractive index needs to be described as a complex dimensionless quantity according to $[109, 149]^1$

$$n(\omega) = 1 - \delta(\omega) + i\beta(\omega) . \qquad (9.1)$$

The real part $\delta(\omega)$ is associated with refraction and the imaginary part $\beta(\omega)$ with absorption of the EM wave in the medium.

The polarization dependence of the refractive index is called "birefringence" and one distinguishes linear and circular birefringence, depending on the polarization of the incident light. The term *refringence* was originally used instead of the term *refraction*, both deriving from the Latin word *frangere*, meaning to break. The polarization dependence of the absorptive part $\beta(\omega)$ is referred to as "dichroism." The term has its origin in the fact that certain crystals may appear dichroic or in two different colors when white light is

¹For isotropic media we have the general relationship $n \equiv \sqrt{\epsilon \mu / \epsilon_0 \mu_0}$, where ϵ / ϵ_0 is the dielectric constant and μ / μ_0 the relative permeability.

incident along two different directions. This is due to the preferential absorption of polarization components and frequencies along different directions. We may summarize these and other optical effects as follows.

- Birefringence. The existence of two different indices of refraction for polarized incident light. One distinguishes linear birefringence and circular birefringence.
- Dichroism. The dependence of photon absorption on polarization. There
 are four main types. Linear dichroism and (natural) circular dichroism depend on the charge distribution. Magnetic linear dichroism and magnetic
 circular dichroism depend on the spin and charge distribution.
- *Optical activity or rotation*. The rotation of the linear polarization direction by a nonmagnetic sample. Optical activity is typically associated with a handedness of the charge distribution in space, i.e., chirality.
- Magneto-optical rotation. The rotation of the linear polarization direction by a magnetic sample. It arises from the presence of aligned magnetic moments, which give the sample a handedness in time through breaking of time-reversal symmetry.

In modern theory, based on time-dependent perturbation theory and the quantum mechanical operator and matrix element method, all interaction effects of polarized photons with matter listed earlier can be cast in terms of a scattering problem. The final formalism has a close resemblance with the classical approach based on the refractive index in that the scattering is expressed in terms of a *complex atomic scattering factor*

$$F(\boldsymbol{Q},\omega) = F^{0}(\boldsymbol{Q}) + F'(\omega) - \mathrm{i} F''(\omega).$$
(9.2)

Here \boldsymbol{Q} is the momentum transfer in the scattering process and $F^0(\boldsymbol{Q})$ is the *atomic form factor*. All factors $F^0(\boldsymbol{Q})$, $F'(\omega)$, and $F''(\omega)$, are real numbers in units of number of electrons per atom. In the soft X-ray range or for scattering in the forward direction, where the momentum transfer \boldsymbol{Q} is small, we obtain an expression similar to (9.1),

$$F(\omega) = Z + F'(\omega) - iF''(\omega) = f_1(\omega) - if_2(\omega).$$
(9.3)

Here Z is the number of electrons per atom and the anomalous scattering factors $F'(\omega)$ and $F''(\omega)$ can be calculated from first principles and represent the refractive and absorptive contributions to scattering. In practice, in the soft X-ray region one can conveniently use the web-tabulated *Henke–Gullikson factors* [362, 363].

The Henke–Gullikson atomic factors are defined as $f_1(\omega) = Z + F'(\omega), \quad f_2(\omega) = F''(\omega).$ (9.4)

They have units of [number of electrons per atom].

It is important to realize that f_1 and f_2 are *atomic* factors that do not include bonding effects associated with atoms in different environments. Fortunately, bonding effects only change the X-ray interactions near absorption edges. In the near edge region the X-ray excitations are associated with specific transitions from core states to empty valence states of the material and the fine structure of the resonances is therefore characteristic of the local bonding environment of the absorbing atom. Outside the near-edge resonance region, the photoelectron is directly excited into free-electron-like continuum states and the excitation cross-section is atom specific and varies smoothly with energy. The X-ray response of the material in this region is therefore simply a superposition of all the individual atomic responses given by the Henke–Gullikson factors. In practice, one rarely measures X-ray absorption or scattering spectra on an absolute intensity or cross-section scale. If needed one converts the measured spectra, including the near-edge resonance region, to an absolute scale by fitting them *outside the resonance region* to the crosssections calculated by means of the Henke–Gullikson factors, as discussed in Sect. 10.3.3.

The real atomic scattering factors $F^0(\mathbf{Q})$, $F'(\omega)$, $F''(\omega)$, $f_1(\omega)$, and $f_2(\omega)$ have units of [number of electrons/atom].

The relationship between $n(\omega)$ in (9.1) and $F(\omega)$ in (9.3) is given by [364]

$$1 - n(\omega) = \frac{r_0 \lambda^2}{2\pi} \sum_j \rho_j F_j(\omega), \qquad (9.5)$$

where $r_0 = e^2/4\pi\epsilon_0 m_{\rm e}c^2 = 2.818 \times 10^{-15}$ m/electron is the classical electron radius, λ is the wavelength, and ρ_j is the number density of atomic species j (atoms/length³), so that the right hand side of (9.5) is dimensionless, as required. Restricting ourselves to a sample with only one atomic species with density $\rho_{\rm a}$ we obtain the simple relations

$$\delta(\omega) = \frac{r_0 \lambda^2}{2\pi} \rho_{\rm a} f_1(\omega), \qquad (9.6)$$

$$\beta(\omega) = \frac{r_0 \lambda^2}{2\pi} \rho_a f_2(\omega). \tag{9.7}$$

 $\delta(\omega)$ and $\beta(\omega)$ are dimensionless.

Scattering and reflectivity experiments depend on both the real, $f_1(\omega) = Z + F'(\omega)$, and imaginary, $f_2(\omega) = F''(\omega)$, parts. In practice, the two scattering factors $F'(\omega)$ and $F''(\omega)$ are rarely determined independently but one is obtained from the other by a Kramers–Kronig transformation, discussed

in Sect. 9.4.4. In particular, $F''(\omega)$ is typically obtained by an X-ray absorption measurement since it is directly proportional to the X-ray absorption cross-section. Experimentally, the real part $F'(\omega)$, is best determined from a measurement of the *polarization rotation* using linearly polarized incident radiation.²

All polarization dependent effects caused by the interaction of an EM wave with matter discussed earlier can therefore be completely described in terms of the scattering factors. The task then boils down to determining the scattering factors in the resonance region where they contain information on the electronic and magnetic structure of the material. There are two important types of measurements to determine them.

- Polarization dependent X-ray absorption measurements completely determine $F''(\omega)$. This is an absolute intensity measurement³ only the incident polarization needs to be known.
- Polarization rotation measurements completely determine $F'(\omega)$. This is an intensity difference measurement involving the polarizations of the incident and transmitted radiation.

9.3 SemiClassical Treatment of X-ray Scattering by Charges and Spins

9.3.1 Scattering by a Single Electron

The semiclassical treatment of magnetic dichroism starts with *nonresonant* X-ray scattering by the charge and spin of a single electron and it provides an intuitive understanding of the processes involved. Below we will review the processes of charge and spin scattering by an electromagnetic wave. While we will give the complete equations for charge scattering, we shall only discuss the spin scattering channel that is of pure spin origin. Other channels arising from the spin–orbit coupling or from the fact that charge and spin are both tied to an electron and that charge motion naturally leads to spin motion will not be considered here [190].

We assume an EM wave with unit polarization vector $\boldsymbol{\epsilon}$ and fields

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{\epsilon} \, E_0 \, \mathrm{e}^{-\mathrm{i}(\omega t - \boldsymbol{k} \cdot \boldsymbol{r})},\tag{9.8}$$

²The rotation angle which is related to $F'(\omega)$ and δ is determined from a relative transmission measurement as a function of polarizer orientation. The ellipticity of the transmitted polarization, which is related to $F''(\omega)$ and β can also be determined by means of polarimetry, yet absorption measurements are easier and more accurate.

³In practice, one often normalizes measured data to the Henke–Gullikson data [362, 363] outside the resonance regions and therefore one performs only a relative intensity measurement.

$$\boldsymbol{B}(\boldsymbol{r},t) = \frac{1}{c} (\boldsymbol{k}_0 \times \boldsymbol{\epsilon}) E_0 e^{-i(\omega t - \boldsymbol{k} \cdot \boldsymbol{r})}.$$
(9.9)

Following convention we have chosen ϵ to be along the *E*-vector and we shall for simplicity assume linear polarization. When this wave is incident on a free electron of charge -e and spin s, both the charge and the spin are set in motion. The electron motion follows the oscillating electric field, creating an electric dipole moment directed along the *E*-vector

$$\boldsymbol{p}(t) = -\frac{e^2}{m_{\rm e}\omega^2} \boldsymbol{E}_0 \,\mathrm{e}^{-\mathrm{i}\omega t}.$$
(9.10)

For spin scattering we consider how the magnetic field acts on the spin. We know from Chapt. 3 that the spin precesses around a constant magnetic field according to the torque equation $T = \hbar ds(t)/dt$,

$$\frac{\mathrm{d}\boldsymbol{s}(t)}{\mathrm{d}t} = -\frac{e}{m_{\mathrm{e}}} \,\boldsymbol{s}(t) \times \boldsymbol{B} \,, \qquad (9.11)$$

For a linearly polarized EM wave the magnetic field $\mathbf{B}(t) = \mathbf{B}_0 e^{-i\omega t}$ oscillates along an axis in space and changes sign periodically. According to (9.11) a sign change in $\mathbf{B}(t)$ leads to a sign change of the torque $\mathbf{T} = \hbar d\mathbf{s}(t)/dt$ direction and thus the vector \mathbf{s} rapidly precesses back-and-forth on a cone around the axis of $\mathbf{B}(t)$, as shown in Fig. 9.1. The component \mathbf{s}_0 is approximately constant while the small perpendicular component \mathbf{s}_d oscillates with the frequency of the EM wave and represents a magnetic dipole. With $\mathbf{m} = -2\mu_{\rm B}\mathbf{s}_{\rm d}$ and $\mu_{\rm B} = e\hbar\mu_0/2m_{\rm e}$ we obtain for the oscillating magnetic dipole moment

$$\boldsymbol{m}(t) = \mathrm{i} \; \frac{e^2 \hbar \mu_0}{\omega m_{\mathrm{e}}^2} \boldsymbol{s} \times \boldsymbol{B}_0 \; \mathrm{e}^{-\mathrm{i}\omega t}, \tag{9.12}$$

where $s \sim s_0$ is the initial spin direction. Whereas the electric dipole oscillates in the direction of E, the magnetic dipole oscillates in a direction that is perpendicular to B and s. This leads to different polarization effects in the scattering as discussed later.

We have now derived the electric and magnetic dipole moments induced by interaction of a polarized EM wave with the charge and spin of an electron. This is the first step in the X-ray scattering process. The second step is simply re-radiation of EM waves by the oscillating electric and magnetic dipoles. The scattered radiation is determined by the dipolar fields in the spatial region far from the dipole which have a rather simple spherical wave form $e^{ik'r}/r$ given by Jackson [149]. For convenience we only list the scattered electric fields denoted $\mathbf{E}'(t)$ since the magnetic field can be simply obtained from (5.9). The fields radiated by an electric dipole $\mathbf{p}(t)$ are

$$\boldsymbol{E}'(t) = \frac{\omega^2}{4\pi\epsilon_0 c^2} \; \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\boldsymbol{r}}}{\boldsymbol{r}} \; [\boldsymbol{k}'_0 \times \boldsymbol{p}(t)] \times \boldsymbol{k}'_0 \tag{9.13}$$

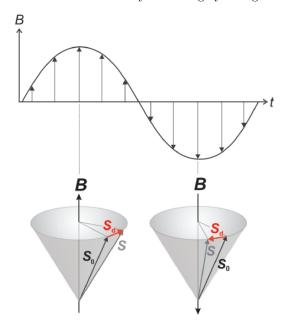


Fig. 9.1. Precessional motion of a spin in the magnetic field B(t) of a linearly polarized EM wave. When the oscillating field changes direction so does the precession direction of s. If we write $s = s_0 + s_d$ the perpendicular component s_d changes sign periodically and therefore represents an oscillating magnetic dipole

and those radiated by a magnetic dipole $\boldsymbol{m}(t)$ are

$$\boldsymbol{E}'(t) = -\frac{\omega^2}{4\pi c} \; \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\boldsymbol{r}}}{\boldsymbol{r}} \; [\boldsymbol{k}'_0 \times \boldsymbol{m}(t)]. \tag{9.14}$$

It is now simple to derive the scattered field for charge scattering by combining (9.10) and (9.13) and we obtain

$$\boldsymbol{E}'(t) = -\frac{1}{4\pi\epsilon_0} \; \frac{e^2}{m_e c^2} \; \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\boldsymbol{r}}}{r} \; [\boldsymbol{k}'_0 \times \boldsymbol{E}(t)] \times \boldsymbol{k}'_0. \tag{9.15}$$

Similarly we can combine (9.12) and (9.14) to obtain the spin scattering amplitude, remembering that $c^2 = 1/\epsilon_0 \mu_0$,

$$\boldsymbol{E}'(t) = \mathrm{i}\frac{1}{4\pi\epsilon_0} \; \frac{e^2}{m_{\mathrm{e}}c^2} \; \frac{\hbar\omega}{m_{\mathrm{e}}c^2} \; \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\boldsymbol{r}}}{r} \; [\boldsymbol{s} \times (\boldsymbol{k}_0 \times \boldsymbol{E}(t))] \times \boldsymbol{k}'_0. \tag{9.16}$$

The two scattering processes are illustrated in Fig. 9.2. Together with the above equations it clearly shows the dipolar nature of the electric and magnetic scattering processes.

There are important differences in the polarization, phase, and amplitude of charge and spin scattering. We note the following important points:

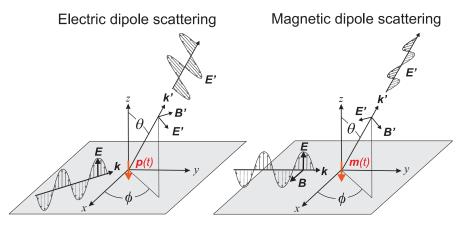


Fig. 9.2. Mechanisms of X-ray dipole scattering from a charge and a spin. Note that charge scattering preserves the polarization direction while spin scattering rotates it

- Charge scattering causes a phase shift of π (minus sign in (9.15)) between the incident and scattered fields.
- Spin scattering introduces a phase shift of $\pi/2$ (factor i in (9.16)) between the incident and scattered fields.
- The spin scattering amplitude is reduced by a factor of $\hbar\omega/m_{\rm e}c^2$ relative to the charge scattering amplitude, where $m_{\rm e}c^2 = 511 \,\rm keV$.
- Charge scattering conserves the polarization while spin scattering causes a rotation of the polarization.

We now touch base with conventional scattering theory by defining the scattering factor of a *single electron*. We assume that by a suitable analyzer we can determine the scattered amplitude and polarization direction ϵ' , which by geometry is perpendicular to the scattered wave vector \mathbf{k}'_0 . This allows us to define the polarization dependent *scattering length*

$$f(\boldsymbol{\epsilon}, \boldsymbol{\epsilon}') = -\frac{r \mathrm{e}^{-\mathrm{i}k'r}}{E} \boldsymbol{E}' \cdot \boldsymbol{\epsilon}'$$
(9.17)

It is in general a complex quantity with the dimension of [length].⁴

By use of (9.15) we obtain the electric dipole scattering length for a single electron,

$$f_{\rm e}(\boldsymbol{\epsilon}, \boldsymbol{\epsilon}') = \frac{1}{4\pi\epsilon_0} \; \frac{e^2}{m_{\rm e}c^2} \; \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' = r_0 \; \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'. \tag{9.18}$$

⁴In general, (9.17) should be written using the complex conjugate vector ϵ'^* to account for imaginary polarization vectors as are used for circularly polarized X-rays.

where $r_0 = e^2/4\pi\epsilon_0 m_e c^2 = 2.82 \times 10^{-6}$ nm is called the *classical electron* radius or the Thomson scattering length. We shall see later that the area r_0^2 , apart from a geometrical factor, gives the X-ray scattering cross-section of a single electron. It is therefore a very important reference number for describing the scattering amplitude of all multielectron systems. For magnetic dipole scattering we obtain from (9.16)

$$f_{\rm s}(\boldsymbol{\epsilon}, \boldsymbol{\epsilon}') = -\mathrm{i} \ r_0 \ \frac{\hbar\omega}{m_{\rm e}c^2} \ \boldsymbol{s} \cdot (\boldsymbol{k}_0 \times \boldsymbol{\epsilon}) \times (\boldsymbol{k}'_0 \times \boldsymbol{\epsilon}'). \tag{9.19}$$

We have conveniently defined the scattering length so that its square is proportional to the intensity scattered into a solid angle Ω , i.e., the *differential* scattering cross-section with dimension [length²/solid angle], given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\boldsymbol{\epsilon}, \boldsymbol{\epsilon}')|^2 \quad . \tag{9.20}$$

Note that by squaring the scattering factor the important phase information that was contained in the complex form of E' is lost. This gives rise to the famous phase problem in X-ray crystallography.

The total scattering cross-section for a single electron is then simply obtained by angular integration of the polarization dependent squared scattering factor. The integration of the polarization factor $\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'$ gives a factor of $8\pi/3$ and we obtain for the charge

$$\sigma_{\rm e} = \int |f(\boldsymbol{\epsilon}, \boldsymbol{\epsilon}')|^2 \mathrm{d}\Omega = r_0^2 \int_0^{2\pi} \int_0^{\pi} \sin^2\theta \,\sin\theta \,\,\mathrm{d}\theta \,\,\mathrm{d}\phi = \frac{8\pi}{3} \,\,r_0^2, \qquad (9.21)$$

which is called the *Thomson cross-section* and has the dimension $[length^2]$.

 $The \ Thomson \ cross-section$

$$\sigma_{\rm e} = \frac{8\pi}{3} r_0^2 = 0.665 \times 10^{-28} \,{\rm m}^2 = 0.665 \,{\rm barn} \tag{9.22}$$

is the total scattering cross-section from the charge of a single electron. Cross-sections are typically listed in units of barn, where $1 \text{ b} = 10^{-28} \text{ m}^2$. Hence one can conveniently remember that the X-ray scattering cross-section for a single electron is about 1 b.

The spin cross-section is obtained by angular integration of (9.19) as

$$\sigma_{\rm s} = \frac{8\pi}{3} \frac{1}{4} \left(\frac{\hbar\omega}{m_{\rm e}c^2}\right)^2 r_0^2 = \frac{\sigma_{\rm e}}{4} \left(\frac{\hbar\omega}{m_{\rm e}c^2}\right)^2. \tag{9.23}$$

Equations (9.21) and (9.23) clearly show that for typical X-ray energies charge scattering is stronger by orders of magnitude than spin scattering. For example, assuming a photon energy of 10 keV, the factor $(\hbar \omega / m_e c^2)^2 = (10/511)^2$

is about 4×10^{-4} and the weak spin scattering signal will only be observable in very special circumstances. An example is an antiferromagnetic lattice where the spin structure has a different periodicity than the charge structure and weak magnetic scattering peaks exist at locations in reciprocal space where charge scattering peaks are absent [365]. When the photon energy $\hbar\omega$ is equal to twice the rest energy of the electron, i.e., $\hbar\omega = 2m_{\rm e}c^2 = 1.022$ MeV, we see that magnetic and charge scattering have the same cross-section.

9.3.2 Scattering by an Atom

It is straightforward to extend the scattering formalism for a single electron to that for a multielectron atom. We simply assume that the total scattered amplitude is the sum of the amplitudes of the individual electrons. However, depending on which electron in the atom the X-ray wave scatters, there will be a tiny length difference in the path of the incident X-ray wave to the detector. Although the path length differences will be of the order of the size of the atom, so is the wavelength of the X-rays. Therefore the small path lengths differences can affect the scattered amplitude through interference effects. This effect is taken into account by the so-called *atomic form factor*

$$F^{0}(\boldsymbol{Q}) = -\frac{1}{e} \int \rho(r) \,\mathrm{e}^{\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}r$$
(9.24)

which makes the scattering process angle dependent, expressed by a wavevector or momentum transfer $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ in the scattering process. The atomic form factor $F^0(\mathbf{Q})$ is the Fourier transform of the number density of electrons in the atomic volume, and it is a real number.

The total charge scattering amplitude or scattering length of the atom is then given by the Thomson scattering length r_0 times the atom-specific form factor times the polarization factor of (9.18), and we obtain for the nonresonant *atomic scattering length*

$$f_{\text{atom}} = f^0(\boldsymbol{Q}) = r_0 \left(\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'\right) F^0(\boldsymbol{Q}) . \qquad (9.25)$$

By use of (9.20) this can be written as a differential scattering cross-section and we have our final result.

The nonresonant differential atomic scattering cross-section can be expressed by means of the real atomic form factor $F^0(\mathbf{Q})$ with units of number of electrons per atom and a polarization dependent term as a multiple of the scattering cross-section of a single electron $\sigma_{\rm e} = 8\pi r_0^2/3$ according to

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{atom}} = r_0^2 \left|\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}'\right|^2 |F^0(\boldsymbol{Q})|^2 = \frac{3}{8\pi} \,\sigma_\mathrm{e} \left|\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}'\right|^2 |F^0(\boldsymbol{Q})|^2. \tag{9.26}$$

For $Q \to \infty$, i.e., when the wavelength λ becomes small relative to the atomic size or when the path difference L becomes large, the waves scattered from different parts of the atom interfere destructively and cause the form factor to vanish, $F^0(\mathbf{Q}) = 0$. In the opposite limit, Q = 0, i.e., forward scattering or when the wavelength λ becomes large relative to the atomic size, there is no path length difference and different volume elements scatter in phase. Thus in the soft X-ray region where λ is of the order of 1 nm, the form factor becomes equal to the number of electrons, $f^0(\mathbf{Q}) = Z$.

9.4 SemiClassical Treatment of Resonant Interactions

So far we have not considered the different binding energies of the atomic electrons, i.e., the shell structure of the atom. In a simple model the massive positively charged nucleus (+Ze) is surrounded by core and valence electrons that have distinct binding energies. It is clear that some kind of "resonance effects" will arise when the X-ray energy is close or equal to these characteristic energies. A proper description of these effects requires quantum theory. In a quantum mechanical one-electron picture the incident photon excites a core electron in an atom to a higher lying empty state. This is the X-ray absorption step. When the electron decays back into the core shell by emission of a photon of the same energy we speak of resonant X-ray scattering, more precisely *elastic* resonant X-ray scattering. This simple picture shows that X-ray absorption and resonant X-ray scattering have a lot of physics in common and we shall connect the two now.

While the proper description and link of these processes indeed requires a quantum theoretical treatment, historically, it was first treated semiclassically. The semiclassical formalism cannot be used to calculate X-ray absorption or resonant scattering cross-sections, but it clearly reveals the link of absorption and scattering. The most important link comes from the so-called Kramers–Kronig formalism. It allows measured absorption cross-sections to be converted to scattering cross-sections and vice versa. Let us take a look at how this comes about.

9.4.1 X-ray Absorption

The importance of X-ray absorption is evident from Röntgen's first experiments, as revealed by the image in Fig. 1.14, showing the preferential absorption in bone over that in tissue. Empirically it was soon found that when X-rays traverse matter the X-ray intensity, given by (5.17) as $I = \epsilon_0 c |\mathbf{E}|^2$, decays exponentially. This fact is easily derived if we assume that each substance has a characteristic length λ_x which leads to an intensity attenuation by a factor 1/e. The quantity $\mu_x = 1/\lambda_x$ with the dimension of [length⁻¹] is called the *linear X-ray absorption coefficient*. Using the geometry of Fig. 9.3 we see that the beam is attenuated by the amount $\mu_x dz$ as it traverses the thin

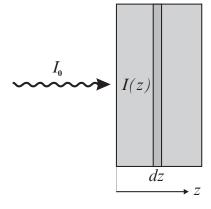


Fig. 9.3. Schematic for the derivation of the absorption law given by (9.28)

sheet of thickness dz at a depth z from the surface. This gives the following condition for the intensity

$$-\mathrm{d}I(z) = I(z)\,\mu_x\,\mathrm{d}z\;.\tag{9.27}$$

The differential equation $dI(z)/dz = -\mu_x I(z)$ has the solution $I(z) = A e^{-\mu_x z}$ and by choosing $A = I_0$ as the incident intensity at the point z = 0 we have our final result.

The X-ray absorption intensity is attenuated upon transmission through a sample with linear absorption coefficient μ_x , according to

$$I(z) = I_0 e^{-\mu_x z}.$$
 (9.28)

The X-ray absorption cross-section σ^{abs} is defined as the number of photons absorbed per atom divided by the number of incident photons per unit area and hence has the dimension [length²/atom]. The number of photons absorbed in the thin sheet dz is $I(z)\mu_x dz$ according to (9.27) and the number incident on the thin sheet per unit area is $I(z)\rho_a dz$, where ρ_a [atoms/volume] is the atomic number density. We have

$$\mu_x = \rho_{\rm a} \,\sigma^{\rm abs} = \frac{N_{\rm A}}{A} \,\rho_{\rm m} \,\sigma^{\rm abs} \tag{9.29}$$

where $\rho_{\rm m}$ [mass/volume] is the atomic mass density, $N_{\rm A} = 6.02214 \times 10^{23}$ [atoms/mol] is Avogadro's number, and A [mass/mol] is the atomic mass number. The quantities $\rho_{\rm m}$, A, and $\rho_{\rm a}$ for the 3d transition metals Fe, Co, Ni are given in Table 10.1.

The linear X-ray absorption coefficient $\mu_x = 1/\lambda_x$ has the dimension [length⁻¹], while the X-ray absorption cross-section σ^{abs} has the dimension [length²/atom].

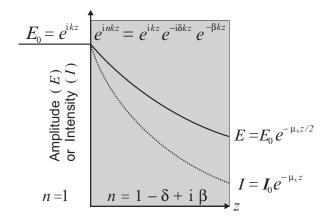


Fig. 9.4. Decay of the amplitude E and intensity $I \propto |E|^2$ of an incident wave $E_0 = e^{ikz}$ during transmission through a homogeneous sample with refractive index $n = 1 - \delta + i\beta$ and linear X-ray absorption coefficient μ_x . In the text we show that $\beta = \mu_x/2k$

Let us now take a look what happens as an EM wave enters into a medium described by a refractive index $n = 1 - \delta + i\beta$ and a linear absorption coefficient μ_x . We assume that the wave is normally incident from vacuum (n = 1) onto the sample along the z direction as shown in Fig. 9.4. For convenience we normalize the amplitude of the incident wave to 1 and ignore the temporal dependence, so that $E_0 = e^{ikz}$.

Inside the sample the electric field is then given by

$$E = e^{inkz} = \underbrace{e^{ikz}}_{E_0} \underbrace{e^{-i\delta kz}}_{\text{phase shift absorption}} \underbrace{e^{-\beta kz}}_{\text{(9.30)}}$$

and we clearly see the complex refractive contribution $e^{-i\delta kz}$ leading to a phase shift δkz and the real absorptive contribution which reduces the incident amplitude E_0 by a factor $e^{-\beta kz}$. By comparing the intensity attenuation law (9.28) with the attenuation law that follows from squaring (9.30), i.e.,

$$|E|^2 = |E_0|^2 e^{-2\beta kz} , \qquad (9.31)$$

we obtain

$$\beta = \frac{\mu_x}{2k} = \frac{\rho_{\rm a}}{2k} \,\sigma^{\rm abs}.\tag{9.32}$$

This shows the direct relationship between the X-ray absorption cross-section and β . By use of (9.7) and $k = 2\pi/\lambda$, where λ is the X-ray wavelength, we can state as follows.

The X-ray absorption cross-section is related to the imaginary part of the refractive index β and the Henke – Gullikson scattering factor f_2 according to

$$\sigma^{\rm abs} = \frac{4\pi}{\lambda \rho_{\rm a}} \,\beta = 2r_0 \lambda \,f_2 \,. \tag{9.33}$$

It is important to state the implicit assumption that went into deriving (9.33). In general, the scattering factor given by (9.2) depends on the scattering direction or \mathbf{Q} . In (9.33) we implicitly assume that $F'' = f_2$ is independent of \mathbf{Q} . This is usually a good assumption in the X-ray region where absorption and resonant scattering are due to electronic excitations of core electrons. Because of the small core shell radius the path length difference experienced by a wave that is scattered anywhere within the core volume, will be small. Therefore the angular or \mathbf{Q} dependence can be neglected when the wavelength is large relative to the atomic size since then $|\mathbf{Q}| \sim 2\pi/\lambda \to 0$. The latter condition is well satisfied in the soft X-ray region with wavelengths in excess of 1 nm.

9.4.2 Resonant Scattering

In the introduction to this section we have given the quantum mechanical picture of resonant scattering, consisting of resonant absorption and emission of a photon. Such a resonant process is semiclassically treated by representing a multielectron atom as a collection of harmonic oscillators. Each oscillator corresponds to a particular quantum mechanical resonant excitation-deexcitation process of a core shell with binding energy E_n . Each atom has then a set of resonance frequencies or energies $E_n = \hbar \omega_n$ and also characteristic damping constants Γ_n . The damping constants describe the dissipation of energy from the applied field and they have the dimension of frequency with $\Gamma_n \ll \omega_n$. The presence of the damping term indicates that the resonating atom can absorb energy from the EM wave and we shall see below that the imaginary term of the scattering cross-section is indeed related to the X-ray absorption cross-section. For a bound electron with coordinates \boldsymbol{x} the equation of motion is that of a forced harmonic oscillator,

$$\frac{\mathrm{d}^2 \boldsymbol{x}}{\mathrm{d}t^2} + \Gamma_n \frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} + \omega_n^2 \boldsymbol{x} = -\frac{e\boldsymbol{E}_0}{m_\mathrm{e}} \,\mathrm{e}^{-\mathrm{i}\omega t},\tag{9.34}$$

where we have neglected the much smaller Lorentz term $-(e/m_e)(\boldsymbol{v} \times \boldsymbol{B})$ which is of the order v/c. Since the incident EM field $\boldsymbol{E} = \boldsymbol{E}_0 e^{-i\omega t}$ impresses its frequency onto the charge, the displacement \boldsymbol{x} and its time derivatives will all have the same $e^{-i\omega t}$ time dependence and the time derivative simply gives $-i\omega$. This yields 9.4 SemiClassical Treatment of Resonant Interactions 365

$$\boldsymbol{x} = \frac{1}{\omega^2 - \omega_n^2 + \mathrm{i}\omega\Gamma_n} \frac{e\boldsymbol{E}_0}{m_\mathrm{e}}$$
(9.35)

and with p = -e x and use of (9.13) and (9.17) we obtain for the frequency dependent scattering length of a bound electron n with resonance frequency ω_n

$$f_n(\omega) = r_0 F_n(\omega) \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' . \qquad (9.36)$$

The resonance factor $F_n(\omega)$ for a core electron n, given by

$$F_n(\omega) = \frac{\omega^2}{\omega^2 - \omega_n^2 + i\omega\Gamma_n} , \qquad (9.37)$$

is a dimensionless quantity that contains the frequency dependence of the scattering factor. With the definition $\sigma_{\rm e} = \int |f_{\rm e}(\omega)|^2 d\Omega$ according to (9.21) we obtain for the angle integrated cross-section

$$\sigma_n^{\text{scat}} = \frac{8\pi}{3} \frac{\omega^4}{(\omega^2 - \omega_n^2)^2 + (\omega\Gamma_n)^2} r_0^2 .$$
(9.38)

At resonance we have $\omega = \omega_n$ and we obtain

$$\sigma_n^{\text{scat}} = \frac{8\pi}{3} \left(\frac{\omega_n}{\Gamma_n}\right)^2 r_0^2 = \left(\frac{\omega_n}{\Gamma_n}\right)^2 \sigma_e . \qquad (9.39)$$

The resonant scattering cross-section is enhanced by a factor $\omega_n^2/\Gamma_n^2 \approx 10^4$ over the nonresonant Thomson cross-section σ_e .⁵

For convenience let us rewrite $F_n(\omega)$ in terms of energy variables, the photon energy $E = \hbar \omega$, the resonance width $\Delta_n = \hbar \Gamma_n$ and the resonance position E_n . We then obtain for the resonance factor in (9.37)

$$F_n(E) = \frac{E^2}{E^2 - E_n^2 + iE\Delta_n} .$$
 (9.40)

Since $\Delta_n \ll E_n$ we can rewrite (9.40) as

$$F_n(E) \simeq 1 + F'_n(E) - iF''_n(E)$$
 (9.41)

with

$$F'_n(E) = \frac{E_n^2(E^2 - E_n^2)}{(E^2 - E_n^2)^2 + (E\Delta_n)^2} .$$
(9.42)

 $F''_n(E)$ can be written as a Lorentzian⁶ and is given by,

⁶This is derived by using the approximation $(E^2 - E_n^2) = (E + E_n)(E - E_n) \simeq 2E(E - E_n)$ which follows from the fact that resonance effects are pronounced only over a small energy range where $E \sim E_n$ [362]. As shown in Appendix A.9, the Lorentzian given by 9.43 is characterized by a position E_n , full width at half maximum (FWHM) Δ_n , height E_n/Δ_n and area $\pi E_n/2$.

⁵In the limit $\omega \gg \omega_n \gg \Gamma_n$ we obtain Thomson's result for the scattering factor given by (9.18) and the scattering cross-section is independent of frequency. In the opposite limit $\omega, \Gamma_n \ll \omega_n$ we obtain the famous Rayleigh law, where the cross-section varies with ω^4 .

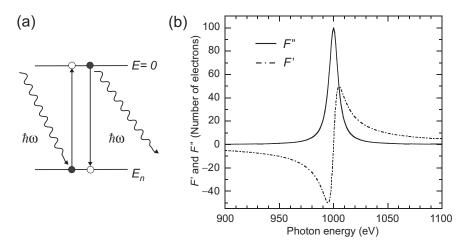


Fig. 9.5. (a) Resonant process in a simple one-electron picture. It consists of absorption of a photon through excitation of a core electron (*filled circle*) to an empty excited state (*open circle*), followed by a de-excitation process with photon emission. The process involves an energy difference E_n , yielding a single resonance. (b) Energy dependent resonance factors F'(E) and F''(E) corresponding to an excitation of a core electron of binding energy $E_n = 1,000 \,\mathrm{eV}$ and resonance width $\Delta_n = 10 \,\mathrm{eV}$, according to (9.42) and (9.43)

$$F_n''(E) = \frac{E_n}{\Delta_n} \frac{(\Delta_n/2)^2}{(E - E_n)^2 + (\Delta_n/2)^2} .$$
(9.43)

The functions $F'_n(E)$ and $F''_n(E)$ are plotted in Fig. 9.5b for typical soft X-ray parameters $E_n = 1,000 \text{ eV}$ and $\Delta_n = 10 \text{ eV}$. Because of its lineshape, $F'_n(E)$ is often called the *dispersion term*.

Let us briefly estimate the relative size of the X-ray absorption and resonant X-ray scattering cross-sections. Using the relationship between $\sigma^{abs}(E)$ and the scattering factor $F''(E) = f_2(E)$ given by (9.33) we can write for the case that the photon energy $E = \hbar \omega$ is near an atomic resonance energy E_n

$$\sigma_n^{\rm abs}(E) = 2r_0 \lambda F_n''(E) = \frac{C^*}{E} F_n''(E) = \frac{C^*}{E} \frac{E_n}{\Delta_n} \frac{(\Delta_n/2)^2}{(E - E_n)^2 + (\Delta_n/2)^2} \,. \tag{9.44}$$

Here $C^* = 2 h c r_0 = 0.70 \times 10^8$ b eV. The absorption cross-section for a core electron in (9.44) has a peak value C^*/Δ_n . In the soft X-ray region $\Delta_n \simeq 10 \text{ eV}$ so that the resonant X-ray absorption cross-section is about 10^7 b. This is to be compared to the scattering cross-section which according to (9.21) is obtained as

$$\sigma_n^{\text{scat}}(E) = \sigma_e \left\{ \left[1 + F'_n(E) \right]^2 + \left[F''_n(E) \right]^2 \right\} = \sigma_e \frac{E^4}{(E^2 - E_n^2)^2 + (E\Delta_n)^2} .$$
(9.45)

with a peak value of $\sigma_{\rm e}(E_n/\Delta_n)^2 \sim 10^4$ b. The resonant X-ray absorption cross-section is seen to be a factor of $\sim 10^3$ larger that the resonant X-ray scattering cross-section.

In our discussion above we have only considered a resonant process associated with one particular core shell of binding energy E_n . When the incident photon energy is near E_n the atomic response will be dominated by the shell n which "resonates." The other shells will not resonate and simply produce a constant "background" contribution due to nonresonant scattering. This background contribution is given by the atomic form factor $F^0(\mathbf{Q})$, defined in (9.24), which is the first term in the general expression of the scattering factor given by (9.2). The \mathbf{Q} -dependent general formulation of resonant scattering can be written in analogy to the nonresonant case given by (9.26). In particular, the differential atomic resonant scattering cross-section is given by

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{scat}} = |f(\boldsymbol{Q}, E)|^2 = |f^0(\boldsymbol{Q}) + f'(E) - \mathrm{i} f''(E)|^2$$
$$= r_0^2 |\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'|^2 |F^0(\boldsymbol{Q}) + F'(E) - \mathrm{i} F''(E)|^2 . \tag{9.46}$$

In the limit of forward scattering we have $\mathbf{Q} = 0$ and $\epsilon = \epsilon'$ and the form factor is simply given by the number of atomic electrons Z, i.e., $F^0(\mathbf{Q} = 0) = F^0 = Z$. This is reflected by replacing the factor 1 for one electron in (9.41) and (9.45) by the factor Z for all electrons in an atom, as assumed in (9.3). This yields the following expression for the resonant forward scattering cross-section

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\boldsymbol{Q}=0}^{\mathrm{scat}} = r_0^2 \left\{ \left[Z + F'(E)\right]^2 + \left[F''(E)\right]^2 \right\} = r_0^2 \left\{ \left[f_1(E)\right]^2 + \left[f_2(E)\right]^2 \right\}.$$
(9.47)

At the end of this section let us summarize the meaning of the different quantities used to describe the resonant scattering amplitude.

- The resonant scattering factor $F(\mathbf{Q}, E) = F^0(\mathbf{Q}) + F'(E) iF''(E)$ has the dimension [number of electrons per atom].
- The resonant scattering length $f(\mathbf{Q}, E) = r_0 \, \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' F(\mathbf{Q}, E)$ depends on polarization and has the dimension [length × number of electrons per atom].
- The Henke-Gullikson factors $f_1(E) = Z + F'(E)$ and $f_2(E) = F''(E)$ describe the case of small |Q| and have the dimension [number of electrons per atom].

9.4.3 Correspondence between Resonant Scattering and Absorption

Expression (9.47) gives the resonant forward scattering cross-section in terms of the real and imaginary parts of the resonant X-ray scattering factor $F(E) = f_1(E) - if_2(E)$. This link is particularly useful at long wavelengths where $|\mathbf{Q}|$ is small and the \mathbf{Q} -dependence may be neglected, in general. This case applies for photon energies below a few keV where the wavelength is much larger than the atomic size and in this "small atom" or "long-wavelength" limit one may conveniently define an *angle-integrated atomic scattering cross-section* similar to that for the single electron case (see (9.21) and (9.22)) by integration of (9.46) with $|\mathbf{Q}| = 0$ over the polarization factor. In the long-wavelength limit the *total atomic scattering cross-section* is given by

$$\sigma^{\text{scat}}(E) = \int \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{|\mathbf{Q}|=0}^{\text{scat}} \mathrm{d}\Omega = \sigma_{\mathrm{e}}\left\{\left[f_1(E)\right]^2 + \left[f_2(E)\right]^2\right\}.$$
 (9.48)

We have also seen above in (9.33) that the X-ray absorption cross-section $\sigma^{abs}(E)$ is directly linked to the imaginary part of the X-ray scattering factor $F''(E) = f_2(E)$. This important result is usually referred to as the *optical theorem*.

The *optical theorem* states that at long wavelengths (small |Q|) the imaginary part of the scattering factor is directly related to the absorption cross-section according to

$$\sigma^{\rm abs}(E) = 2 r_0 \lambda \, {\rm Im}[F(\boldsymbol{Q}, E)]_{\boldsymbol{Q} \to 0} = \frac{C^*}{E} f_2(E) \,, \qquad (9.49)$$

where $C^* = 2 h c r_0 = 0.70 \times 10^8 \text{ b eV}.$

The scattering factors and cross-sections for Fe metal, taken from the work of Kortright and Kim [353], are plotted in Fig. 9.6 in the vicinity of the L_3 and L_2 edges. Note the strong similarity of the lineshape of the scattering factors with those in Fig. 9.5.

9.4.4 The Kramers–Kronig Relations

The idea is to have a formalism that links both $F'_n(E)$ and $F''_n(E)$ to the X-ray absorption cross-section σ_n^{abs} which is easily measured. While this formalism naturally emerges from quantum mechanics, which allows transitions to both bound and continuum states, we shall nevertheless continue with our semiclassical model. It will yield the same results and lead us to the famous and important Kramers–Kronig relations.

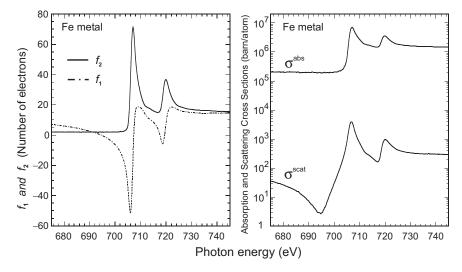


Fig. 9.6. Left: Measured energy dependent resonance factors f_1 and f_2 for the $L_{3,2}$ edges of Fe metal $(2p_{3/2}, 2p_{1/2} \rightarrow 3d \text{ transitions})$ [353]. Right: Energy dependent
cross-sections for X-ray absorption (top) and scattering (bottom) calculated from
the scattering factors according to (9.49) and (9.48), respectively

The Kramers–Kronig relation allows the determination of $F'_n(E)$ from the measured absorption cross-section $\sigma_n^{abs}(\epsilon)$ according to

$$F'_n(E) = \frac{1}{C} P_0^{\infty} \frac{\epsilon^2 \sigma_n^{\text{abs}}(\epsilon)}{(E^2 - \epsilon^2)} \,\mathrm{d}\epsilon \;. \tag{9.50}$$

Here $C = C^* \pi/2 = \pi h c r_0 = 1.098 \times 10^8$ beV. In (9.50) we have replaced the lower integration limit by zero because the cross-section $\sigma_n^{abs}(\epsilon)$ and hence the integral is zero for $\epsilon < E_n$. In practice, the integration is tricky because of the singularity for $\epsilon = E$ and at a given photon energy E the integral has to be evaluated by integrating from 0 to $E - \delta$ and from $E + \delta$ to ∞ and then taking the limit $\delta \to 0$. This is indicated by the "Pf" symbol, meaning "principal value" integral. Today this task is readily accomplished with modern mathematical software packages. In text books two Kramers– Kronig relations are typically found that relate the two resonance factors. The first one is obtained from (9.50) by use of the relation $\sigma_n^{abs}(\epsilon) = C^* F_n''(\epsilon)/\epsilon$ in (9.49)

$$F'_n(E) = \frac{2}{\pi} P_0^{\infty} \frac{\epsilon F''_n(\epsilon)}{(E^2 - \epsilon^2)} d\epsilon , \qquad (9.51)$$

and the second one allows the opposite transformation

$$F_n''(E) = \frac{2E}{\pi} P_0 \int_0^\infty \frac{F_n'(\epsilon)}{(E^2 - \epsilon^2)} \,\mathrm{d}\epsilon \;. \tag{9.52}$$

Again, the "Pf" symbol means principal value integral.

9.5 Quantum-Theoretical Concepts

9.5.1 One-Electron and Configuration Pictures of X-ray Absorption

In the simplest picture of resonant X-ray absorption a photon transfers its energy to a core electron and the electron is excited into an unoccupied electronic state. In this so-called *one-electron picture* we simply follow what happens to the photoelectron. This is also referred to as the *active electron approximation* [189] since we ignore what happens to all other "passive" electrons in the atom during the excitation process. Although this picture is not entirely correct since the "passive" electrons are not passive, it is quite intuitive, and because of its simplicity the picture is often used in the X-ray absorption literature.

Let us illustrate the one-electron picture for the L-edge X-ray absorption spectrum of a 3d transition metal atom, as shown in Fig. 9.7a. In the "initial

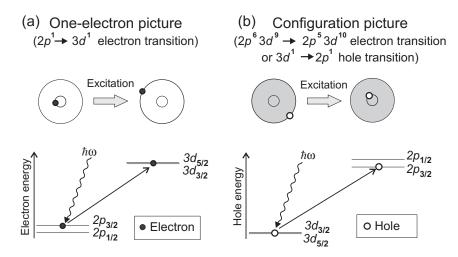


Fig. 9.7. Description of resonant L-edge X-ray absorption in two pictures, (a) one electron picture and (b) d^9 configuration picture. Each energy level is labeled by its quantum numbers $n, l, j = l \pm s$. In (a) the quantum numbers label oneelectron states, in (b) they label hole states for the special case of a $3d^9$ electronic ground state, containing nine electrons or equivalently one hole. The two pictures are equivalent for the description of the electronic transitions

state" or 2p core state, the active electron has an angular momentum l = 1 and spin s = 1/2, so that the spin–orbit coupling, discussed in Sect. 6.4, produces two energy states with $j = l \pm s$. The four substates of $2p_{3/2}$ with $j_+ = 3/2$ experience an energy shift $E_{j_+} = \zeta_l/2$ and the two substates of $2p_{1/2}$ with $j_- = 1/2$ are shifted by $E_{j_-} = -\zeta_l$, with the separation given by the *Landé* interval rule $E_{j_+} - E_{j_-} = \zeta_l j_+$. In the "final state" the active electron is located in the 3d shell with angular momentum l = 2 and spin s = 1/2. The spin–orbit coupling again produces two energy states with $j = l \pm s$, i.e., the states $3d_{5/2}$ with j = 5/2 and $3d_{3/2}$ with j = 3/2, as shown in Fig. 9.7a. Because the core shell is more compact its spin–orbit coupling constant ζ_{2p} is considerably larger (of order 15 eV) than that of the valence shell ζ_{3d} (of order 50 meV), and the $2p_{3/2} - 2p_{1/2}(L_3 - L_2)$ splitting dominates, as seen in the experimental spectrum of Fe metal in Fig. 9.6.

The one-electron picture of Fig. 9.7a is misleading, however, especially to the photoemission community, in that it depicts the spin-orbit splitting of the p core shell as an "initial state" effect. It is clear that in reality the p shell is filled in the ground state and there is therefore no observable effect of the spin-orbit interaction. In the proper description of the X-ray absorption process, based on a *configuration picture*, an atom is excited from a ground or initial state configuration to an excited or final state configuration. In discussing transitions between configurations one typically omits all closed subshells since they are spherically symmetrical and their net angular momentum is zero [182]. Listing only the active shells, resonant L-edge absorption is described by an initial state electron configuration $2p^6d^n$ and a final state configuration $2p^5d^{n+1}$.

For transition metal atoms with configurations $1 \le n \le 9$ it is particularly easy to deal with the configuration d^9 in X-ray absorption, which is the configuration for Cu^{2+} (see Fig. 10.1a). In this case the initial state contains a filled p^6 shell and nine electrons in the *d* shell. A d^9 electron configuration is equivalent to a d^1 hole configuration and by taking proper care of signs it is often more convenient to carry out calculations in the corresponding hole rather than the electron picture. We shall do so in the following. Because of the cancellation of angular momenta in a filled shell we can simply describe the initial state as a d^1 hole configuration. The final state $p^5 d^{10}$ has a closed d-shell and a p^5 electron or p^1 hole configuration. Hence for a d^9 ground state, L-edge spectra in a configuration hole picture are described by a transition from the configuration d^1 to p^1 . The spin-orbit splitting of the p shell is therefore properly described as a final state effect, as shown in Fig. 9.7b. We see that the two pictures in Fig. 9.7 are completely equivalent in describing the electronic transitions. Note that the energy order of the j states is inverted in the two schemes because electrons and holes have opposite spin.⁷

⁷This is expressed by Hund's third rule stating that the electronic ground state has the minimum possible j value for a less than half filled shell and the maximum possible j value for a more than half full shell.

In general, the one electron and configuration pictures are not equivalent. Differences arise when open shells with two or more holes or electrons need to be considered. In such cases exchange and correlation effects between the particles may be large as discussed in Chap. 7. Such effects lead to multiplet structure in the ground state, i.e., between the d electrons, as well as in the excited state, between the core p and valence d electrons. The simplest two-particle case is that of a p^6d^8 ground state configuration leading to a p^5d^9 excited state. This situation, which is encountered in NiO, can also be described (taking proper care of signs) by the equivalent case of a ground state d^2 hole configuration and an excited state we have to consider the exchange and correlation between two holes. We shall discuss multiplet effects in more detail in Sect. 9.7.8.

Next we shall discuss how to calculate transition probabilities associated with X-ray excitation and de-excitation processes.

9.5.2 Fermi's Golden Rule and Kramers–Heisenberg Relation

The X-ray absorption and X-ray scattering cross-sections are both calculated by consideration of the time-dependent perturbation of the sample by the EM field. The time-dependent EM field induces transitions between an initial state $|i\rangle$ and final state $|f\rangle$, where both states contain an electronic and a photon part. If the system evolves directly from state $|i\rangle$ to $|f\rangle$ we speak of a first-order process, if some intermediate states $|n\rangle$ are involved we call it a second-order process. As illustrated schematically in Fig. 9.8, X-ray absorption is a first order and resonant X-ray scattering a second-order process.

The associated formalism was derived by Kramers and Heisenberg [366] and by Dirac [367] and the transition probability up to second order can be written as follows.

The transition probability per unit time, T_{if} , from a state *i* to a state *f* is given up to second order by,

$$T_{if} = \frac{2\pi}{\hbar} \left| \langle f | \mathcal{H}_{\text{int}} | i \rangle + \sum_{n} \frac{\langle f | \mathcal{H}_{\text{int}} | n \rangle \langle n | \mathcal{H}_{\text{int}} | i \rangle}{\varepsilon_i - \varepsilon_n} \right|^2 \delta(\varepsilon_i - \varepsilon_f) \rho(\varepsilon_f).$$
(9.53)

The sum is over all possible states of energy ε_n . The dimension of T_{if} is $[time^{-1}]$.

For X-ray absorption and resonant elastic scattering (including magnetic resonant scattering) the interaction Hamiltonian consists of the product of the momentum operator p and the vector potential A according to [147, 178, 368, 369]

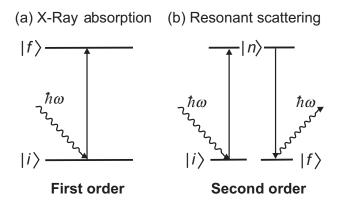


Fig. 9.8. Description of X-ray absorption and resonant elastic X-ray scattering as transitions between quantum mechanical states which are products of electronic and photon states. The X-ray absorption process corresponds to a *first-order* transition process between an initial state $|i\rangle$ and an excited state $|f\rangle$. The resonant scattering process is a *second-order* process that involves intermediate states $|n\rangle$. The system can pass through the intermediate states in a virtual sense that does not require energy conservation until the final state $|f\rangle$ is reached

$$\mathcal{H}_{\rm e}^{\rm int} = \frac{e}{m_{\rm e}} \, \boldsymbol{p} \cdot \boldsymbol{A} \; . \tag{9.54}$$

Since in free space $\mathbf{E} = -\partial \mathbf{A}/\partial t$ this expression means that the electronic transition is driven by the electric field \mathbf{E} of the EM wave. The states and energies in (9.53) reflect those of the combined photon plus atom system. The wave functions $|i\rangle$ and $|f\rangle$ are products of electronic and photon states and the energies are sums of electronic and photon energies. The quantity $\rho(\varepsilon_f)$ is the density of final states per unit energy.

The first-order term in (9.53) was originally derived by Dirac [367] and called by Fermi the "Golden Rule No. 2" [370]. It is therefore often called by the somewhat misleading name *Fermi's golden rule*. The second-order term, referred to by Fermi as "Golden Rule No. 1" [370], was originally derived by Kramers and Heisenberg [366] and today is usually called the *Kramers– Heisenberg relation*. It gives the transition probability from $|i\rangle$ to $|f\rangle$ via a range of virtual intermediate states $|n\rangle$. The system can pass through the intermediate states in a virtual sense that does not require energy conservation until the final state is reached. This energy conservation is reflected by the delta function that involves only the initial and final states. With the dimensions of \hbar [energy × time], $\rho(\varepsilon_f)$ [1/energy] and $|\mathcal{H}_{int}|^2$ [energy²], we obtain the dimension of T_{if} as [1/time].

The total cross-section is obtained from the transition probability per unit time T_{if} by normalization to the incident photon flux Φ_0 .

$$\sigma = \frac{T_{if}}{\Phi_0} \ . \tag{9.55}$$

The numerator has the dimension [1/time] and the incident photon flux Φ_0 , given by (5.18), has the dimension $[1/(\text{time} \times \text{area})]$, so that σ has the dimension [area].

The differential cross-section $d\sigma/d\Omega$ reflects the number of transitions per unit time into the solid angle $d\Omega$ and is given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{T_{if}}{\Phi_0 \,\mathrm{d}\Omega} \,. \tag{9.56}$$

9.5.3 Resonant Processes in the Electric Dipole Approximation

We now want to give the basic quantum mechanical expressions used for the calculation of polarization dependent X-ray absorption and resonant scattering processes. We would like to calculate the intensities of strong resonances like those associated with $2p_{3/2}, 2p_{1/2} \rightarrow 3d$ transitions in Fig. 9.6, commonly called "white lines" for historical reasons. In the early days, when photographic plates were used as detectors, the strong absorption resonances appeared etched into the black detector emulsion as white lines. In the following we shall adopt this terminology and often speak of the "white line intensity."

By quantizing the electromagnetic field [371] one can separate the matrix elements in (9.53) into electronic and photon parts, evaluate the photon part, and obtain the matrix elements in terms of transitions between two electronic states $|a\rangle$ and $|b\rangle$. The relevant matrix elements have the general form

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon} e^{i\boldsymbol{k} \cdot \boldsymbol{r}} | a \rangle , \qquad (9.57)$$

where p is the electron momentum vector, ϵ the unit photon polarization vector, and k the photon wave vector. For the purpose of the present book it is sufficient to stay within the *dipole approximation*. Within this approximation one eliminates the k-dependence of the matrix element and rewrites the electron momentum operator p in terms of the *length operator* r according to

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon} (1 + \mathrm{i} \boldsymbol{k} \cdot \boldsymbol{r} + ...) | a \rangle \simeq \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon} | a \rangle = \mathrm{i} m_{\mathrm{e}} \omega \langle b | \boldsymbol{r} \cdot \boldsymbol{\epsilon} | a \rangle \qquad (9.58)$$

As before, m_e is the electron rest mass and $\omega = \omega_b - \omega_a$ the photon frequency associated with the transition from state $|a\rangle$ to state $|b\rangle$. The dipole approximation assumes that the size of the absorbing atomic shell is small relative to the X-ray wavelength, i.e., $|\mathbf{r}| \ll 1/|\mathbf{k}| = \lambda/2\pi$, so that the electric field which drives the electronic transition is constant over the atomic volume. In our case we are interested mostly in the photon energy range $\hbar\omega \leq 1,000 \text{ eV}$ corresponding to a wavelength $\lambda \geq 1.2 \text{ nm}$ and transitions from the 2p core shell of radius $|\mathbf{r}| \simeq 0.01 \text{ nm}$ so that we have $|\mathbf{r}| \simeq 0.01 \text{ nm} \ll \lambda/2\pi \simeq 0.2 \text{ nm}$, and it is reasonable to use the dipole approximation.

In the dipole approximation the X-ray absorption cross-section is given by

$$\sigma^{\rm abs} = 4\pi^2 \frac{e^2}{4\pi\epsilon_0 \hbar c} \hbar \omega |\langle b| \,\boldsymbol{\epsilon} \cdot \boldsymbol{r} |a\rangle|^2 \,\delta[\hbar \omega - (E_b - E_a)] \,\rho(E_b) \,, \qquad (9.59)$$

where the density of final states per unit energy, $\rho(E_b)$, depends on the normalization of the electronic wavefunctions $|a\rangle$ and $|b\rangle$. The X-ray absorption resonance intensity, $I_{\rm res}$, is the energy integral over the cross-section and if we assume that the functions $|a\rangle$ and $|b\rangle$ have been volume normalized to unity one obtains the following expression that will be used throughout this chapter [190, 372].

The polarization dependent X-ray absorption resonance intensity in the dipole approximation is given by

$$I_{\rm res} = \mathcal{A} |\langle b| \, \boldsymbol{\epsilon} \cdot \boldsymbol{r} |a \rangle|^2 \,. \tag{9.60}$$

The proportionality factor, given by

$$\mathcal{A} = 4\pi^2 \frac{e^2}{4\pi\epsilon_0 \hbar c} \hbar \omega \tag{9.61}$$

contains the dimensionless fine structure constant $\alpha_{\rm f}$

$$\alpha_{\rm f} = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.04}.$$
(9.62)

The intensity I_{res} has the dimension [length²× energy] and is usually expressed in units of [Mb eV], where $1 \text{ Mb} = 10^{-22} \text{ m}^2$.

If there are more than one discrete final state we need to sum the intensities associated with different final states. This is often expressed as a separate density of final state factor in the equation for the transition intensity, but we have included it in (9.60) into our final state description.

We see that the calculation of $I_{\rm res}$ boils down to the evaluation of the polarization dependent transition matrix element $\langle b | \boldsymbol{\epsilon} \cdot \boldsymbol{r} | a \rangle$. In the following we may therefore loosely refer to the squared matrix element with dimension [length²] as the "transition intensity." The true intensity given by (9.60) has the dimension [energy × length²].

Similarly, one can also evaluate the second-order term in (9.53) to obtain an expression for the resonantly scattered X-ray intensity. In the dipole approximation one again neglects the k dependence in the transition matrix elements.⁸ By using the short hand notation for the resonant energies $E_{\rm R}^n = E_n - E_a$ and denoting the finite full width at half maximum (FWHM) of the intermediate state energy distributions as Δ_n one obtains the following differential resonant scattering cross-section.

⁸The same result is also obtained by assuming forward scattering, i.e., $k_1 = k_2$.

The polarization dependent differential resonant X-ray scattering crosssection in the dipole approximation is given by

$$\left(\frac{\mathrm{d}\,\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{scat}} = \left|f(\hbar\omega)\right|^2 = \frac{\hbar^2\omega^4}{c^2} \alpha_{\mathrm{f}}^2 \left|\sum_{n} \frac{\langle a|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_2^*|n\rangle\langle n|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_1|a\rangle}{(\hbar\omega - E_{\mathrm{R}}^n) + \mathrm{i}(\Delta_n/2)}\right|^2. \quad (9.63)$$

Here $\alpha_{\rm f}$ is the dimensionless fine structure constant and ϵ_1 and ϵ_2 are the unit polarization vectors of the incident and scattered radiation.

In the following we shall establish the form of the polarization dependent dipole operator $\boldsymbol{\epsilon} \cdot \boldsymbol{r}$ and the form of the wavefunctions $|a\rangle$ and $|b\rangle$.

9.5.4 The Polarization Dependent Dipole Operator

According to (9.60) the *polarization dependent dipole operator* is given by the dot product $\boldsymbol{\epsilon} \cdot \boldsymbol{r}$. Here \boldsymbol{r} is the electron position vector, given in Cartesian coordinates by

$$\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z \ . \tag{9.64}$$

We are particularly interested in the X-ray absorption intensity for pure linear or circular polarization since we have seen in Sect. 4.4.1 that such pure polarization states can be produced today by suitable undulators. We have also discussed their mathematical description in Sect. 5.4. Here we want to distinguish cases of different polarization and different X-ray incidence directions in the (x, y, z) coordinate system of the sample. We express the angular momentum as $q\hbar$ so that q = 0 refers to linearly polarized light and $q = \pm 1$, or $q = \pm$ for short, to circularly polarized light.

For *linearly polarized X-rays*, the direction of the E vector determines the X-ray absorption intensity, and for the three extreme cases where E is aligned along x, y, and z we have the corresponding real unit polarization vectors

$$\boldsymbol{\epsilon}_x^0 = \boldsymbol{\epsilon}_x = \boldsymbol{e}_x \qquad \boldsymbol{\epsilon}_y^0 = \boldsymbol{\epsilon}_y = \boldsymbol{e}_y \qquad \boldsymbol{\epsilon}_z^0 = \boldsymbol{\epsilon}_z = \boldsymbol{e}_z \ . \tag{9.65}$$

For *circularly polarized* X-rays we consider the cases where the angular momenta, which are parallel to the X-ray wavevector \mathbf{k} , are aligned along x, y, and z. For circularly polarized X-rays with $\mathbf{k} \parallel z$ we write the unit polarization vector in accordance with (5.35) and (5.36) as

$$\boldsymbol{\epsilon}_{z}^{\pm} = \mp \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_{x} \pm \mathrm{i} \, \boldsymbol{\epsilon}_{y}), \qquad (9.66)$$

and for propagation along x or y we use a similar notation according to a right handed coordinate system, e.g., for $k \parallel x$

$$\boldsymbol{\epsilon}_x^{\pm} = \mp \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_y \pm \mathrm{i} \, \boldsymbol{\epsilon}_z). \tag{9.67}$$

The dipole operators $P_{\alpha}^{q} = \boldsymbol{\epsilon} \cdot \mathbf{r} = \boldsymbol{\epsilon}_{\alpha}^{q} \cdot \mathbf{r}$ in (9.60) can then be rewritten in terms of the familiar spherical harmonics $Y_{l,m}(\theta, \phi)$ [181, 182], and for $\alpha = z$ we have

$$P_{z}^{\pm} = \boldsymbol{\epsilon}_{z}^{\pm} \cdot \mathbf{r} = \pm \frac{1}{\sqrt{2}} \left(x \pm iy \right) = r \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}, \qquad (9.68)$$

$$P_z^0 = \boldsymbol{\epsilon}_z \cdot \mathbf{r} = \qquad z \qquad = r \sqrt{\frac{4\pi}{3}} Y_{1,0}. \tag{9.69}$$

Because of the prefactors of the spherical harmonics, it is more convenient to express the dipole operators in terms of *Racah's spherical tensor operators*.

Racah's spherical tensor operators are defined as [181],

$$C_m^{(l)} = \sqrt{\frac{4\pi}{2l+1}} Y_{l,m}(\theta,\phi) , \qquad \left(C_m^{(l)}\right)^* = (-1)^m C_{-m}^{(l)} .$$
 (9.70)

We have listed these spherical tensors for $0 \le l \le 4$ in Table A.3. The polarization dependent electric dipole operators are related to Racah's tensor operators of rank l = 1, and we have for example

$$P_z^0 = r C_0^{(1)} = r \cos \theta = z, \qquad (9.71)$$

$$P_z^{\pm} = r C_{\pm 1}^{(1)} = \mp r \frac{1}{\sqrt{2}} \sin \theta \, \mathrm{e}^{\pm \mathrm{i}\phi} = \mp \frac{1}{\sqrt{2}} \, (x \pm \mathrm{i}y). \tag{9.72}$$

The dipole operators for all polarization cases $(q = 0, \pm 1)$ and orientations of the principal axes $\alpha = x, y, z$ of our sample coordinate system are listed in Table A.4. They can be written in the general form

$$P_{\alpha}^{q}/r = \sum_{p=0,\pm 1} e_{\alpha,p}^{q} C_{p}^{(1)} = e_{\alpha,1}^{q} C_{1}^{(1)} + e_{\alpha,0}^{q} C_{0}^{(1)} + e_{\alpha,-1}^{q} C_{-1}^{(1)} , \qquad (9.73)$$

where the coefficients $a_{\alpha,p}^q$ may be imaginary with $\sum_p |e_{\alpha,p}^q|^2 = 1$. The above discussion leads to the following form of the matrix element in (9.60) in terms of the polarization dependent dipole operators P_{α}^q ,

$$\langle b|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|a\rangle = \langle b|P^q_{\alpha}|a\rangle.$$
 (9.74)

We can then rewrite (9.60) in its final form, to be used from now on.

The X-ray absorption resonance intensity for different X-ray propagation directions α and polarization states q can be written as

$$I_{\rm res} = \mathcal{A} |\langle b| P^q_{\alpha} |a\rangle|^2, \qquad (9.75)$$

where \mathcal{A} is given by (9.61) and the polarization dependent dipole operators P_{α}^{q} with $\alpha = x, y$, or z and q = +1, 0, or -1 are listed in Table A.4.

9.5.5 The Atomic Transition Matrix Element

The calculation of the transition matrix element depends on the wavefunctions $|a\rangle$ and $|b\rangle$. In a one-electron picture, the "initial state" $|a\rangle$ is given by the core electron wavefunction. The "final state" $|b\rangle$ consists of the valence electron wavefunctions.

The simplest wave functions are the atomic spin orbitals of the central field form given by (6.12) or

$$R_{n,l}(r) Y_{l,m_l} \chi_{s,m_s} = |R_{n,l}(r); l, m_l, s, m_s\rangle, \qquad (9.76)$$

where the Dirac bra-ket notation is given on the right. $R_{n,l}(r)$ is the radial component of a shell n with angular momentum l, the spherical harmonics Y_{l,m_l} characterize the angular part and χ_{s,m_s} is the spin part. We shall see below that a general wavefunction appropriate for an atom in a solid, i.e., a ligand field or band state that includes bonding, exchange and spin-orbit effects, can in fact be written as a linear combination of atomic basis functions of the form (9.76). The atomic functions (9.76) are therefore of paramount importance and we shall first take a look at the calculation of transition matrix elements with such functions.

In a one-electron picture a "initial" state wavefunction for a core shell n with angular momentum c is given by

$$|a\rangle = |R_{n,c}(r); c, m_c, s, m_s\rangle , \qquad (9.77)$$

where $R_{n,c}(r)$ is the radial component of the core shell with principal quantum numbers n and orbital quantum number c, and $|s = 1/2, m_s\rangle$ describes the spin state of the electron.

The "final" state will be of the form

$$|b\rangle = |R_{n',l}(r); l, m_l, s, m'_s\rangle$$
, (9.78)

where $R_{n',l}$ is the radial component of the valence state of shell n' with angular momentum l. The exclusion principle does not allow electrons to be excited into occupied states, and hence the final states are determined by the empty states in the l subshell. The task before us is then to calculate the transition matrix element

$$\langle b | P^{q}_{\alpha} | a \rangle = \langle R_{n',l}(r); l, m_{l}, s, m'_{s} | P^{q}_{\alpha} | R_{n,c}(r); c, m_{c}, s, m_{s} \rangle,$$
(9.79)

with the direction and polarization dependent dipole operators P^q_{α} given in Table A.4. We see from (9.73) that the matrix element in (9.79), in general, involves a sum over matrix elements of the Racah operators $C^{(1)}_q$. For a transition from a core shell with angular momentum c to an unfilled valence shell with angular momentum l we obtain

$$\langle b | P_{\alpha}^{q} | a \rangle = \underbrace{\delta(m'_{s}, m_{s})}_{\text{spin}} \underbrace{\langle R_{n',l}(r) | r | R_{n,c}(r) \rangle}_{\text{radial}} \underbrace{\sum_{m_{c}, m_{l}, p} e_{\alpha, p}^{q} \langle l, m_{l} | C_{p}^{(1)} | c, m_{c} \rangle}_{\text{angular}},$$

$$(9.80)$$

where the coefficients $e_{\alpha,p}^q$ are those in Table A.4. The matrix elements factors into spin, radial, and angular parts. We see that the dipole operator does not act on the spin and only transitions are allowed that preserve the spin. The polarization dependence is entirely contained in the angular part of the wavefunctions. The radial part determines the angle integrated transition strength.

The Radial Part of the Atomic Transition Matrix Element

The radial dipole matrix element is given by

$$\mathcal{R} = \langle R_{n',l}(r) | r | R_{n,c}(r) \rangle = \int_0^\infty R_{n',l}^*(r) R_{n,c}(r) r^3 \mathrm{d}r , \qquad (9.81)$$

where $\{n, c\}$ and $\{n', l\}$ describe the shell and subshell quantum numbers of the initial and final states, respectively.

The radial parts of the wavefunctions $R_{nl}(r)$ obey the normalization condition

$$\int_{0}^{\infty} |R_{nl}(r)|^2 r^2 \,\mathrm{d}r = 1 \,. \tag{9.82}$$

In order to picture the radial extent of the transition matrix element \mathcal{R} given by (9.81) we compare in Fig. 9.9 the function $r^3 R_{2p}(r) R_{3d}(r)$ for a $2p \to 3d$ transition to the functions $r^2 R_{nl}^2(r)$ for nl = 1s, 2p, 3d, using parameterized radial functions given by Griffith [228] for the Mn²⁺ ion.

The localization of \mathcal{R} in the core region of the atom leads to some fundamental differences between X-ray absorption spectroscopy (XAS) and optical spectroscopy. Because of the small energy (of order of 1 eV) of optical transitions, electronic excitations occur only between filled and empty *valence* states. In many systems the probed valence states are extended states which are not localized on a specific atom and the intensity of optical transitions is determined by the group theoretical symmetry of the valence states, dictated by the molecule or crystal. In contrast, XAS is based on transitions involving core electrons which are localized on specific atoms. The function $R_{\text{core}} R_{\text{valence}} r^3$ which determines the integral \mathcal{R} has its major contribution close to the atomic core, as shown in Fig. 9.9. It gives X-ray absorption spectroscopy its elemental specificity and local character. XAS may be viewed as an inverted linear combination of atomic orbitals (LCAO) scheme. The

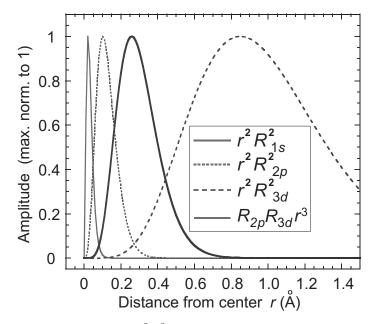


Fig. 9.9. Top: Radial functions $r^2 R^2(r)$ for the 1s, 2p, and 3d orbitals of the Mn²⁺ ion, representing the probability of finding the electron at a distance r from the nucleus. Their maxima are often associated with the Bohr radii. Also plotted is the function $R_{2p}(r) R_{3d}(r) r^3$ (thick solid line), describing the localization of the $2p \rightarrow 3d$ transition matrix element, according to (9.81). All functions are plotted for the distance r from the atomic center and the amplitudes have been normalized to 1. The plotted Slater type functions are taken from Griffith [228]

LCAO scheme composes molecular functions from atomic functions, XAS decomposes the molecular functions into its atomic constituents. This is often referred to as the *one center approximation*.

The strong localization of the core shell makes X-ray absorption spectroscopy element-specific and sensitive to the valence shell properties within the atomic volume.

The Angular Part of the Atomic Transition Matrix Element

The angular part of the transition matrix element (9.80) is determined by matrix elements of the form $\langle l, m_l | C_q^{(1)} | c, m_c \rangle$. For convenience, we have tabulated the nonzero matrix elements in Table 9.1.

By inspection of the nonvanishing matrix elements we can read off the *dipole selection rules*.

$m C_{-q}^{(1)} L, M\rangle$. Nonlisted matrix elements are zero. ^a		
$\langle l+1,m C_{0}^{(1)} l,m\rangle$		
$\langle l-1,m C_0^{(1)} l,m angle$	=	$\sqrt{\frac{l^2 - m^2}{(2l - 1)(2l + 1)}}$
$\left\langle \left. l+1,m+1\right C_{1}^{\left(1\right) }\left l,m\right\rangle \right.$	=	$\sqrt{\frac{(l+m+2)(l+m+1)}{2(2l+3)(2l+1)}}$
$\frac{\langle l-1,m+1 C_1^{(1)} l,m\rangle}{2}$	=	$-\sqrt{\frac{(l-m)(l-m-1)}{2(2l-1)(2l+1)}}$
$\langle l+1, m-1 C_{-1}^{(1)} l, m \rangle$	=	$\sqrt{\frac{(l-m+2)(l-m+1)}{2(2l+3)(2l+1)}}$
$\langle l-1, m-1 C_{-1}^{(1)} l, m \rangle$	=	$-\sqrt{\frac{(l+m)(l+m-1)}{2(2l-1)(2l+1)}}$

Table 9.1. Nonvanishing angular momentum dipole matrix elements $\langle L, M | C_q^{(1)} | l, m \rangle$. The matrix elements are real, so that $\langle L, M | C_q^{(1)} | l, m \rangle^* = \langle L, M | C_q^{(1)} | l, m \rangle = (-1)^q \langle l, m | C_{-q}^{(1)} | L, M \rangle$. Nonlisted matrix elements are zero.^a

^aThe matrix elements $\langle l', m' | C_q^{(1)} | l, m \rangle = c^{k=1}(l'm'; lm)$ are tabulated by Condon and Shortley and by Slater [373]. Care has to be taken with the direction of the transition because it affects the sign according to $c^k(l'm'; lm) = (-1)^{m-m'}c^k(lm; l'm')$.

The dipole selection rules for transitions between states of the form $|n, l, m_l, s, m_s\rangle$ are: $\Delta l = l' - l = \pm 1$, $\Delta m_l = m'_l - m_l = q = 0, \pm 1$, $\Delta s = s' - s = 0$, $\Delta m_s = m'_s - m_s = 0$. where $q\hbar$ is the X-ray angular momentum.

9.5.6 Transition Matrix Element for Atoms in Solids

Since solids, not atomic systems, are of main interest in magnetism research we need to discuss the calculation of the transition matrix element with more realistic initial and final state wavefunctions. Fortunately, within reasonable approximations, the wavefunctions of bonded atoms can be linked to the form of the atomic matrix element (9.80) because all wavefunctions can be written as linear combinations of the atomic functions, as seen from the form of the LF wavefunctions (7.30) and the \mathbf{k} -dependent band functions (7.22) or (7.23). If we use a tight binding band function written as

$$|\psi_i(\mathbf{k}, r)\rangle = |R_{n,L}(r)\rangle |\phi_i(\mathbf{k})\rangle$$

= $|R_{n,L}(r)\rangle \sum_{M=-L}^{+L} a_{i,M}(\mathbf{k}) |L M \chi^+\rangle + b_{i,M}(\mathbf{k}) |L M \chi^-\rangle, (9.83)$

with energy $E_i(\mathbf{k})$, the X-ray absorption transition intensity is given by

$$I_{\alpha}^{q} = \mathcal{A} \sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m, j}} |\langle \psi_{i}(\mathbf{k}, r) | P_{\alpha}^{q} | \varphi_{m}^{j}(r) \rangle|^{2}$$
$$= \mathcal{A} \mathcal{R}^{2} \sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m, j}} \left| \left\langle \phi_{i}(\mathbf{k}) \left| \sum_{p=0, \pm 1} e_{\alpha, p}^{q} C_{p}^{(1)} \right| c m \chi^{j} \right\rangle \right|^{2}.$$
(9.84)

By making use of the fact that the dipole operator does not act on spin we can separately sum over the orthogonal spin states χ^+ and χ^- and the resonance intensity takes the form

$$I_{\alpha}^{q} = \mathcal{A} \mathcal{R}^{2} \sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m}} \left| \sum_{p, M} a_{i, M}(\mathbf{k}) \ e_{\alpha, p}^{q} \left\langle L \ M | C_{p}^{(1)} | c \ m \right\rangle \right|^{2} + \left| \sum_{p, M} b_{i, M}(\mathbf{k}) \ e_{\alpha, p}^{q} \left\langle L \ M | C_{p}^{(1)} | c \ m \right\rangle \right|^{2}.$$
(9.85)

Although the band states contain wavevector-dependent expansion coefficients, the matrix elements involve only atomic orbitals. We shall see later that the summation over \boldsymbol{k} , which in general is done by computer, can be done analytically for the case that one averages over all polarization states q or over three X-ray incidence angles $\alpha = x, y, z$. This yields an important sum rule that allows the determination of the number of unoccupied states.

Another important form of the wavefunctions are the spin-orbit basis functions $|R_{n,l}(r); l, s, j, m_j\rangle$. For example, as shown in Fig. 9.6, the L-edge spectra of the transition metals have 2p core spin-orbit splitting of about 15 eV, and one therefore needs to carry out the evaluation of the transition matrix element with the $2p_{3/2}$ and $2p_{1/2}$ eigenfunctions of the spin-orbit Hamiltonian (see Sect. 6.4.3 and 6.6.1). The angular parts of the spin-orbit coupled functions $|l, s, j, m_j\rangle$ can be expressed as a linear combination of the uncoupled functions $|l, s, m_l, m_s\rangle$ according to

$$|l, s, j, m_j\rangle = \sum_{m_l, m_s} C_{m_l, m_s; j, m_j} |l, s, m_l, m_s\rangle,$$
 (9.86)

where the $C_{m_l,m_s;j,m_j}$ are the famous *Clebsch–Gordon* coefficients,⁹ written in Slater's notation [225]. The radial parts are the same as before. For

⁹They are readily calculated by computer programs, e.g., *Mathematica*.

convenience, we given the s, p, and d functions in the bases $|l, s, j, m_j\rangle$ and $|l, s, m_l, m_s\rangle$ in Table A.5. We see that the calculation of the transition matrix element with spin–orbit coupled functions is just a little more complicated but follows the form (9.80).

Some Important General Rules

The X-ray absorption process for an atom in different environments and the states involved are illustrated Fig. 9.10. We have the following important rules:

- The sum over all basis states of a shell with angular momentum ℓ is spherically symmetric. Examples of basis states are the spherical harmonics, valence orbitals or spin–orbit states shown in Fig. 9.10.
- The one-electron $j = \ell \pm s$ manifolds created by the spin-orbit interaction are each spherically symmetric.
- The t_{2g} and e_g manifolds (see Fig. 9.10) of the *d* orbitals are each spherically symmetric.
- For a spherically symmetric shell the associated transition intensity does not depend on the choice of the basis states.
- If at least two of the three parts of the dipole matrix element $\langle b | P_{\alpha}^{q} | a \rangle$ are spherically symmetric, the squared matrix element or intensity becomes independent of the direction α and polarization q.

In general, the measured X-ray absorption spectra of atoms in magnetic solids depend on three key parameters:

- The sample orientation
- The X-ray polarization
- The external magnetic field

From a pedagogical point of view it is best to distinguish and consecutively discuss two general cases. The first case corresponds to measurements that *average over all sample orientations* relative to the X-ray beam. In practice, this is simply accomplished by averaging over three orthogonal measurements. The significance of this procedure, discussed later, is that the so-determined spectral intensities are directly related by simple sum rules to important physical quantities per atom, like the number of empty valence states, the spin magnetic moment and the orbital magnetic moment.

The second case is more complicated and corresponds to a single measurement that *depends on the orientation of the sample*. Now the measured spectral intensities no longer correspond to quantities that are integrated over the atomic volume but they may also contain anisotropic, i.e., direction dependent, contributions. For example, if the spin density in the atomic volume is not spherical, the XMCD intensity measured for different sample orientations will not simply determine the (isotropic) spin moment but rather the anisotropic spin density.

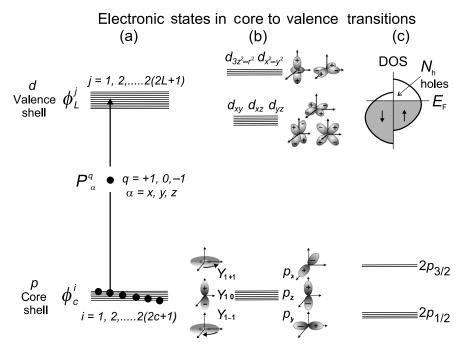


Fig. 9.10. Schematic of electronic core and valence states, and dipole transitions between them in a one-electron model. (a) Atomic case, illustrating a transition from a filled core state $|\phi_c^i\rangle$ in shell n, given by (9.77), to an empty valence state $|\phi_L^j\rangle$ in shell n', described by (9.78). Both states are labeled by their angular momenta l = cand l = L and there are 2(2l + 1) substates or spin orbitals within each manifold l. The electric dipole operator P^q_{α} is one of the operators given in Table A.4, where q = +1, 0, -1 labels the possible angular momentum transfer and $\alpha = x, y, z$ the direction. (b) Ligand field case for the case of $p \rightarrow d$ transitions (L-edge). The filled core shell is spherically symmetric and can be described either in a basis of spherical harmonics or p orbitals given in Table A.2. The valence states are linear combinations of the atomic states (9.77) and (9.78) and correspond to the *d* orbitals in Table A.2. The upper two d orbitals are the $e_{\rm g}$, while the lower three are the $t_{\rm 2g}$ orbitals. Each set is spherically symmetric. (c) States for a transition metal. The valence shell is represented by spin-up and spin-down d states with a total number of empty dstates above the Fermi energy $E_{\rm F}$, called the number of valence holes, $N_{\rm h}$, ("up" plus "down" spins). The core state is assumed to be spin-orbit split into $2p_{3/2}$ and $2p_{1/2}$ states, giving rise to the L₃ and L₂ edges in experimental spectra, respectively. Note that each core manifold j = 3/2 and j = 1/2 is spherically symmetric

For these reasons we shall separately discuss the two cases later. We will apply the theoretical concepts developed above for the calculation of angle integrated and polarization dependent transition intensities. In the process the link between the transition intensities and physical parameters will emerge.

9.6 The Orientation-Averaged Intensity: Charge and Magnetic Moment Sum Rules

In understanding the significance of the resonance intensity in X-ray absorption spectra it is best to first discuss measurements that eliminate magnetic effects, if present, and give charge-related information only. In the following we shall specifically discuss the important case of the L-edge spectra of transition metals. We will show that such spectra, properly averaged over all sample orientations yield the total number of unoccupied valence states or holes.

9.6.1 The Orientation-Averaged Resonance Intensity

For our discussion it is useful to start by defining an X-ray absorption resonance or white-line intensity that is independent of sample orientation. We shall assume that our sample has higher than monoclinic symmetry so that the unit cell axes are orthogonal. One can then define an orientation averaged absorption intensity as the average over three orthogonal measurements. If we use the notation (9.73) (also see Table A.4) for our polarization (q) and X-ray propagation (α) dependent dipole operator P^q_{α} , one can show as done in Sect. 9.6.2, that the average may involve either a sum over q or α according to

$$\langle I \rangle = \frac{1}{3} \left(I_x^q + I_y^q + I_z^q \right) = \frac{1}{3} \left(I_\alpha^{-1} + I_\alpha^0 + I_\alpha^{+1} \right) .$$
(9.87)

Let us illustrate this average for different cases. The simplest case is a *nonmagnetic polycrystalline* sample. In this case the polarization of the incident X-rays does not matter since the electric field vector \boldsymbol{E} that drives the electronic transition is oriented at random relative to the crystallographic directions of the sample. The recorded spectrum therefore corresponds to a true angular average.

For nonmagnetic single crystals with higher than monoclinic symmetry the same angle-averaged intensity can be obtained by averaging over three orthogonal measurements according to (9.87). For the special case of cubic symmetry the measured spectral intensity is isotropic and a single measurement suffices. For lower symmetry, the required average over α depends on the polarization labelled by q. For linear polarized X-rays (q = 0) one averages over spectra for \boldsymbol{E} along the x, y, and z axes of the crystal. For natural light or circularly polarized light ($q = \pm 1$)¹⁰ one averages over three measurements with \boldsymbol{k} along x, y, and z. For a fixed crystalline direction α the average over q (0, ± 1) ensures that the \boldsymbol{E} -vector can equally drive the transition along the x, y, and z axes of the crystal (see Table A.4), and therefore an effective average is performed.

¹⁰ For circularly polarized X-rays the photon spin does not matter for nonmagnetic samples. To the absorbing charge the light looks naturally polarized with E lying somewhere in the plane perpendicular to k.

For magnetic single crystals one can use the same method as for nonmagnetic single crystals if one uses linearly polarized light. For circularly polarized X-rays one must eliminate magnetic effects by saturating the sample with the field parallel and antiparallel to the direction α and summing over the two intensities. The angle-averaged resonance intensity obeys an important intensity sum rule that can be stated as follows.

The angle-averaged intensity of the combined L_3 and L_2 resonances is directly proportional to the total number of d states above the Fermi level, i.e., the number of holes in the d band.

This is demonstrated in Fig. 9.11a for the $L_{3,2}$ white-line intensity of the absorption spectra of the pure metals Fe, Co, Ni, and Cu. The shown spectra were recorded for polycrystalline and magnetically not aligned samples so that polarization dependent effects are automatically averaged out. Of interest is the white-line resonant intensity associated with $2p \rightarrow 3d$ transitions, shown shaded in the inset of Fig. 9.11a, which sits on a step-like background due to nonresonant excitation channels. The nonresonant channels produce steps at the L_3 and L_2 positions with a step ratio of 2 to 1 reflecting the number of core electrons in the $p_{3/2}$ and $p_{1/2}$ core states.

The white line intensity near threshold dramatically decreases along the series. This is due to filling of the 3d band with increasing number of electrons or atomic number Z, in accordance with the densities of states shown in Fig. 12.1. In total, the d shell can hold 10 electrons and by going from Fe to Cu one adds approximately one electron per atom. By summing for each energy the number of d states over the Brillouin zone one obtains the d band density of states, $\rho(E_{3d})$, as schematically shown in Fig. 9.11b. By energy integration $N_{\rm h} = \int_{E_{\rm F}}^{\infty} \rho(E) dE$ from the Fermi level up one obtains the total number of empty d band states or d holes. When the resonance intensity is plotted against the theoretically obtained number of 3d holes one obtains a linear relationship as shown in Fig. 9.11c. The resonance intensity of the spectrum, defined as the shaded peak area in the inset of Fig. 9.11a, is the energy integral over the cross-section and has the dimension [area × energy], and in Fig. 9.11 is given in units of Mb eV.

9.6.2 Derivation of the Intensity Sum Rule for the Charge

Figure 9.11b shows the electronic states appropriate for a transition metal. The total number of empty d states above the Fermi energy $E_{\rm F}$, called the number of valence holes, $N_{\rm h}$, is simply the number of spin up plus down states. In the one-electron model the core state is assumed to be spin-orbit split into $2p_{3/2}$ and $2p_{1/2}$ states, giving rise to the L₃ and L₂ edges in experimental spectra, respectively. The sum rule states that the transition intensity is proportional to the total number of empty d states $N_{\rm h}$ when we sum over the $2p_{3/2}$ and $2p_{1/2}$ contributions. This is intuitively correct since the intensity should increase if we make more empty final states available for the transition.

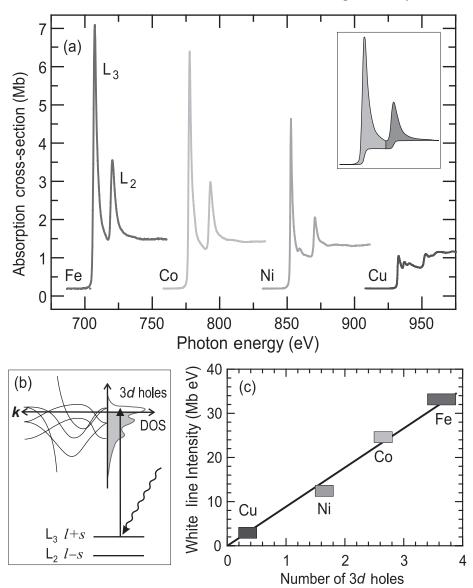


Fig. 9.11. (a) L-edge X-ray absorption spectra, plotted on an absolute cross-section scale, for the 3d transition metals Fe, Co, Ni, and Cu. When the sum of the L_3 and L_2 intensities, defined as the area shown *shaded* in the inset, is plotted against the calculated number of 3d holes a linear relationship is obtained within experimental error as shown in (c). We have used the following values for the number of holes: 1.5–1.78 for Ni, 2.5–2.80 for Co and 3.4–3.93 for Fe (also see Sect. 12.2.2 and Fig. 12.16). The correlation follows from a sum rule, discussed in the text, that links the integrated resonance cross-section or resonance intensity to the number of empty valence states in the electronic ground state. The number of empty states is obtained from the integrated density of states (DOS), as shown in (b)

Let us derive the sum rule using a tight binding band picture for the 3d valence states of the transition metals. The intensity of an electronic transition between core states of angular momentum c and valence states of angular momentum L = c + 1 is given by (9.85). By separating off the diagonal and cross terms we have

$$I_{\alpha}^{q} = \mathcal{A} \mathcal{R}^{2} \sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m}} \sum_{p, M} \left[|a_{i,M}(\mathbf{k})|^{2} + |b_{i,M}(\mathbf{k})|^{2} \right] |e_{\alpha,p}^{q}|^{2} |\langle L M | C_{p}^{(1)} | c m \rangle |^{2}$$

+ $\mathcal{A} \mathcal{R}^{2} \sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m}} \sum_{\substack{p \neq p' \\ M \neq M'}} e_{\alpha,p}^{q} (e_{\alpha,p'}^{q})^{*} \langle L M | C_{p}^{(1)} | c m \rangle \langle L M' | C_{p'}^{(1)} | c m \rangle^{*}$
 $\times \left[a_{i,M}(\mathbf{k}) (a_{i,M'}(\mathbf{k}))^{*} + b_{i,M}(\mathbf{k}) (b_{i,M'}(\mathbf{k}))^{*} \right].$ (9.88)

We can now perform an orientation average according to (9.87) by either summing of the three orthogonal polarization states $q = 0, \pm 1$ or over crystal directions $\alpha = x, y, z$. In both cases the cross term in (9.88) vanishes because $\sum_{q} e^{q}_{\alpha,p}(e^{q}_{\alpha,p'})^{*} = \sum_{\alpha} e^{q}_{\alpha,p}(e^{q}_{\alpha,p'})^{*} = 0$ for all p, p' combinations (see Appendix A.6), and the polarization averaged transition intensity is given by

$$\langle I \rangle = \frac{1}{3} \mathcal{AR}^{2} \underbrace{\sum_{\substack{E_{i} > E_{F} \\ i, \mathbf{k}, M}} (|a_{i,M}(\mathbf{k})|^{2} + |b_{i,M}(\mathbf{k})|^{2})}_{N_{h}} \underbrace{\sum_{p,m} |\langle L M | C_{p}^{(1)} | c m \rangle|^{2} \underbrace{\sum_{q \text{ or } \alpha} |e_{\alpha,p}^{q}|^{2}}_{= 1}}_{= L/2L + 1}$$
$$= \mathcal{AR}^{2} \frac{L}{3(2L+1)} N_{h}.$$
(9.89)

Here we have used (A.25) and (A.27) and the sum rule (A.21), and $N_{\rm h}$ is the total number of holes according to (7.25). This is an important result and we need to put a box around it. For the L-edge of the 3*d* transition metals the sum rule reads as follows.

The orientation averaged "white line" intensity of a core to valence $nc \rightarrow n'L$ transition with c = L - 1 is directly related to the total number of valence holes $N_{\rm h}$ in the electronic ground state according to

$$\langle I \rangle = C N_{\rm h} \ . \tag{9.90}$$

where

$$C = \mathcal{A}\mathcal{R}^2 \frac{L}{3(2L+1)} , \qquad (9.91)$$

 $\mathcal{A} = 4\pi^2 \hbar \omega / 137$ and \mathcal{R} is the radial $nc \to n'L$ matrix element.

Note that according to (9.87), we have defined the angle-averaged intensity $\langle I \rangle$ to be equivalent to that obtained for a randomly oriented sample in a single measurement. It is of great importance, as stated above, that $N_{\rm h}$ is the total number of valence holes in the *electronic ground state*, not the excited electronic state. This is not obvious from our one-electron model calculation but can be proven in a more general configuration based model of the X-ray absorption process [100, 101]. For the special case of a $p \rightarrow d$ transition we have

$$\langle I \rangle = \frac{2 \mathcal{A} \mathcal{R}^2}{15} N_{\rm h} . \qquad (9.92)$$

9.6.3 Origin of the XMCD Effect

The important intensity sum rule for the number of holes suggests that if we could make the absorption process spin dependent we could measure an intensity difference that corresponds to the difference between the number of spin-up and spin-down holes, i.e., the magnetic moment. This can indeed be done by using circularly polarized photons and is the basis of XMCD spectroscopy.

Before we proceed we need to specifically state our assumptions. In using the important concept of proportionality of the white line intensity and the number of valence holes from the previous sections we implicitly assume that the measured white line intensity is independent of the sample crystallography. In the following we shall therefore assume that the sample is either polycrystalline or that we average three dichroism measurements along orthogonal crystalline directions.¹¹

In order to understand the essence of the XMCD effect we assume a oneelectron picture where the valence states exhibit a Stoner splitting as discussed in Sect. 7.4.2, and shown on the left side of Fig. 9.12. The shown density of states actually correspond to that calculated for Fe metal by band theory (see Fig. 12.1).

For maximum XMCD effect the magnetization direction M of the sample and the photon spin or angular momentum $L_{\rm ph}$ are chosen to be *collinear*. As illustrated on the left side of Fig. 9.12, the dichroism effect is then given by the difference of the $p \rightarrow d$ transition (X-ray absorption) intensities, measured for photons with positive angular momentum (q = +1, $L_{\rm ph}$ points in direction of wavevector k) and negative angular momentum (q = -1, $L_{\rm ph}$ points in direction of -k) aligned along the fixed magnetization direction M of the sample. An equivalent way is to fix the X-ray photon spin direction and switch the magnetization directions [374].

On the right of Fig. 9.12 we show experimental L-edge XMCD spectra for Fe metal [96,375] that have been corrected to correspond to 100% circularly

¹¹More specifically, we also assume that the sample symmetry is higher than monoclinic so that the unit cell axes are orthogonal.

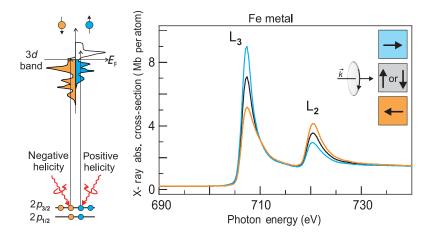


Fig. 9.12. The XMCD effect illustrated for the L-edge absorption in Fe metal. The shown density of spin-up and spin-down states closely resembles that calculated for Fe metal (compare Fig. 12.1). The experimental data on the right are from Chen et al. [96] and have been corrected to correspond to 100% circular polarization. We show the case of circularly polarized X-rays with positive angular momentum (helicity), and the color coded spectra correspond to the shown sample magnetization directions

polarized X-rays and parallel alignment of the photon spin and the magnetization. The dichroism effect is seen to be very large. If the photon spin is aligned perpendicular to the magnetization the cases of perpendicular "up" and "down" magnetization directions cannot be distinguished.

Denoting the magnetization M and photon angular momentum $L_{\rm ph}$ directions by arrows, the dichroism effect is only dependent on the relative alignment of the two arrows. The convention adopted by the XMCD community is to plot the dichroism intensity of the 3*d* transition metals Fe, Co, and Ni so that the L₃ dichroism is negative (also see Fig. 10.12). According to Fig. 9.12 this corresponds to the definition,

$$\Delta I = I^{\uparrow\downarrow} - I^{\uparrow\uparrow}. \tag{9.93}$$

Note that the *minority* electron spin direction (= majority hole spin direction) is the same as that of the sample magnetization. The importance of the so defined XMCD intensity can be expressed as follows.

The XMCD difference intensity, defined as the white-line intensity difference between antiparallel and parallel orientations of the sample magnetization and the incident photon spin is directly proportional to the atomic magnetic moment.

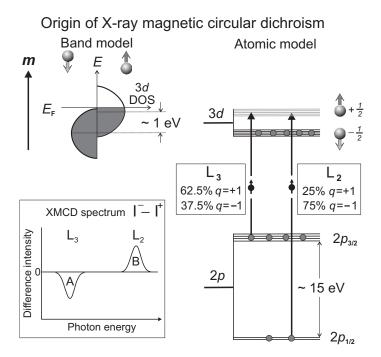


Fig. 9.13. Illustration of the L-edge X-ray absorption processes of circularly polarized photons with angular momentum $q = \pm 1$ (in units of \hbar). For the *d* valence shell we show the correspondence between the Stoner band picture of a magnetic material and an atomic one-hole *d* shell model. We have chosen our magnetization direction such that the "down-spins" are filled and the "up-spins" partially unfilled. In the atomic model we assume one "spin-up" hole and show the possible 2p core to 3dvalence transitions assuming circularly polarized light with angular momentum *q*. The fraction of "up-spin" electrons excited from the *p* core shell through absorption of X-rays with angular momentum $q = \pm 1$ is listed for the L₃ and L₂ edges. Here we have assumed the X-rays to be incident parallel to the atomic magnetic moment *m*. In the inset we show the XMCD difference spectrum calculated with the atomic model according to (9.95) and assuming the shown resonant peak shapes

The quantum mechanical origin of the XMCD effect at the L-edge is explained in more detail by the simple atomic model of Fig. 9.13. Here we have assumed the case of a "strong" ferromagnet with one filled spin channel. With the sample magnetized in the "up" direction, the spin-down states are filled and the spin-up states are only partially filled as shown in Fig. 9.13. For simplicity we ignore the weak spin-orbit interaction among the d electrons so that our sample has only a spin magnetic moment and the orbital moment is zero. We also show the correspondence between the Stoner band picture of a magnetic material and an atomic d shell model. In both cases the five spin-down d states are filled and the spin-up states are assumed to be par-

tially filled. For an empty spin-up shell the magnetic moment is $5 \mu_{\rm B}$ in our simple atomic model and as we fill in more electrons it decreases by $1 \mu_{\rm B}$ per (spin-up) electron.

For the special situation of a completely filled majority band shown in Fig. 9.13, the charge sum rule of Sect. 9.6.1 would actually be sufficient to give us the magnetic moment since it is equal to the total number of holes. In general, of course, we have to allow for partially filled majority and minority bands and therefore we need to make the X-ray absorption process spin dependent in order to determine the difference in majority and minority population.

For our quantum mechanical calculation we use the atomic model shown on the right side of Fig. 9.13 and calculate the dichroism effect by considering the angular part of the squared transition matrix element from the $p_{3/2}$ and $p_{1/2}$ states to the empty spin-up states of the *d*-band. We write the $p_{3/2}$ and $p_{1/2}$ wave functions in the basis $|l = 1, m_l, s, m_s\rangle$, as is done in Table A.5. For the spin-up 3*d* hole states we use the five *d* orbitals listed in Table A.2 with spin up $|\chi^+\rangle = |m_s = +1/2\rangle$. They are linear combinations of basis functions $|l=2, m_l, s, m_s\rangle$ so that all matrix elements can be calculated from the expressions in Table 9.1 under the assumption of spin conservation. The individual transition intensities (angular part only) are given by

$$|\langle d_n, \chi^+| \frac{P_z^q}{r} |p_j, m_j \rangle|^2 \tag{9.94}$$

with index values n = 1, ..., 5, j = 3/2, 1/2, $m_j = \pm 3/2, \pm 1/2$ and $q = 0, \pm 1$. The individual squared transition matrix elements are given in Fig. 9.14.

From the individual transition intensities in Fig. 9.14 we can now derive the XMCD effect. With the definition of (9.93) it is given by the difference of the $p \rightarrow d$ transition intensities with negative (q = -1) and positive (q = +1)photon spin,

$$\Delta I = I^{\uparrow\downarrow} - I^{\uparrow\uparrow} = I^- - I^+. \tag{9.95}$$

By summing the appropriate intensities and differences in Fig. 9.14 we obtain for the L_3 and L_2 dichroism effects:

$$\Delta I_{\mathrm{L}_{3}} = \mathcal{AR}^{2} \sum_{n,m_{j}} |\langle d_{n}, \chi^{+} | C_{-1}^{(1)} | p_{3/2}, m_{j} \rangle|^{2} - |\langle d_{n}, \chi^{+} | C_{+1}^{(1)} | p_{3/2}, m_{j} \rangle|^{2}$$
$$= -\frac{2}{9} \mathcal{AR}^{2} , \qquad (9.96)$$

and

$$\Delta I_{L_2} = \mathcal{AR}^2 \sum_{n,m_j} |\langle d_n, \chi^+ | C_{-1}^{(1)} | p_{1/2}, m_j \rangle|^2 - |\langle d_n, \chi^+ | C_{+1}^{(1)} | p_{1/2}, m_j \rangle|^2$$

= $+ \frac{2}{9} \mathcal{AR}^2$. (9.97)

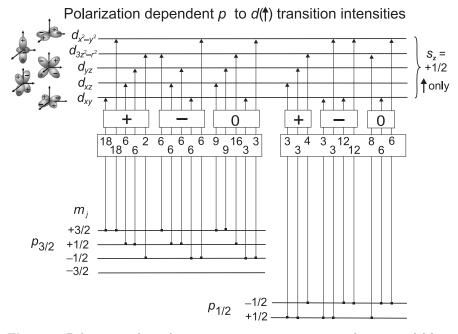


Fig. 9.14. Polarization dependent transition intensities in a one-electron model from spin-orbit and exchange split p core states $|j, m_j\rangle$ to spin-up $(m_s = +1/2) d$ valence orbitals (Table A.2), assumed to be split by the exchange interaction. The listed intensities each need to be divided by 90 to get the proper absolute values in units of \mathcal{AR}^2 . We have chosen the z-axis as the spin quantization axis and the transition intensities are for circular polarization with $k \parallel z$ and angular momenta q = +1 (labeled +) and q = -1 (labeled -) and for linear polarization with $E \parallel z$ (labeled q = 0). We have assumed a splitting of the p states by the exchange interaction, lifting the degeneracy in m_j . Note that this causes an opposite order of m_j states for $p_{3/2}$, l + s and $p_{1/2}$, l - s because of the opposite sign of s

The relevant XMCD intensities are summarized in Fig. 9.13. The dichroism signal at the L₃ and L₂ edges are identical in magnitude but of opposite sign. At the L₃ edge, X-rays with positive (q = 1) photon spin excite more *spin-up* electrons than X-rays with negative (q = -1) photon spin, and at the L₂ edge the opposite is found. It is easy to show that for the calculation of the dichroism effect it is equivalent to fix the X-ray spin and switch the magnetization direction [374]. In principle, L-edge X-ray absorption spectra contain contributions from both $p \to d$ and $p \to s$ transitions, but in practice the $p \to d$ channel dominates by a factor > 20. [376]

9.6.4 Two-Step Model for the XMCD Intensity

The model calculations in Figs. 9.13 and 9.14 suggest a particularly simple two-step model.

In the first X-ray absorption step, conservation of angular momentum requires a transfer of the angular momentum of the incident circularly polarized X-rays to the excited photoelectrons. If the photoelectron is excited from a spin-orbit split level, e.g., the $2p_{3/2}$ level (L₃ edge), the angular momentum of the photon can be transferred in part to the spin through the spin-orbit coupling and the excited photoelectrons are spin polarized. The spin polarization is opposite for incident X-rays with positive $(+\hbar)$ and negative $(-\hbar)$ photon spin. Also, since the $2p_{3/2}$ (L₃) and $2p_{1/2}$ (L₂) levels have opposite spin-orbit coupling (l + s and l - s, respectively) the spin polarization will be opposite at the two edges. The photoelectron spin quantization axis is identical to that of the photon spin, i.e., it is parallel or antiparallel to the X-ray propagation direction.

In the *second* step the exchange split valence shell with unequal spinup and spin-down populations acts as the detector for the spin of the excited photoelectrons. For optimum detection the valence shell spin quantization axis (the "detector" axis) has to be aligned with the photon spin or photoelectron spin quantization axis.

For the specific case shown in Fig. 9.13 only spin-up electrons can be excited from the 2p core to the partially unfilled spin-up 3d valence shell because the dipole operator does not act on spin and therefore does not allow spin-flips during excitation. At the L₃-edge, X-rays with positive spin (q = +1) excite 62.5% spin-up electrons and negative spin X-rays (q = -1) excite 37.5% spin-up electrons, while for the L₂ edge the numbers are 25% spin-up electrons for q = +1 and 75% spin-up electrons for q = -1. Taking into account the two times higher population of the $2p_{3/2}$ state, one finds the dichroic intensity differences at the L₃ and L₂ edges calculated according to (9.96) and (9.97) where $\Delta I_{L_3} = A$ and $\Delta I_{L_2} = B$, to be identical in magnitude but of opposite sign, as shown in the inset of Fig. 9.13.

The results of Fig. 9.13 are readily extended to the general case where both majority and minority bands are partially empty since for transitions to spindown (majority) states the same excitation percentages given in Fig. 9.13 are found, except with q = +1 and q = -1 interchanged. Thus the minority and majority band contributions to the dichroism intensity have opposite signs. If both contribute equally the dichroism signal vanishes, as required for a nonmagnetic material.

Note that the pure photon spin configurations with angular momenta $\pm \hbar$ are not converted into pure (100%) electron spin configurations. Some of the photon angular momentum is converted into electron orbital momentum which is also carried by the photoelectron. The photoelectron thus carries the angular momentum absorbed from the photon as spin and orbital momentum degrees of freedom. The orbital momentum of the photoelectron is detected if the valence shell has an orbital moment. A particularly interesting case is that of K-shell excitations.

K-shell Dichroism

For K-shell excitation the 1s core shell has zero angular momentum and hence no spin-orbit coupling. It may, however, exhibit a small splitting into $m_s = \pm 1/2$ states due to the exchange field or an external magnetic field. In Fig. 9.15 we give the polarization dependent transition intensities for two cases.

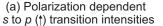
On the left side of Fig. 9.15 we show transitions from the spin-split 1s shell to empty exchange split 2p orbitals with $m_s = +1/2$ given by

$$|\langle p_n, m_s = +1/2| \frac{P_z^q}{r} |s, m_s\rangle|^2$$
(9.98)

for n = 1...3 and $q = 0, \pm 1$. On the right we show transitions from the spin–split 1s shell to empty spin–orbit coupled $2p_j$ (j = 3/2, 1/2) orbitals, further split by an external magnetic field into $-3/2 \le m_j \le +3/2$ Zeeman components,

$$|\langle p_j, m_j| \frac{P_z^q}{r} |s, m_s\rangle|^2 \tag{9.99}$$

for j = 3/2, 1/2, $m_j = \pm 3/2, \pm 1/2, m_s = \pm 1/2$, and $q = 0, \pm 1$. Note that our results for this case confirm those given earlier in Fig. 8.1.



(b) Transition intensities between spin-orbit and Zeeman split *s* and *p* states

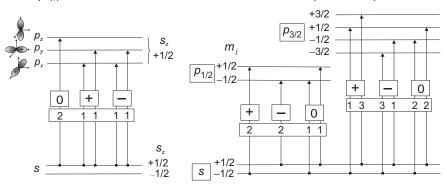


Fig. 9.15. (a) Polarization dependent transition intensities in a one-electron model between exchange (or Zeeman) split s core states and empty spin-up ($s_z = +1/2$) p valence orbitals, assumed to be separated from the full spin-down shell by the exchange interaction. The listed intensities each need to be divided by 6 to get the proper absolute values in units of \mathcal{AR}^2 . We have chosen the z-axis as the spin quantization axis and the transition intensities are for circular polarization with $k \parallel z$ and angular momenta q = +1 (labeled +) and q = -1 (labeled -) and for linear polarization (labeled q = 0) and $E \parallel z$. (b) Transition intensities between exchange (or Zeeman) split s core states and spin-orbit coupled and Zeeman split p_j valence states denoted by quantum numbers m_j (see Table A.5). The listed intensities each need to be divided by 9 to get the proper absolute values. The coordinate system is the same as in (**a**).

For the K-edge excitation the 1s state has only a spin and no orbital angular momentum. Since the spin does not interact directly with the electric field, the photon spin is transferred to the photoelectron as an orbital angular momentum, either \hbar or $-\hbar$. The orbital angular momentum of the photoelectron can only be detected by the valence shell if it possesses an orbital magnetic moment itself, that means if the valence band empty density of states has an imbalance of states with quantum numbers $+m_l$ and $-m_l$. If the valence shell does not possess an orbital moment, photoelectrons with orbital momenta \hbar and $-\hbar$ cannot be distinguished and no dichroism effect will be observable. This is true even if the valence shell has a net spin polarization as in the Stoner model. Therefore, for K-shell excitation a dichroism effect exists only if the p valence shell possesses an orbital moment [377]. Sensitivity to the spin magnetic moment of the p shell arises only indirectly through the spin–orbit interaction.

Summary for the XMCD Intensity

We can summarize the models shown in Figs. 9.13–9.15 by the following twostep model of XMCD [374].

The two-step model of XMCD:

• In the *first step*, circularly polarized X-rays generate photoelectrons with a spin and/or orbital momentum from a localized atomic inner shell.

• In the *second step*, the 3*d* shell serves as the detector of the spin or orbital momentum of the photoelectron. For maximum effect, the photon spin needs to be aligned with the magnetization direction.

The size of the dichroism effect depends on three important parameters:

- The degree of circular photon polarization $P_{\rm circ}$,
- The expectation value of the magnetic moment of the 3d shell $\langle \boldsymbol{m} \rangle$
- The angle θ between the directions of the photon angular momentum $L_{\rm ph}$ and the magnetic moment m

This can be cast into the following dependence of the XMCD intensity,

$$I_{\rm XMCD} \propto P_{\rm circ} \ \boldsymbol{m} \cdot \boldsymbol{L}_{\rm ph} \propto P_{\rm circ} \langle \boldsymbol{m} \rangle \cos \theta \ .$$
 (9.100)

In theory we define the XMCD difference intensity according to (9.95), assuming $P_{\rm circ} = 1$. For our later discussion of the resonant magnetic scattering intensity is useful to write the XMCD absorption intensity in a form that involves matrix elements of Racah's spherical tensors, as done for the L₃ and L₂ signals in (9.96) and (9.97). By use of the short form

$$\langle C_q^{(1)} \rangle = \langle d_n, \chi^+ | C_q^{(1)} | p_j, m_j \rangle,$$
 (9.101)

we can state as follows.

The XMCD difference intensity for X-ray propagation and magnetization direction aligned along z may be written in terms of angular matrix elements of the Racah spherical tensors according to,

$$\Delta I_{\rm XMCD} = \mathcal{AR}^2 \sum_{\rm states} |\langle C_{-1}^{(1)} \rangle|^2 - |\langle C_{+1}^{(1)} \rangle|^2.$$
(9.102)

The factor \mathcal{A} is given by (9.61) and \mathcal{R} is the radial transition matrix element given by (9.81).

9.6.5 The Orientation Averaged Sum Rules

In this section we want to formally state three important sum rules for orientation averaged intensities [100–102, 240, 241, 378–383]. The sum rules link the measured polarization dependent resonance intensities with valence band properties, in particular the number of empty states or "holes" $N_{\rm h}$ per atom, the spin magnetic moment m_s per atom and the orbital magnetic moment m_o per atom. Since these latter atomic quantities are defined by integration over the atomic volume and are therefore *isotropic* quantities, one needs to be sure that the measurement eliminates anisotropic effects caused by anisotropic charge and spin densities in the crystallographic unit cell. It is therefore necessary, in general, to first define a coordinate system for the crystallographic axes, so that one can properly average out anisotropies by suitable measurements.

In the following we shall assume that the crystal symmetry is higher than monoclinic so that we can chose the unit cell axes along the x, y, and z directions of a cartesian coordinate system. For a measurement we then specify the X-ray polarization and the magnetization direction in this frame and define a suitable intensity average according to (9.87). With this definition we can now use intensity averages of three measurements to determine physical quantities.

First we can determine the number of empty valence states per atom by measuring the transition intensity of core electrons into the empty valence states, as illustrated schematically in Fig. 9.16a for the L-edge in the magnetic 3d transition metals. We then have the first of three important sum rules, which we shall call the *charge sum rule*. It relates the measured averaged peak intensity to the number of empty states $N_{\rm h}$. We can state it as follows.

The charge sum rule links the measured averaged X-ray absorption resonance intensity of a core to valence transition to the number of empty valence states $N_{\rm h}$ per atom

$$\langle I \rangle = C N_{\rm h}, \tag{9.103}$$

where C is the proportionality constant given by (9.91).

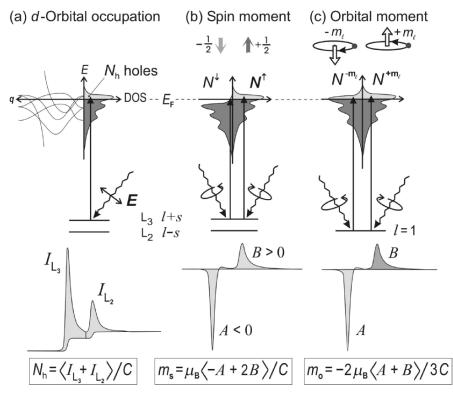


Fig. 9.16. Schematic of processes, spectra, and intensities underlying the quantitative determination of valence band properties such as the number of empty d states $N_{\rm h}$, and the spin moment $m_s = \mu_{\rm B}(N_{\rm h}^{\dagger} - N_{\rm h}^{\downarrow}) = \mu_{\rm B}(N_{\rm h}^{+m_s} - N_{\rm h}^{-m_s})$ and orbital moment $m_o = \mu_{\rm B}(N_{\rm h}^{+m_\ell} - N_{\rm h}^{-m_\ell})$. At the bottom we indicate the relationship between measured spectral intensities and the valence band properties. Note the sign of the dichroism difference intensities. In the shown cases we have A < 0 and B > 0

For the special case of the transition metal L-edges one needs to determine the total core to valence intensity given by the sum of the two spin–orbit split components as shown in Fig. 9.16a and (9.103) takes the form [102]

$$\langle I_{\rm L_3} + I_{\rm L_2} \rangle = C N_{\rm h} \ . \tag{9.104}$$

If the X-ray absorption spectrum is determined in terms of the absolute crosssection (with the dimension [area]) then the measured intensity I, given by the energy integration of the cross-section, has the dimension [area × energy], and therefore C is typically given in conventional units of [Mb eV]. For the 3d transition metals it has a value of about 10 Mb eV (see Fig. 9.17) [384].

In order to derive the magnetic spin moment for the 3d transition metals according to a sum rule due to Carra et al. [101] we also need to carry out an average as proposed by Stöhr and König [102]. One uses circularly polarized light and measures XMCD spectra for k along the three crystallographic directions x, y, z. For each measurement one magnetically saturates the sample along the direction of k and determines the dichroic (difference) intensities Aand B at the L₃ and L₂ edges as shown in Fig. 9.16b by either switching the photon spin for a given magnetization direction or by switching the magnetization direction for a given photon spin. Note that large fields of several Tesla may be needed for full magnetic alignment of the sample. One then performs the average of the difference intensities according to (9.87). This leads to the so-called spin sum rule. Note that in the case shown in Fig. 9.16 the areas Aand B have opposite signs.

The *spin sum rule* links the angle averaged dichroism intensities with the size of the spin moment per atom according to

$$\langle -A + 2B \rangle = \frac{C}{\mu_{\rm B}} \ m_s \ . \tag{9.105}$$

where the constant C is the same as in the charge sum rule.

For Fe, Co, and Ni the orbital, m_o , and spin, m_s , moments are parallel because the *d* shell is more than half full. While the spin moment becomes anisotropic only in higher order through the spin-orbit coupling which is significantly smaller than the dominant isotropic exchange interaction, the orbital moment may be strongly anisotropic. The origin of this anisotropy lies in the ligand field which may preferentially destroy the orbital motion of the electrons about certain crystal axes as discussed in Sect. 7.9. One therefore also needs to average over three directions to determine the average orbital moment. The three measurements are identical to those for the spin moment yet for the sum rule analysis one takes a different linear combination of the dichroism intensities. The orbital moment is determined by use of the *orbital moment sum rule* due to Thole et al. [100]

The *orbital moment sum rule* links the angle averaged dichroism intensities with the size of the average orbital moment per atom according to

$$-\langle A+B\rangle = \frac{3C}{2\mu_{\rm B}} m_o . \qquad (9.106)$$

The constant C is the same as in the charge and spin sum rules.

In practice, the determination of m_o requires high quality data and careful data analysis since A + B is typically a small number, obtained by subtraction of two large numbers since A < 0 and B > 0. If the two intensities have the same size but opposite signs the orbital moment is zero.

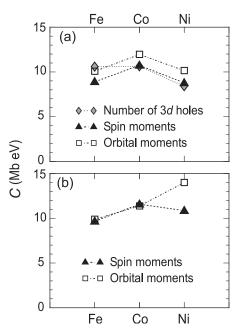


Fig. 9.17. Values for the constant C in the X-ray absorption sum rules determined by use of (9.103)–(9.106) from experimentally measured intensities and literature values for $N_{\rm h}, m_s$, and m_o [384]. In (**a**) we used the values $N_{\rm h}, m_s$, and m_o obtained by density functional theory including orbital polarization [385, 386] and in (**b**) the spin and orbital moments determined from the gyromagnetic ratio [387]

Figure 9.17 shows results for the constant C determined for Fe, Co, and Ni from experimental data and "known" values for the magnetic moments and the d shell occupation. A true determination of C is more difficult than first imagined since even for the elemental transition metals, there are some discrepancies between experimental and theoretical values for the moments. Furthermore, XMCD only measures the d electron contribution to the moments because $2p \rightarrow 4p$ transitions are not allowed by the dipole selection rule and $2p \rightarrow 4s$ transitions have much smaller cross-sections [376] than $2p \rightarrow 3d$ transitions.

If the intensities are not angle averaged, additional terms arise for the charge and spin moment sum rules that can be written in terms of a intraatomic quadrupolar charge contribution and a nonspherical intraatomic spin distribution. These terms average to zero when an angular average is performed as assumed earlier [102]. We shall come back to these anisotropic terms in Sect. 9.7.9.

9.7 The Orientation-Dependent Intensity: Charge and Magnetic Moment Anisotropies

In Sect. 9.6 we have treated the case of angle averaged X-ray absorption intensities. We assumed that the sample is either polycrystalline, of cubic symmetry or that a suitable angular average of three orthogonal crystalline directions is performed. In modern magnetism research, one often encounters single crystal samples or thin films with anisotropic bonding. We shall now discuss the Xray absorption spectra of such samples, which may be magnetically oriented, for the cases of linearly and circularly polarized X-rays. In the process we shall encounter the generalization of the three orientation averaged sum rules discussed in Sect. 9.6.5.

The discussion of the orientation-dependent intensities naturally leads to the distinction between spectra recorded with linearly polarized X-rays and circularly polarized X-rays and we shall discuss the two cases in turn.

9.7.1 Concepts of Linear Dichroism

The term "linear dichroism" describes angle dependent effects when the direction of the linear polarized \boldsymbol{E} vector is changed relative to the sample.¹² In nonmagnetic systems the anisotropy arises from an anisotropic charge distribution about the absorbing atom caused by bonding. For magnetic samples an additional anisotropy may exist relative to the magnetization direction of the sample. It is important to realize that in all cases the measured anisotropy arises from a nonspherical charge distribution. If the origin of the charge anisotropy is due to bonding alone we speak of "natural" linear dichroism, when it has a magnetic origin we use the term "magnetic" linear dichroism. Both may co-exist and in this case they can be separated either by temperature dependent studies or, for ferromagnets, by rotation of the magnetic alignment field relative to the fixed X-ray polarization .

Because of the close connection between the "natural" and "magnetic" dichroism effects we need to discuss both. We start with the case of nonmagnetic systems and present the physical origin of natural linear dichroism.

9.7.2 X-ray Natural Linear Dichroism

The easiest way to visualize the polarization dependence underlying X-ray natural linear dichroism or XNLD is the "search light effect" [189]. It can be stated as follows.

¹²Note that natural or circular polarized light defines a polarization plane perpendicular to the propagation direction \mathbf{k} and therefore both also give rise to an angular polarization effect when the sample is turned in the beam. For nonmagnetic samples this case can be treated by assuming that one has two orthogonal linearly polarized \mathbf{E} -vector components perpendicular to \mathbf{k} , and the intensities $\propto |\mathbf{E}_i|^2$ (i = 1, 2) associated with the two components are added incoherently, i.e., there is no interference term.

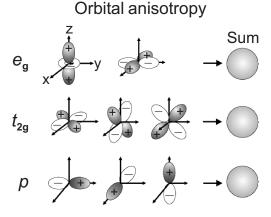


Fig. 9.18. Spatial orientation of p and d orbitals. All individual orbitals are anisotropic but the sums of the $e_{\rm g}$ and $t_{\rm 2g} d$ orbitals or the sum of the p orbitals is spherically symmetric as shown

In an X-ray absorption experiment electrons are excited from a selected core shell to empty valence states. For *linear polarized X-rays* the electric field vector \boldsymbol{E} acts like a *search light* for the direction of the maximum and minimum number of empty valence states. The transition intensity is directly proportional to the number of empty valence states in the direction of \boldsymbol{E} .

In an X-ray absorption measurement we sum over all degenerate levels of the core state. In accordance with Fig. 9.18 this leads to a spherically symmetric core contribution. This is obvious for K-edge spectra where the 1s core state is spherically symmetric. For L-edge spectra we also get a spherical core contribution if we sum over the $p_{3/2}(L_3)$ and $p_{1/2}(L_2)$ intensities. The dependence of the X-ray absorption intensity on \boldsymbol{E} -vector orientation is then entirely determined by the spatial distribution of the *empty valence states*.

The search light effect can be readily demonstrated for the case of K- and L-edges, where the electronic transitions involve $1s \rightarrow 2p$ and $2p \rightarrow 3d$ coreto-valence excitations. All we have to look for is the spatial charge distribution of the empty valence states involved in the transitions. For convenience we can do this by picturing the valence states by the familiar real p and d orbitals, as illustrated in Fig. 9.18. In a cubic ligand field the d orbitals form the $e_{\rm g}$ and $t_{\rm 2g}$ irreducible representations. The sum of the orbitals within each representation is spherically symmetric. The p orbitals are not split in cubic symmetry and their sum is also spherically symmetric. In cubic symmetry the X-ray absorption intensity in nonmagnetic materials is therefore independent of \boldsymbol{E} -vector orientation relative to the sample. It is clear that the charge distribution of the *individual* p and d orbitals is asymmetric in space, and therefore as the symmetry is lowered below cubic, transitions to individual p and d orbitals will depend on the orientation of the E-vector relative to the x, y, z coordinate system of the crystal. This is the origin of the natural linear dichroism effect. Some of the most beautiful examples of this effect are found for small molecules or organic molecules with directional covalent bonds as discussed in detail in the book NEXAFS Spectroscopy [189].

For the K-edge we readily recognize the foundation of the search light effect, since the p orbitals have directions of maximum charge density and perpendicular nodal planes where the charge density is zero. The X-ray absorption intensity is maximum when E is aligned along the orbital and is zero when E lies in the *nodal plane*. One can remember the search light effect by the following simple picture. The photoelectron is ejected from the spherically symmetric core state along the direction of the E-vector. The E-vector "search light" then senses the hole density of the valence orbital. If the density in the direction of E is zero the transition intensity vanishes. In general, the transition intensity scales directly with the orbital density along E. For L-edges the transition intensity is zero if the E-vector lies along the d orbital *nodal axis*, which is the intersection of two nodal planes (see Fig. 9.19).

9.7.3 Theory of X-ray Natural Linear Dichroism

The "search light effect" follows from a quantum mechanical calculation of the angle dependent transition matrix element which we shall outline now.

In order to facilitate our discussion we shall assume that we are dealing with a nonmagnetic sample. Since XNLD does not depend on spin we can use the same formalism as above but only consider one spin. Inclusion of the other spin would simply give a factor 2 higher intensity. We therefore start with (9.85), written for one spin, and take care of the other spins by a factor of 2. We have,

$$I_{\alpha}^{q} = 2\mathcal{A}\mathcal{R}^{2}\sum_{\substack{E_{i} > E_{\mathrm{F}} \\ i, \mathbf{k}, m}} \left| \sum_{p, M} a_{i, M}(\mathbf{k}) \ e_{\alpha, p}^{q} \left\langle LM | C_{p}^{(1)} | c \, m \right\rangle \right|^{2}.$$
(9.107)

This equation is valid for an atom in a solid described by a band-like valence electron wavefunction

$$\psi_i(\mathbf{k}, r) \rangle = |R_{n',L}(r)\rangle |\phi_i(\mathbf{k})\rangle$$

= $|R_{n',L}(r)\rangle \sum_M a_{i,M}(\mathbf{k}) |LM\rangle$. (9.108)

There are 2L + 1 such states for a given *L*-manifold. If we drop the *k* dependence, the state (9.108) also describes a ligand field state. For the *d* orbitals,

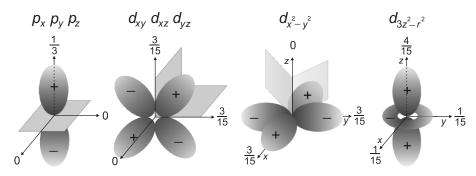


Fig. 9.19. Polarization dependent core to valance transition intensities (square of the transition matrix elements) for E along the principal coordinate axes. Listed are the intensities for the four basic symmetry cases, $s \to p_i$ (i = x, y, z), $p \to d_{ij}$ $(i \neq j = x, y, z)$, $p \to d_{x^2-y^2}$ and $p \to d_{3z^2-r^2}$. All intensities are per orbital per spin in units of \mathcal{AR}^2

for example, the coefficients $a_{i,M}$ would be the coefficients in Table A.2. Equation (9.107) is valid for transitions from a spherically symmetric core manifold $|c\,m\rangle$ and the sum is over all 2c + 1 orbital substates. In the measurement of XNLD we therefore assume that we sum over any spin-orbit split states in the core. This is automatically fulfilled for K-edge spectra, and for L-edge spectra we add the L₃ and L₂ intensities. Because in XNLD one wants to learn about the anisotropy of the valence charge around the absorbing atom one best uses linearly polarized light since the directional \boldsymbol{E} -vector acts like a search light, as discussed later. We shall therefore restrict our discussion to linearly polarized X-rays.

The search light effect is most clearly seen by considering transitions from a core manifold to specific molecular orbitals. Results for the squared transition matrix elements are summarized in Fig. 9.19. In particular, we list the polarization-dependent transition intensities

$$|\langle 2p_n|\frac{P_{\alpha}^0}{r}|1s\rangle|^2 \tag{9.109}$$

from a s core state to the p_x, p_y , and p_z valence orbitals, assuming linearly polarized light with $E \parallel x, y, z$, and similarly the intensities

$$|\langle 3d_n|\frac{P^0_{\alpha}}{r}|2p\rangle|^2\tag{9.110}$$

from a p core state to the five d_n orbitals, assuming linearly polarized light with $E \parallel x, y, z$.

For all $s \to p_i$, (i = x, y, z) transitions (e.g., K-edge) we have a transition intensity 1/3 when the **E**-vector is along the p_i orbital lobe and zero otherwise. The polarization averaged intensity per p_i orbital is $\langle I \rangle = 1/9$. For all transitions from p core states to the clover-leaf-shaped d orbitals, shown in the middle of Fig. 9.19, we have a transition intensity 3/15 for E along the two axes that lie in the plane of the orbital and zero along the perpendicular nodal direction. The transition intensity to the $d_{3z^2-r^2}$ orbital is different as illustrated in Fig. 9.19. For $p \rightarrow d_i$ transitions (e.g., L-edge) we have the polarization-averaged intensity per d_i orbital $\langle I \rangle = 2/15$.

In practice, one often encounters the case where the sample has cylindrical symmetry about an axis. Let us consider a nonmagnetic system with cylindrical symmetry about z. For E along z the X-ray absorption intensity for a transition between states $|a\rangle$ and $|b\rangle$ is obtained with the dipole operator P_z^0 in Table A.4 as,

$$I_z^0 = \mathcal{A} \mathcal{R}^2 \left| \langle b | C_0^{(1)} | a \rangle \right|^2.$$
(9.111)

Similarly we obtain the intensities for E along x and y as

$$I_x^0 = I_y^0 = \frac{1}{2} \mathcal{A} \mathcal{R}^2 \left[\left| \langle b | C_{-1}^{(1)} | a \rangle \right|^2 + \left| \langle b | C_1^{(1)} | a \rangle \right|^2 \right].$$
(9.112)

The cross terms vanish because only one of the operators $C_q^{(1)}$ couples a given pair of substates $|cm\rangle$ and $|LM\rangle$ with L = c + 1 and $M - m = q = 0, \pm 1$, according to the dipole selection rule. For later reference it is important to state that one obtains the same intensity as in (9.112) for circularly or natural light incident along z (operators P_z^{\pm} in Table A.4), i.e.,

$$I_{z}^{+1} = I_{z}^{-1} = \frac{1}{2}\mathcal{AR}^{2} \left[\left| \langle b|C_{-1}^{(1)}|a\rangle \right|^{2} + \left| \langle b|C_{1}^{(1)}|a\rangle \right|^{2} \right].$$
(9.113)

For a spherically symmetric charge distribution we have $I^q_{\alpha} = I^q_{\alpha'} = I^{q'}_{\alpha}$.

The Angle-Dependent XNLD Intensity

More generally, the measured intensity can be written as a function of the angle θ of the *E*-vector with the symmetry axis (labeled ||) and the intensity has the form [388]

$$I(\theta) = I_{\parallel} \cos^2 \theta + I_{\perp} \sin^2 \theta . \qquad (9.114)$$

This expression is valid for higher than three fold symmetry about the axis labeled \parallel . The intensities I_{\parallel} and I_{\perp} are determined by the projection of the charge distribution along the symmetry axis and a direction perpendicular to it.¹³ If the charge distribution has a node perpendicular to the symmetry axis, we have $I_{\perp} = 0$, and the linear dichroism intensity has the famous cosine squared polarization dependence.

¹³The charge distribution function itself cannot be determined by XNLD but only its projections along the cartesian coordinate axes. The projections $f_{\parallel} = I_{\parallel}/(I_{\parallel} + 2I_{\perp})$ and $f_{\perp} = I_{\perp}/(I_{\parallel} + 2I_{\perp})$ are called *orientation factors* [388].

For a uniaxially aligned system the X-ray linear dichroism intensity varies as $I(0) = I = \frac{2}{2} 0 = 2(I) = \frac{2}{2} 0 = 0$ (0.115)

 $I(\theta) = I_{\parallel} \cos^2 \theta = 3\langle I \rangle \cos^2 \theta, \qquad (9.115)$

where θ is the angle of the *E*-vector with the symmetry axis and $\langle I \rangle$ is the angle averaged intensity (9.103).

9.7.4 XNLD and Quadrupole Moment of the Charge

We have seen that polarized X-ray absorption spectroscopy can probe the local anisotropy of the charge density, in particular the hole density, around the absorbing atom. Because the core shell is so localized, XNLD is very sensitive to deviations of the local valence charge in the atomic volume from spherical symmetry. In a picture based on the search light effect the measured X-ray absorption intensity is proportional to the projection of the number of holes in the direction of \boldsymbol{E} . By measuring X-ray absorption along three orthogonal directions, i.e., $\boldsymbol{E} \parallel x, y, z$, we can determine the projection of the number of holes along the three directions, as illustrated in Fig. 9.19.

Sometimes it is useful to describe the origin of polarization dependent X-ray absorption in another way. Starting from the fact that the polarization-averaged intensity is a constant according to (9.103), i.e.,

$$\langle I \rangle = C N_{\rm h}, \tag{9.116}$$

one may write the intensity for a given direction α as a deviation from the constant. For a given polarization direction, say along z, we write $I_z = \langle I \rangle - f(z^2)$. The general formalism given in Appendix A.8 yields the expression

$$I_{\alpha}^{0} = CN_{\rm h} \left(1 - \mathcal{B} \langle Q_{\alpha\alpha} \rangle\right) \qquad (9.117)$$

where $\langle Q_{\alpha\alpha} \rangle$ is the quadrupole moment of the charge distribution. The other factors are

$$C = \mathcal{A} \mathcal{R}^2 \frac{L}{3(2L+1)}$$
, $\mathcal{B} = \frac{2L+3}{2L}$, (9.118)

with $\mathcal{A} = 4\pi^2 \hbar \omega \left(e^2 / 4\pi \epsilon_0 \hbar c \right)$ and \mathcal{R} being the radial transition matrix element. One can make the following general statement.

The *angle-dependent XNLD intensity* is proportional to the sum of the total number of valence holes and the quadrupole moment of the spatial hole density.

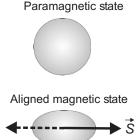


Fig. 9.20. Illustration how a spherical charge density may be modified in the presence of a magnetic alignment of the spins in the sample. The charge distortion arises from the spin–orbit coupling and an asymmetry is induced relative to the spin axis (not direction!). The effect exists in both collinear ferromagnets and antiferromagnets

This formalism appears rather complicated but it is very powerful. We shall see later that it also describes the angle dependent XMCD intensity for the important 3d transition metals. In that case the isotropic term proportional to $N_{\rm h}$ in (9.117) is replaced by the isotropic spin moment m_s and the quadrupolar charge distribution by a quadrupolar spin distribution.¹⁴

9.7.5 X-ray Magnetic Linear Dichroism

In order to differentiate magnetic from natural linear dichroism let us assume a sample of cubic symmetry where no XNLD is present. We also assume that the sample becomes magnetically aligned, either ferromagnetic or antiferromagnetic, below the magnetic transition temperature. In the paramagnetic state above the transition temperature the core and valence charge density is then spherically symmetric according to Sect. 9.7.2. As the sample is cooled into a magnetic state with collinear spin alignment, the spin-orbit coupling may lead to a deformation of the charge. This charge distortion is of uniaxial symmetry about the spin direction as shown schematically in Fig. 9.20. Now the X-ray absorption intensity will be different for E aligned parallel and perpendicular to the spin direction.

The *XMLD effect* arises from a nonspherical distortion of the atomic charge by the spin–orbit interaction when the *atomic spins* are axially aligned by the exchange interaction.

In order to illustrate the effect of the spin-orbit coupling on the charge density we plot in Fig. 9.21 the charge densities of the individual $|j, m_j\rangle$ components of the spin-orbit split $p_{1/2}$ and $p_{3/2}$ manifolds. This is readily done by use of the wavefunctions listed in Table A.2. We see that all individual densities (squares of wavefunctions) are anisotropic in space relative to the z alignment axis of the spin. In contrast, the sum over all m_j substates of each j manifold are spherically symmetric. We can therefore conclude that a linear magnetic dichroism effect will only exist if somehow the m_j substates in

¹⁴The latter term is the infamous T_z term derived by Carra et al. [101].

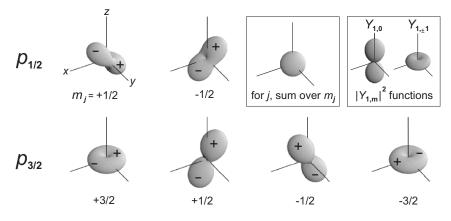


Fig. 9.21. Orbital densities for the $p_{1/2}$ and $p_{3/2}$ manifolds calculated with the functions given in Table A.5. The substates $|l, s, j, m_j\rangle$, for j = 1/2 and j = 3/2 are labelled for brevity by the quantum numbers m_j . In all cases the spin quantization axis is taken to be the z axis. The charge distributions are seen to be asymmetric in space and they give rise to different X-ray absorption intensities when the E-vector is aligned along z and perpendicular to z. One inset shows the spherically symmetric charge density obtained when summing over all m_j states and also when for a given j the m_j states are summed. The upper right inset shows a plot of the charge density $|Y_{l,m}|^2$ for $l = 1, m = 0, \pm 1$, associated with the spherical harmonic basis functions for the p states. They are important when the $|j, m_j\rangle$ states are expressed as a function of spin-up and spin-down functions as given in Table A.5

either the initial or final states of the electronic transition are split and do not contribute equally to the X-ray absorption intensity. In magnetic materials a splitting between m_j substates in the valence and core shells naturally arises in the presence of the exchange interaction below the magnetic transition temperature, as discussed in Sect. 6.6.2.

An unequal spectral contribution of such energetically split m_j substates may arise via two effects. First, if at low temperature the substates have an unequal population [389]. Second, if the energetic splitting between the substates can be observed experimentally.

The XMLD effect for the *ferromagnetic transition metals* predominantly arises from the second mechanism, as shown by Kuneš and Oppeneer [390]. We shall discuss their model in Sect. 9.7.6.

9.7.6 Simple Theory of X-ray Magnetic Linear Dichroism

The XMLD model of Kuneš and Oppeneer [390] is illustrated in Fig. 9.22.

To illustrate the origin of the XMLD effect for the 3d transition metals we start with a Stoner-like band model as previously used for the explanation of the XMCD effect in Fig. 9.13. Again we simplify the description of the d states in an atomic model assuming that the ("down") majority spins are filled. We

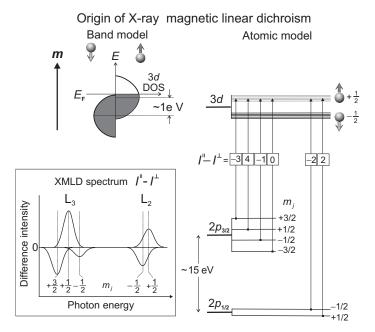


Fig. 9.22. Illustration of the L-edge X-ray absorption processes of linearly polarized photons with angular momentum $q = \pm 1$. For the *d* valence shell we show the correspondence between the Stoner band picture of a magnetic material and an atomic one-hole d shell model. We have chosen our magnetization direction such that the "down-spins" are filled and the "up-spins" partially unfilled. In the atomic model we assume one "spin-up" hole and show the possible 2p core to 3d valence transitions assuming circularly polarized light with angular momentum q. The fraction of "upspin" electrons excited from the p core shell through absorption of X-rays with angular momentum $q = \pm 1$ is listed for the L₃ and L₂ edges. Here we have assumed the X-rays to be incident parallel to the atomic magnetic moment m. We have assumed a splitting of the p states by the exchange interaction, lifting the degeneracy in m_j . Note that this causes an opposite order of m_j states for $p_{3/2}$, l+s and $p_{1/2}$, l-sbecause of the opposite sign of s. Listed are the relative difference intensities which can be obtained from Fig. 9.14 according to $I^{\parallel} - I^{\perp} = I^0 - (I^+ + I^-)/2$. The absolute difference intensities in units of \mathcal{AR}^2 are obtained by dividing the listed values by a factor of 90

then consider electronic transitions from the spin-orbit split p core states to the d minority spin states, as shown in Fig. 9.22. From our earlier discussion we know that a magnetic linear dichroism can only exist if we can differentiate transitions between states that are not spherically symmetric.

In our simple model we assume that the empty 3d density of minority spin states is spherically symmetric, so that we describe the d shell simply by an equal weighting of all spin-up d_i orbitals. Our assumption is reasonable for band-like systems with cubic symmetry like Fe and Ni where an effec-

tive averaging of the k-dependent states over the Brillouin zone leads to an equal contribution of the d_i orbitals. In addition the spin–orbit interaction in the 3d valence shell is small (~ 50 meV) compared to the exchange interaction (1–2 eV) and for the moment we shall neglect it altogether. We shall see later that the spin–orbit interaction in the valence shell actually leads to the distinction of two kinds of magnetic linear dichroism.

From Fig. 9.21 we know that the total 2p core state is also spherically symmetric, and so are the two individual spin-orbit components $2p_{3/2}$ and $2p_{1/2}$. However, the charge density of the individual m_j substates are anisotropic. Indeed, in a ferromagnet the exchange field (which only acts on the spin) leads to a small exchange splitting of the m_j substates of the $2p_{3/2}$ and $2p_{1/2}$ states, as discussed in Sect. 6.6.2 and shown in Fig. 9.22. For the 3*d* metals the splitting between the individual m_j states is rather small, of order 0.2 eV [390–392]. The spin enters in our model since only spin-conserving coreto-valence transitions are allowed by the dipole transition operator.¹⁵

The XMLD difference intensity is obtained from two measurements with E-vector parallel and perpendicular to the sample magnetization direction M,

$$\Delta I_{\rm XMLD} = I^{\parallel} - I^{\perp}. \tag{9.119}$$

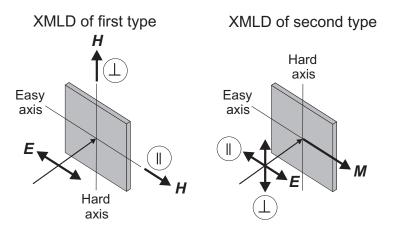
A simple atomic-like model calculation which is similar to that carried out in conjunction with Fig. 9.14, shows that an XMLD effect exists for the various individual transition intensities as illustrated in Fig. 9.22. The XMLD difference spectrum then consists of the sum of all the individual difference intensities. Assuming magnetic alignment along the z-axis, the energy dependent XMLD difference intensity is given by the difference of the intensities measured for $\boldsymbol{E} \parallel z$ and $\boldsymbol{E} \perp z$. With the dipole operators in Table A.4 we obtain for example, for \boldsymbol{E} along z and x,

$$\Delta I_{\text{XMCD}} = \mathcal{AR}^2 \sum_{n,j,m_j} \left| \langle d_n, \chi^+ | C_0^{(1)} | p_j, m_j \rangle \right|^2 -\frac{1}{2} \left| \langle d_n, \chi^+ | C_{-1}^{(1)} - C_{+1}^{(1)} | p_j, m_j \rangle \right|^2.$$
(9.120)

The cross terms can be shown to vanish and by use of the short form (9.101) we obtain the following expression for the *XMLD difference intensity*,

$$\Delta I_{\rm XMLD} = \frac{1}{2} \mathcal{AR}^2 \sum_{\rm states} 2|\langle C_0^{(1)} \rangle|^2 - |\langle C_{-1}^{(1)} \rangle|^2 - |\langle C_{+1}^{(1)} \rangle|^2 .$$
(9.121)

¹⁵The effective charge asymmetry that enters into the transition matrix element is actually not that of the j, m_j core functions but that of their spherical harmonic components. This comes about because the dipole operator only links the minority (up-spin) projections of the p functions given by $Y_{1,m}\chi^+$ (see Table A.5) to the minority d valence states of the form $Y_{2,M}\chi^+$. However, the "spherical" harmonics $Y_{1,m}$ with m = -1, 0, +1 are actually very anisotropic as shown in the upper right inset of Fig. 9.21 (also see Table A.2).



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Fig. 9.23. The two methods to record XMLD spectra, called XMLD of the first and second kind. XMLD of the *first kind* is measured with a fixed sample orientation relative to the linearly polarized X-rays, and the magnetization of the sample is rotated between the easy and the hard directions by a sufficiently strong magnetic field. The measured effect is a pure magnetic effect. XMLD of the *second kind* corresponds to saturating the sample along the easy axis and measuring the absorption with the easy axis either parallel or perpendicular to the *E*-vector. This can be done either by rotating the *E*-vector relative to the sample, as shown, or the sample relative to the *E*-vector. In all cases shown the measured intensities are labeled \parallel and \perp , as shown, with the XMLD signal defined by (9.119)

We shall come back to this expression later in conjunction with the resonant magnetic scattering intensity in Sect. 9.8.

9.7.7 XMLD of the First and Second Kind

In the above discussion we have assumed that we have a sample of cubic symmetry that is magnetically aligned. The assumption of cubic symmetry eliminates any XNLD effect. This would also be true for a polycrystalline sample. In such cases the linear dichroism signal will only be due to a magnetic effect, namely the charge deformation about the magnetic axis. In single crystal samples with lower than cubic symmetry both XNLD and XMLD effects can be present. The expressions for the general case when both natural and magnetic dichroism effects are present are more complicated and have been discussed by Carra et al. [378].

In principle we can eliminate any XNLD effect by performing a different type of measurement as illustrated in Fig. 9.23. The two depicted types of measurements explained in the figure caption are often referred to XMLD of the *first* and *second* type, following Guo et al. [380].

Although experimentally more demanding, the XMLD effect of the first kind has the advantage that it eliminates the XNLD effect.¹⁶ It also contains useful information on the magnetocrystalline anisotropy (MCA) as discussed below. If the MCA of the sample is negligible and the sample has either cubic symmetry or is polycrystalline the two types of XMLD measurements give the same result. For example, polycrystalline films of the elemental ferromagnets typically have an in-plane easy axis and a weak in-plane anisotropy. In lowest order it then does not matter whether we measure the XMLD effect by either rotating the magnetization direction M with a field relative to the fixed E-vector or whether we rotate E relative to the fixed magnetization M. Therefore, our theory developed above should describe the experimental XMLD spectra.

The lineshape predicted by our simple model is indeed observed as shown in Fig. 9.24 [393, 394]. The measurements actually correspond to the XMLD effect of the first kind.¹⁷ The size of the XMLD effect plotted in Fig. 9.24 corresponds to a per-atom normalization of the original spectra, with the edge jump set to unity. The XMLD difference intensity is seen to be significantly smaller than the corresponding XMCD effect in Fig. 9.12. This confirms the expectations from our model calculation.

Despite the larger linewidth ($\sim 1 \, \text{eV}$) of the individual transitions than the core exchange splitting $(\sim 0.2 \,\mathrm{eV})$ the small energy shifts of the individual components still have a pronounced effect on the measured XMLD line shape. As shown in the bottom left inset of Fig. 9.22, the small energetic shifts of the individual transitions leads to a pronounced differential resonance line shape at both the L_3 and L_2 . It arises from shifted positive and negative components which, when added, give a similar differential lineshape from negative to positive intensity for both edges. The same lineshape at the two edges is a consequence of the fact that for the $p_{3/2}$, (l+s) and $p_{1/2}$, (l-s) levels the signs of both s and m_i are inverted as discussed already in Sect. 6.6.2 in conjunction with Fig. 6.18. The intensity of the largest peak in the XMLD (difference) spectrum in the inset of Fig. 9.22 is $(4/90)\mathcal{AR}^2$. This compares to the value $(2/9)\mathcal{AR}^2$ for the XMCD difference, given by (9.96) or (9.97), and indicates that the XMLD effect should be considerably smaller than the XMCD effect. XMLD spectra can also be measured by analyzing the polarization of the X-rays rather than measurement of the absorption. Such magnetooptical polarization spectroscopy, discussed in Sect. 8.7.4, can be performed in several different geometries [395], and is complementary to X-ray absorption spectroscopy.

¹⁶In *antiferromagnets* one can, in principle also "flop" the magnetization axis from the easy into the hard direction, but typically very large fields are required.

¹⁷Note that the geometry used in reference [393] is opposite to the one shown in Fig. 9.23 and therefore the measured difference denoted $\alpha^{\perp} - \alpha^{\parallel}$ by the authors actually agrees with our definition in (9.119).

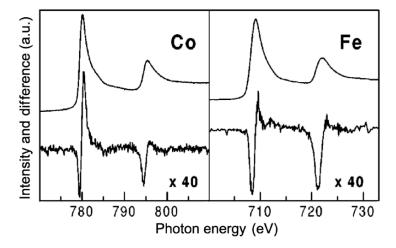


Fig. 9.24. X-ray absorption spectra and XMLD difference spectra for Co and Fe metal [393]. The plotted intensities of the difference spectra correspond to $I^{\parallel} - I^{\perp}$, with the original spectra normalized to an edge jump of 1, far above the edges. The measurements actually correspond to XMLD of the first kind, but because of the weak magnetocrystalline anisotropy and the polycrystalline nature of the samples, the difference between spectra of the first and second kind is negligibly small

XMLD of the first kind, which is measured by fixing the X-ray polarization vector E along either the hard axis or easy axis and then rotating the magnetic axis by 90° using a sufficiently strong external magnetic field, avoids any natural linear dichroism contribution because only the magnetically induced change in charge distribution is measured. In addition, we know from Sect. 7.9.3 that the energy associated with the rotation of the magnetic axis is the magnetocrystalline anisotropy $\Delta E_{\rm so}$. It is therefore not surprising that XMLD measurements of the first kind can indeed measure the magnetocrystalline anisotropy. This was first pointed out by van der Laan [396] who also established a sum rule that links the magnetocrystalline anisotropy with a linear combination of the XMLD intensity measured at the L₃ and L₂ edges, according to

$$\frac{\Delta I_{\rm L_3} - 2\Delta I_{\rm L_2}}{\langle I_{\rm L_3} + I_{\rm L_2} \rangle} = \frac{16\sqrt{3}}{5\,\zeta_{3d}} \frac{\Delta E_{\rm so}}{N_{\rm h}} \,. \tag{9.122}$$

Here $\Delta E_{\rm so}$ is the magnetocrystalline anisotropy energy given by (7.50), ζ_{3d} the spin–orbit parameter defined in (6.87), $N_{\rm h}$ is the number of 3*d* holes, and $\langle I_{\rm L_3} + I_{\rm L_2} \rangle$ is the white line intensity defined in (9.104). The sum rule was experimentally verified by Dhesi et al. [394].

It is interesting to note that the magnetocrystalline anisotropy energy values derived from XMLD are significantly larger than the energies measured with conventional methods. This is similar to the determination of the magne-

tocrystalline anisotropy energies from the angular dependence of the orbital moment, as discussed in Sect. 7.9.3. The origin for these discrepancies are not understood [333, 394].

Summary for the XMLD Intensity

We can summarize as follows.

X-ray magnetic linear dichroism, XMLD, arises from charge anisotropies induced by the exchange and spin–orbit interactions relative to the easy magnetic *axis* of the sample. The effect arises from *uniaxial* spin alignment and exists for both ferromagnets and antiferromagnets.

In practice, the measured magnitude of the XMLD intensity depends on three important parameters,

- The degree of linear polarization $P_{\rm lin}$
- The expectation value of the square of the magnetic moment $\langle m^2
 angle$
- The angle θ between the *E*-vector and the magnetic axis

This can be cast into the following general dependence of the XMLD intensity,

$$I_{\rm XMLD} \propto P_{\rm lin} |\boldsymbol{m} \cdot \boldsymbol{E}|^2 \propto P_{\rm circ} \langle \boldsymbol{m}^2 \rangle \cos^2 \theta$$
 (9.123)

In theory, one calculates the maximum linear dichroism effect by assuming $P_{\text{lin}} = 1$ and assuming two perpendicular measurements with \boldsymbol{E} parallel and perpendicular to \boldsymbol{m} . In this case one obtains (9.121) for the XMLD difference intensity. We can state as follows.

The XMLD difference intensity for a system with its magnetic axis along z may be written in terms of angular matrix elements of the Racah spherical tensors according to,

$$\Delta I_{\rm XMLD} = \frac{\mathcal{AR}^2}{2} \sum_{\rm states} 2|\langle C_0^{(1)} \rangle|^2 - |\langle C_{-1}^{(1)} \rangle|^2 - |\langle C_{+1}^{(1)} \rangle|^2 . \quad (9.124)$$

The factor \mathcal{A} is given by (9.61), and \mathcal{R} is the radial transition matrix element given by (9.81).

It is important to note the difference between the expectation value $\langle m^2 \rangle$ measured by XMLD and the quantity $\langle m \rangle^2$ which can be determined by XMCD [93]. The difference between the two quantities plays an important

role in the temperature dependence of the XMLD intensity [93, 105, 106], as discussed by Regan [284].¹⁸

9.7.8 Enhanced XMLD through Multiplet Effects

In our discussion above we have used a simple one-electron model which describes the electronic excitation of an "active" electron and ignores its coupling to the other atomic electrons, which are therefore assumed to be "passive". In practice, such a model only works if correlation effects are small. The success of our simple treatment of the XMLD effect in the magnetic transition metals is largely based on the fact that they can be reasonably well described by density functional theory which is largely based on an independent-electron picture as discussed in Chapter 7.

For strongly correlated systems such as the transition metal oxides, we have seen in Chapter 7 that multiplet effects have to be taken into account. In particular we have discussed multiplet effects that arise from the coupling between the electrons within the 3d valence shell. Such coupling leads to ${}^{2S+1}L$ ionic terms that are furthermore split by the ligand field and the exchange and spin-orbit interactions. The electronic ground state is the lowest-energy state. For such systems one can no longer describe X-ray absorption in a one-electron model but one needs to use a configuration based approach, as discussed in Sect. 9.5.1.

For 3d transition metals, the configuration picture calculates the X-ray absorption spectrum as transitions from the electronic ground to an excited configuration [266, 267, 397, 398]. The electronic ground configuration consists of a filled $2p^6$ core shell and a $3d^N$ shell with N electrons. In the final configuration one electron has been removed from the core shell and added to the 3d shell. We have the *electron* excitation scheme,

Electron excitation picture:
$$2p^6 \, 3d^N \to 2p^5 \, 3d^{N+1}$$
. (9.127)

If the 3d shell is more than half full it simplifies things to use the concept of holes instead of electrons. This is possible because we have learned in Sect. 6.5 that for a given shell the Coulomb and exchange interactions can be equivalently treated in either an electron or hole picture if we take care of signs. For

$$\frac{\langle \boldsymbol{m}^2 \rangle}{\mu_0} = \frac{\langle \boldsymbol{m} \rangle^2}{\mu_0} + k_{\rm B} T \chi. \tag{9.125}$$

If the susceptibility χ is not known one may use a molecular field expression to relate the two expectation values according to [93]

$$\langle \boldsymbol{m}^2 \rangle = g_J^2 \mu_{\rm B}^2 J (J+1) - g_J \mu_{\rm B} \langle \boldsymbol{m} \rangle \coth\left(\frac{g_J \mu_{\rm B} H_{\rm ext}}{2k_{\rm B}T}\right).$$
(9.126)

 $^{^{18}}$ The two quantities, $\langle \boldsymbol{m}^2\rangle$ and $\langle \boldsymbol{m}\rangle^2$ are related by the magnetic susceptibility χ and temperature T according to

example, Hund's third rule states that the spin-orbit interaction changes sign and the LF splitting is upside down as shown in Fig. 7.16. With these rules we can use instead of (9.127) the following *hole* excitation scheme,

Hole excitation picture:
$$2p^0 3d^{10-N} \rightarrow 2p^1 3d^{9-N}$$
. (9.128)

We can state as follows.

L-edge spectra for multielectron $3d^N$ valence systems may be derived by considering either electron or hole configurations. The two schemes give the same ${}^{2S+1}L$ free ion multiplets but the sign of the spin–orbit and LF splittings have to be inverted.

The simplest case involves initial (ground) and final (excited) configurations with only two particles. It is encountered for NiO which has a (predominantly) $2p^6 3d^8$ ground state and a $2p^5 3d^9$ excited state configuration. The hole picture involves a $p^0 d^2 \equiv d^2$ ground and $2p^1 3d^1 \equiv 2p 3d$ final configuration. Hence we see that in this case the hole picture is simpler and involves the interactions between two-holes, both in the initial and final configurations. The X-ray absorption spectrum then corresponds to transitions between these two configurations. Let us take a look at the electronic states involved in the corresponding L-edge X-ray absorption spectrum.

The energy states involved in the L-edge transitions for Ni²⁺ in an octahedral ligand field (e.g., NiO) are shown in Fig. 9.25. The electronic ground configuration $2p^6 3d^8$ ($p^0 d^2 \equiv d^2$ hole state) consists of a filled 2p core shell and 8 electrons in the 3d shell which are coupled by the strong Coulomb and exchange interactions (total splitting about $\sim 5 \,\mathrm{eV}$), resulting in a ${}^{3}F$ free ion ground state which lies below the next higher states $({}^{1}D, {}^{3}P)$ by about 2 eV [266]. The ${}^{3}F$ state is split by the LF as shown in Fig.7.16 $(10D_q \simeq 1.5 \text{ eV})$ with a lowest energy ${}^{3}A_{2g}$ orbital singlet state with a spin S = 1, corresponding to a spin moment of $2\mu_{\rm B}$ and a quenched orbital moment. From Table 7.7 we see that the $d^8({}^{3}A_{2g}, t_{2g}^6 e_g^2)$ ground state can be thought of as two holes of the same spin in the two e_g orbitals $d_{3z^2-r^2}$ and $d_{x^2-y^2}$. According to Table A.2 these d orbitals correspond to the spherical harmonics $Y_{2,0}$ and $Y_{2,\pm 2}$, respectively. Thus the ${}^{3}A_{2g}$ state can be written as products of the two one-electron functions $\hat{A}(Y_{2,0}Y_{2,\pm 2})$, where \hat{A} means that the product has been properly antisymmetrized, i.e., is a Slater determinant. With the angular momentum addition rules $M_L = m_\ell^1 + m_\ell^2$, where $m_\ell^i = 0, \pm 1$ are the magnetic quantum numbers of the two electrons, one can then see that the state ${}^{3}\!A_{2g}$ has the form

$$|{}^{3}\!A_{2g}\rangle \sim |\hat{A}(Y_{2,0}Y_{2,\pm 2})\rangle \sim |{}^{3}\!F, M_{L} = \pm 2, M_{S}\rangle.$$
 (9.129)

The ${}^{3}A_{2g}$ state is further split by the superexchange interaction. The exchange field felt by the Ni²⁺ ion consists of the sum over the six nearest neighbors [399]

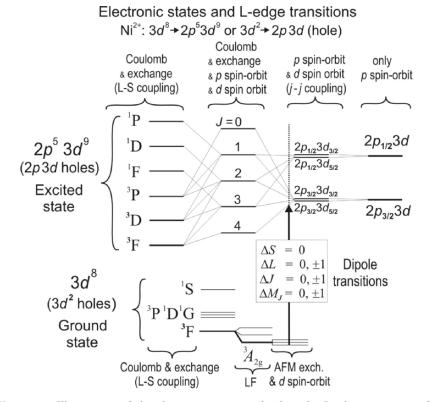


Fig. 9.25. Illustration of the electron states involved in the L-edge transitions for Ni²⁺ in an octahedral ligand field (e.g., NiO) as discussed in the text. The $2p^6 3d^8$ electronic ground state configuration, corresponding to a $2p^0 3d^2 \equiv 3d^2$ hole configuration, is coupled by the strong Coulomb and exchange interactions to a ${}^{3}F$ free ion ground state which is split in an octahedral LF, resulting in a lowest energy ${}^{3}A_{2g}$ ground state. The $2p^5 3d^9$ electronic final state configuration (2p 3d hole configuration) is dominated by the strong 2p core spin–orbit interaction, as shown on the right. In practice, the two-hole final states are described by an "intermediate" coupling scheme, indicated by the dotted vertical line. These states may be written as linear combinations of L - S coupling (left) or j - j coupling states (second from right), whose correspondence may be seen by means of the common J states (second from left) [182]. We have also listed the dipole selection rules in L-S-J coupling

and is about $0.15 \,\mathrm{eV}$. It aligns the atomic moments into an antiferromagnetic arrangement, as shown in Fig. 7.25. Together with the even weaker spin-orbit interaction ($\zeta_{3d} \sim 50 \,\mathrm{meV}$) it leads to a magnetic splitting of the ${}^{3}A_{2\mathrm{g}}$ state, where the lowest energy state may be written in the form¹⁹

¹⁹The 3*d* spin–orbit interaction also mixes the ${}^{3}A_{2g}$ LF ground state with the higher energy ${}^{3}T_{2g}$ and ${}^{3}T_{1g}$ LF states, resulting in a small orbital moment.

$$|\text{GS}\rangle = \sum_{\substack{J=4,3,2\\M_J}} a_{J,M_J} |{}^3F_J, M_J\rangle .$$
 (9.130)

The $2p \, 3d$ hole final configuration of the electronic excitation cannot simply be treated in L-S coupling because the largest interaction is the spinorbit coupling for the 2p hole, which leads to a $2p_{3/2} - 2p_{1/2}$ splitting of about 15 eV, and is larger than the $2p \, 3d$ Coulomb and exchange interaction ($\sim 5 \, \text{eV}$). Hence the final state corresponds to a coupling scheme [182] that is "intermediate" between that where the Coulomb and exchange interaction is turned off, schematically shown on the right side of Fig. 9.25 and the L-S scheme shown on the left side. For reference we also show a j-j coupling scheme, assuming a small spin-orbit interaction in the 3d shell. In general, there are n energetically different final states which form two separate spin-orbit split groups and within each group exhibit multiplet structure. They can also be written as linear combinations of $|L, S, J, M_J\rangle$ states according to²⁰

$$|\mathrm{FS}\rangle_n = \sum_{\substack{J=4,3,2\\M_J}} b^n_{J,M_J} |{}^3\!F_J, M_J\rangle + \sum_{\substack{J=3,2,1\\M_J}} c^n_{J,M_J} |{}^3\!D_J, M_J\rangle .$$
(9.131)

The fine structure of the L-edge absorption spectrum calculated by van der Laan and Thole [402] for a $3d^8$ electronic ground state and different strengths of the spin–orbit and Coulomb interactions in the $2p^53d^9$ final state is shown in Fig. 9.26a. Here the evolution of the spectrum is shown between two extreme cases. If the Coulomb and exchange interactions are zero, the spectrum (top trace) shows one-electron like behavior with two peaks separated by the 2pspin-orbit splitting. In the other extreme of zero 2p core spin-orbit splitting but strong Coulomb and exchange splitting, the spectrum (bottom trace) is that calculated in pure L-S coupling. It consists of two peaks, corresponding to the allowed $(\Delta S=0, \Delta L=0, \pm 1)$ transitions ${}^{3}F \rightarrow {}^{3}D$ and ${}^{3}F \rightarrow {}^{3}F$. In the intermediate region, where both the 2p core spin-orbit and 2p-3d Coulomb and exchange splitting are present, a more complicated L-edge spectrum is found. The situation encountered in practice for Ni²⁺ in octahedral symmetry is indicated by an arrow on the left, and the calculated spectrum is shown in Fig. 9.26b [402]. The agreement with experiment demonstrates the power of multiplet calculations.

The enhancement of the XMLD effect in the presence of multiplet splitting arises from the same physical principle as in the one-electron case. An XMLD effect will only exist if the exchange and spin–orbit interactions break the spherical symmetry in either or both of the initial and final states involved in the electronic transitions. The origin of the magnetically induced charge

 $^{^{20}}$ In general, one can always express functions written in one coupling scheme as a linear combination of functions written in another coupling scheme. In practice, this is done today by use of the elegant scheme developed by Racah [400] and Wigner [401], which is treated in detail by Cowan [182] and Shore and Menzel [181].

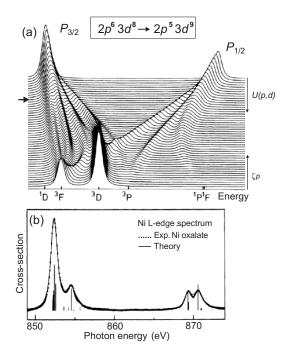


Fig. 9.26. (a) Calculated L-edge transition probability from a $2p^6 3d^8$ configuration with a ${}^{3}F$ free ion ground state to the $2p^5 3d^9$ electronic *final state* configuration [402]. The horizontal scale corresponds to excitation energy, while the 2p-3dCoulomb and exchange interaction U(p, d) and the 2p spin–orbit coupling ζ_p are varied vertically. The top trace correspond to pure 2p spin–orbit coupling (U(p, d) = 0)and the lowest trace to pure L-S coupling ($\zeta_p = 0$). The case corresponding to experiment is marked with an *arrow* on the *left side*. (b) Experimental (*dotted line*) and calculated L-edge spectra (*data points*) for Ni oxalate [402]

asymmetry in the ground state (9.130) and the excited states (9.131) is best seen by realizing that any multiplet state $|^{2S+1}L_J\rangle = |L, S, J\rangle$ is spherically symmetric, similar to the one-electron case shown in Fig. 9.21. Only when the M_J -degeneracy is lifted through magnetic interactions do the $|L, S, J, M_J\rangle$ substates exhibit a charge asymmetry.

Both the ground state (9.130) and the excited states (9.131) are seen to consist of a linear combination of M_J substates, weighted by coefficients a_{J,M_J}, b_{J,M_J}^n , and c_{J,M_J}^n and are therefore, in general, not spherically symmetric. In addition, the dipole operator couples the M_J -states in the ground state and the M'_J states in the excited states differently for linearly polarized light along z, namely $M'_J - M_J = 0$, and for linearly polarized light perpendicular to z, namely $M'_J - M_J = \pm 1$. One may summarize the reasons for the enhanced XMLD effect in spectra with multiplet effects as follows. The XMLD effect is enhanced in the presence of multiplet effects for the following reasons:

- The X-ray absorption spectrum for a sample with a $2p^63d^N$, 1 < N < 9, ground configuration consists of several resonances that are due to the multiplet structure of the final configuration $2p^53d^{N+1}$.
- In general, for magnetically aligned samples both the electronic ground state of the $2p^63d^N$ ground configuration and the excited states of the final configuration $2p^53d^{N+1}$ are not spherically symmetric.
- The dipole operator selects and weights the various resonant transitions depending on the light polarization, often with opposite intensity changes for energetically separated resonances.

The XMLD effect measured for a thin epitaxial NiO film grown on MgO(100) is shown in Fig. 9.27 [403]. In this case the XMLD effect arises from the preferential alignment of the antiferromagnetically coupled spins perpendicular to the film surface. In comparison, the results of a multiplet

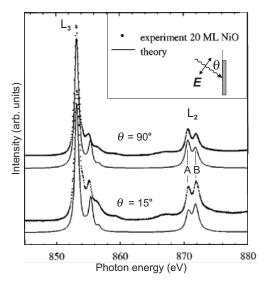


Fig. 9.27. Experimental (dotted line) polarization dependent Ni L-edge spectra for a 20 monolayer (ML) thick epitaxial NiO(100) film grown on MgO(100) [403], measured at room temperature. The angle $\theta = 90^{\circ}$ corresponds to normal incidence with \boldsymbol{E} in the plane of the film and $\theta = 15^{\circ}$ to grazing incidence with \boldsymbol{E} nearly along the surface normal. The theoretical spectra (solid line) were calculated with a multiplet theory including an octahedral LF and assuming an exchange interaction along a magnetic axis that lies nearly perpendicular to the surface along $\langle \pm 2 \pm 1 \pm 1 \rangle$

calculation are also shown. They are found to be in good agreement with the data. Particularly important is the strong change of the two peaks A and B associated with the L₂-edge. By comparison of experiment and theory one can establish the following rule: when the E-vector is aligned along the magnetic axis the higher energy peak B has maximum intensity. The peak intensity ratio is often used to determine changes in the orientation of the magnetic axis [105, 403–405].

The magnetic origin of the observed linear dichroism effect may be proven by heating the sample above the Curie temperature, as illustrated for strontium doped LaFeO₃ in Fig. 9.28. If about 40% of the La atoms are replaced by Sr, the high Néel temperature of LaFeO₃ (1013 K) is reduced to around 200 K. The Fe $L_{2,3}$ NEXAFS spectra of such a La_{0.6}Sr_{0.4}FeO₃ sample recorded below and above the Néel temperature are plotted in Fig. 9.28a, b, respectively. The spectra recorded at 100 K, well below the expected Néel temperature, reveal the presence of a strong polarization dependence, which completely vanishes in case of the room temperature spectra. This clearly demonstrates the purely magnetic origin of the linear dichroism observed for La_{0.6}Sr_{0.4}FeO₃ below its Néel temperature.

Both LaFeO₃ (see Fig. 10.9) and $La_{0.6}Sr_{0.4}FeO_3$ have the same crystal structure with six oxygen atoms surrounding each Fe atom. Since the oxygens have a higher electronegativity than Fe, $LaFeO_3$ is an ionic compound in which Fe has a valency of 3+ and a d^5 high spin ground state. Correspondingly, the rich fine structure of the spectra can be explained by a multiplet calculation performed for an Fe^{3+} ion in a high-spin ground state [407], which considers the multiplet coupling of the five Fe 3d valence electrons (or holes) in the ground state, and the multiplet coupling of the four 3d holes and the 2p core hole in the final state. The oxygen ligands surrounding the Fe³⁺ ion give rise to an octahedral crystal field, which is taken into account via the cubic 10Dq crystal field parameter. In general, more than one multiplet state contributes to each of the peaks in the absorption spectrum. Since these different states typically differ in their polarization dependence, the intensities of the absorption structures typically vary between two finite extreme values and do not vanish completely for any orientation of the electric field vector relative to the AFM axis.

9.7.9 The Orientation-Dependent Sum Rules

In Sect. 9.6.5 we established relationships between orientation-averaged Xray absorption resonance intensities and physical quantities which represent averages over the atomic volume, like the number of valence holes per atom and the atomic spin and orbital moments. It turns out that these orientation averaged sum rules are integrated versions of more general orientationdependent sum rules. The latter link the intensities of orientation-dependent XNLD, XMLD, and XMCD spectra to the same atomic-volume integrated physical quantities plus an orientation-dependent term related to the quadru-

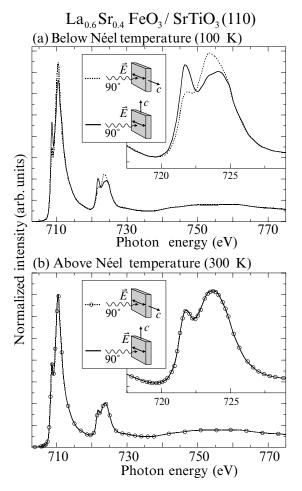


Fig. 9.28. Saturation corrected electron yield spectra at the Fe $L_{2,3}$ -edge of $La_{0.6}Sr_{0.4}FeO_3$, grown as a 40 nm thin $La_{0.4}Sr_{0.6}FeO_3$ film on a $SrTiO_3(110)$ substrate, for the two indicated geometries, (a) below and (b) above the Néel temperature. The absence of any dichroism above the Néel temperature demonstrates the magnetic origin of the linear dichroism effect observed below the Néel temperature. Spectra taken from Lüning et al. [406]

pole moment. The orientation-dependent term simply integrates to zero when an orientational average is performed.

In the context of this book we restrict our discussion to the generalized form of three sum rules of Sect. 9.6.5. In particular, we simply state their form since a more detailed discussion has been given elsewhere [102, 333, 384, 408]. Also, there are other sum rules for the case of XMLD, and we refer the interested reader to the original papers [378, 382, 383].

When generalized, the *charge sum rule* (9.103) takes the form (9.117) or A.31 which we can write in simplified form as (see Appendix A.8),

$$[I_{L_3} + I_{L_2}]_{\alpha} = C(N_h + N_Q^{\alpha}).$$
(9.132)

We have characterized the anisotropy by an index α that specifies the orientation of E (linear polarization) or k (circular polarization). The sum rule correlates the polarization dependent white line intensity with the total number of d holes $N_{\rm h}$ and a quadrupole term N_O^{α} which expresses the anisotropy of the charge density in the atomic volume as discussed in Sect. 9.7.4 and Appendix A.8. The term N_Q^{α} vanishes when an angular average is performed, $\sum_{\alpha}^{1} N_Q^{\alpha} = N_Q^x + N_Q^y + N_Q^z = 0$ yielding the isotropic sum rule (9.103). For 3d compounds the *spin sum rule* (9.105) originally derived by Carra

et al. [101] takes the general form [102, 408]

$$[-A+2B]_{\alpha} = \frac{C}{\mu_{\rm B}}(m_s + m_D^{\alpha}) \ . \tag{9.133}$$

We see that its form closely resembles the charge sum rule, and in fact its derivation in a one-electron model proceeds along the same lines as that of (9.132). In general, the term m_D^{α} arises from the anisotropic spin density in the atomic volume. It is given by $m_D^{\alpha} = -7 \langle T_{\alpha} \rangle \mu_{\rm B} / \hbar$ [408] where $\boldsymbol{T} = \boldsymbol{S} - 3 \hat{\boldsymbol{r}} (\hat{\boldsymbol{r}} \cdot \boldsymbol{S})$ is the intra-atomic magnetic dipole operator [101]. In general we have T_{α} = $\sum_{\beta} Q_{\alpha\beta} S_{\beta}$, so that the charge (expressed by the quadruple operator Q, see Appendix A.8) and spin (S) components of T are coupled. If the atomic spinorbit coupling is comparable to the ligand field effects experienced by the magnetic atom, the charge distribution is no longer decoupled from the spin distribution and in this case the term m_D^{α} is always present in addition to the spin moment. This provides a problem since the spin moment cannot be independently determined. We shall not discuss this difficult case here but refer the reader to references [409–411].

If the spin-orbit coupling is weak relative to the ligand field effects, the atomic spin density closely follows the atomic charge density. The term m_D^{α} is then mainly determined by the anisotropy of the charge due to bonding and it may be eliminated by three orthogonal measurements, provided the ligand field symmetry is not too low [102, 333].

Many 3d compounds fall in this category since the spin-orbit coupling is small. In this case there is more than a formal similarity between the charge sum rule (9.132) and the spin sum rule (9.133). In this case the total number of holes, $N_{\rm h}$, and the charge density term, N_Q^{α} in (9.132), are simply replaced by the isotropic spin moment, m_s , and a spin density term $m_D^{\alpha} = (7/2) \sum_i Q_{\alpha}^i m_s^i$ in (9.133), respectively. The latter consists of a sum over the d_i -orbital projected spin moments m_s^i and the quadrupole matrix elements Q_{α}^i of the d_i orbitals defined in (A.32). This term is nonzero in anisotropic bonding environments and reflects the fact that the number of spins in the atomic volume differs along different crystallographic (bonding) directions. Polarized X-rays

therefore offer the capability of probing the angular distribution of the spins in the atomic volume, whereas conventional magnetometry only probes the integrated number of spins, i.e., the essentially isotropic spin moment per atom. For small spin–orbit coupling, the term m_D^{α} vanishes when an angular average is performed because of its link to the quadrupole moment. We then have $(1/3) \sum_{\alpha} m_D^{\alpha} = 0$, and the isotropic sum rule (9.105) is obtained. The angular average requires that in all measurements the sample is magnetically saturated by a strong external magnetic field along the X-ray propagation direction.

Finally, we discuss the general orbital moment sum rule. When an XMCD measurement is performed for a given sample orientation in the presence of an external magnetic field which is sufficiently large to magnetically saturate the sample along the X-ray propagation direction \mathbf{k} , the orbital moment m_o^{α} along the field direction α can be directly determined by use of the sum rule

$$-[A+B]_{\alpha} = \frac{3C}{2\mu_{\rm B}} \ m_o^{\alpha} \ . \tag{9.134}$$

Note that in contrast to the quantities $N_{\rm h}$ and m_s which by definition correspond to isotropic atomic quantities, the orbital moment m_o^{α} is in general anisotropic, as discussed in Sect. 7.9.3. We have also seen in that section that the difference between the orbital moments measured along the easy and hard magnetization directions is related to the magnetocrystalline anisotropy.

9.8 Magnetic Dichroism in X-ray Absorption and Scattering

We conclude this chapter by connecting the magnetic dichroism effects observed in X-ray absorption and resonant scattering. We have seen in Sect. 9.4.2 that the X-ray absorption cross-section is given by the imaginary part $f_2(E) =$ F''(E) of the resonant forward scattering factor F(E), according to the optical theorem (9.49) or

$$\sigma^{\rm abs}(E) = 2 r_0 \lambda \, {\rm Im}[F(\boldsymbol{Q}, E)]_{\boldsymbol{Q}=0} = \frac{C^*}{E} f_2(E) \,, \qquad (9.135)$$

where $C^* = 2 h c r_0 = 0.70 \times 10^8$ b eV. This general relationship also holds for dichroic absorption and scattering. For example, if we measure the XMCD absorption cross-section $\sigma^{abs}(E)$ we can use the Kramers–Kronig transformation to obtain the dichroic scattering factors, and by their use we obtain the resonant scattering cross-section in the long-wavelength limit according to (9.48) or

$$\sigma^{\text{scat}} = \sigma_{\text{e}} \left(\left[f_1(E) \right]^2 + \left[f_2(E) \right]^2 \right).$$
(9.136)

As an example we show in Fig. 9.29 the L-edge dichroic absorption and scattering cross-sections for Fe metal, using the data of Kortright and Kim [353].

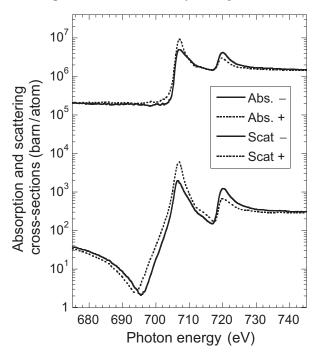


Fig. 9.29. Fe L-edge XMCD cross-sections for the absorbed and elastically scattered intensity [353]. The shown cross-sections are the polarization-dependent versions of those in Fig. 9.6 in the presence of magnetic alignment

The plot is the dichroic version of that in Fig. 9.6. The figure shows that magnetic effects are prominent both in X-ray absorption and resonant scattering.

In Sect. 9.5.3 we have stated the quantum mechanical results for the X-ray absorption cross-section, given by (9.59), and the resonant scattering cross-section in the long-wavelength limit, given by (9.63). We now want to establish the link between these expressions, which in essence constitutes the proof of dichroic version of the optical theorem (9.49).

9.8.1 The Resonant Magnetic Scattering Intensity

We start with expression (9.63) for the differential cross-section for the resonantly scattered intensity in the dipole approximation, i.e.,

$$\left(\frac{\mathrm{d}\,\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{scat}} = r_0^2 \left|F(\hbar\omega)\right|^2 = \frac{\hbar^2 \omega^4}{c^2} \alpha_{\mathrm{f}}^2 \left|\sum_n \frac{\langle a|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_2^*|n\rangle\langle n|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_1|a\rangle}{(\hbar\omega - E_R^n) + \mathrm{i}(\Delta_n/2)}\right|^2 \quad (9.137)$$

For a magnetic sample, we define the z quantization axis to lie along the magnetization direction. One can then express the double matrix element in terms of matrix elements of spherical tensors $C_q^{(1)}$ $(q = 0, \pm 1)$ and products

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involving the unit polarization vectors and the unit vector $\hat{\boldsymbol{m}} = \boldsymbol{e}_z$ according to [412]

$$\langle a | \boldsymbol{r} \cdot \boldsymbol{\epsilon}_{2}^{*} | n \rangle \langle n | \boldsymbol{r} \cdot \boldsymbol{\epsilon}_{1} | a \rangle = \frac{\mathcal{R}^{2}}{2} \left[(\boldsymbol{\epsilon}_{2}^{*} \cdot \boldsymbol{\epsilon}_{1}) \left\{ |C_{+1}|^{2} + |C_{-1}|^{2} \right\} + i(\boldsymbol{\epsilon}_{2}^{*} \times \boldsymbol{\epsilon}_{1}) \cdot \hat{\boldsymbol{m}} \left\{ |C_{-1}|^{2} - |C_{+1}|^{2} \right\} + (\boldsymbol{\epsilon}_{2}^{*} \cdot \hat{\boldsymbol{m}})(\boldsymbol{\epsilon}_{1} \cdot \hat{\boldsymbol{m}}) \left\{ 2|C_{0}|^{2} - |C_{-1}|^{2} - |C_{+1}|^{2} \right\} \right],$$
(9.138)

where $\mathcal{R} = \langle a|r|n \rangle$ is the radial transition matrix element and the factors $|C_q|^2$ are dipole matrix elements of the Racah spherical tensors given by

$$|C_q|^2 = |\langle a|C_q^{(1)}|n\rangle|^2.$$
(9.139)

This gives the following key result for the *resonant magnetic scattering factor*, defined in (9.20) [365, 412].

The elastic resonant magnetic scattering factor in units [number of electrons] is given by

$$F(\hbar\omega) = \frac{\hbar\omega^2 \alpha_{\rm f} \mathcal{R}^2}{2cr_0} \left[\underbrace{\underbrace{(\boldsymbol{\epsilon}_2^* \cdot \boldsymbol{\epsilon}_1) \, G_0}_{\rm charge} + \underbrace{\mathbf{i}(\boldsymbol{\epsilon}_2^* \times \boldsymbol{\epsilon}_1) \cdot \hat{\boldsymbol{m}} \, G_1}_{\rm XMCD} + \underbrace{(\boldsymbol{\epsilon}_2^* \cdot \hat{\boldsymbol{m}})(\boldsymbol{\epsilon}_1 \cdot \hat{\boldsymbol{m}}) \, G_2}_{\rm XMLD}}_{\rm XMLD} \right],$$
(9.140)

where $\alpha_{\rm f}$ is the dimensionless fine structure constant given by (9.62), \mathcal{R}^2 the radial transition matric element, r_0 the classical electron radius, and

$$G_0 = \sum_n \frac{|\langle a|C_{+1}^{(1)}|n\rangle|^2 + |\langle a|C_{-1}^{(1)}|n\rangle|^2}{(\hbar\omega - E_R^n) + i(\Delta_n/2)} , \qquad (9.141)$$

$$G_1 = \sum_n \frac{|\langle a|C_{-1}^{(1)}|n\rangle|^2 - |\langle a|C_{+1}^{(1)}|n\rangle|^2}{(\hbar\omega - E_R^n) + i(\Delta_n/2)} , \qquad (9.142)$$

and

$$G_2 = \sum_n \frac{2|\langle a|C_0^{(1)}|n\rangle|^2 - |\langle a|C_{-1}^{(1)}|n\rangle|^2 - |\langle a|C_{+1}^{(1)}|n\rangle|^2}{(\hbar\omega - E_R^n) + i(\Delta_n/2)} .$$
(9.143)

The first term in (9.140) is independent of the magnetic moment. The numerator of G_0 has the form of the natural linear dichroism intensity given by (9.112) for linear polarization and (9.113) for circular polarization. As indicated in (9.140) it describes the resonant scattering from a *spherical* charge

distribution. The polarization dependence $(\epsilon_2 \cdot \epsilon_1)$ is the same as for Thomson scattering. The scalar product is finite only if the incident and scattered polarizations are collinear, that is the photon polarization is not rotated upon scattering.

The second term has a linear dependence on the magnetic moment and the numerator of the matrix element G_1 has the same form as (9.102), describing XMCD. It therefore describes magnetic *circular* dichroism. The polarization dependence is $(\epsilon_2 \times \epsilon_1)$ so that the polarization is rotated on scattering.

The third term is quadratic in the magnetic moment and the matrix elements in G_2 are of the same form as those for XMLD given by (9.124). Hence the term describes magnetic *linear* dichroism. The polarization dependence is more complicated and in general the polarization is partially rotated in the scattering process.

9.8.2 Link of Magnetic Resonant Scattering and Absorption

In order to establish the link between the imaginary part $f_2(\hbar\omega)$ of the magnetic resonant scattering factor and the X-ray absorption cross-section $\sigma^{abs}(\hbar\omega)$, we start from $F(\hbar\omega)$ given by (9.137). For simplicity we restrict ourselves to one well-defined resonant transition via a state $|n\rangle = |b\rangle$ so that we can drop the sum. This gives

$$F(\hbar\omega) = \frac{\hbar\omega^2}{cr_0} \alpha_{\rm f} \frac{\langle a|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_2^*|b\rangle\langle b|\boldsymbol{r}\cdot\boldsymbol{\epsilon}_1|a\rangle}{(\hbar\omega - E_{ba}) + {\rm i}(\Delta_b/2)} . \tag{9.144}$$

where $E_{ba} = E_b - E_a$ is the resonant energy and Δ_b is the FWHM of the intermediate state.

We now want to prove the relationship (9.135). Without dealing with the different polarization cases, which we shall do later, let us quickly see how the scattering factor transforms into the absorption cross-section. If we assume that the unit polarization vectors are real and consider *forward scattering* so that $\epsilon_1 = \epsilon_2 = \epsilon$ we get $\langle a | \boldsymbol{r} \cdot \boldsymbol{\epsilon} | b \rangle \langle b | \boldsymbol{r} \cdot \boldsymbol{\epsilon} | a \rangle = |\langle b | \boldsymbol{r} \cdot \boldsymbol{\epsilon} | a \rangle|^2$. Next we rewrite the denominator in (9.144) as a real and imaginary part

$$\frac{1}{(\hbar\omega - E_{ba}) + \mathrm{i}(\Delta_b/2)} = \frac{\hbar\omega - E_{ba}}{(\hbar\omega - E_{ba})^2 + (\Delta_b/2)^2} - \mathrm{i}\pi \underbrace{\frac{2}{\pi\Delta_b} \frac{(\Delta_b/2)^2}{(\hbar\omega - E_{ba})^2 + (\Delta_b/2)^2}}_{\rho(E_b)}$$
(9.145)

The imaginary term denoted by an under-bracket represents a normalized Lorentzian of unit area and dimension [1/energy] according to Appendix A.9. As indicated we can use this function to represent the density of states $\rho(E_b)$ associated with the intermediate state $|b\rangle$. By substituting into (9.144) and with $\hbar\omega = E$ we obtain the desired result

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$$\operatorname{Im}[F(\hbar\omega)] = f_2(\hbar\omega) = \frac{\pi\omega}{cr_0} \alpha_{\rm f} \,\hbar\omega \,|\langle b|\,\boldsymbol{\epsilon}\cdot\boldsymbol{r}|a\rangle|^2 \,\rho(E_b) \,.$$
$$= \frac{\omega}{4\pi cr_0} \,\sigma^{\rm abs}(\hbar\omega) = \frac{\hbar\omega}{2h\,c\,r_0} \,\sigma^{\rm abs}(\hbar\omega) = \frac{E}{C^*} \,\sigma^{\rm abs}(\hbar\omega) \,. \tag{9.146}$$

Here we have used (9.59), with implicit requirement of the energy conserving δ -function. Our result (9.146) constitutes a quantum mechanical proof of the optical theorem (9.49), extended to magnetic systems. Let us now take a closer look at the detailed polarization-dependent terms in the resonant magnetic scattering factor given by (9.140).

Linear Polarization

For linearly polarized incident X-rays, ϵ is real and only the first and third terms are nonzero. By use of (9.145) we obtain from (9.140)

$$f_{2}(\hbar\omega) = \underbrace{\frac{\hbar\omega}{2hcr_{0}}}_{E/C^{*}} \underbrace{4\pi^{2}\alpha_{f}\hbar\omega}_{\mathcal{A}} \mathcal{R}^{2} \rho(E_{b}) \left[\underbrace{\frac{1}{2} \left\{ |C_{+1}|^{2} + |C_{-1}|^{2} \right\}}_{\text{charge}} + \underbrace{\frac{1}{2} |\boldsymbol{\epsilon} \cdot \hat{\boldsymbol{m}}|^{2} \left\{ 2|C_{0}|^{2} - |C_{-1}|^{2} - |C_{+1}|^{2} \right\}}_{\text{XMLD}} \right].$$
(9.147)

In comparing the terms labelled "charge" and "XMLD" to the relevant expressions for the X-ray absorption *intensities* we need to ignore the conversion factor E/C^* and integrate the density of states factor $\rho(E_b)$ over energy which per our definition gives unity (see Appendix A.9). Our result for the charge term is then found to be identical to the X-ray absorption intensity for linear polarized X-rays given by (9.112). Since the result does not depend on the orientation of the polarization vector $\boldsymbol{\epsilon}$ in space, we see that this term reflects absorption by a spherically symmetric charge density.

The XMLD term is identical to our previous result given by (9.124) if we take the difference of the intensities for $\boldsymbol{\epsilon} \parallel \hat{\boldsymbol{m}}$ and $\boldsymbol{\epsilon} \perp \hat{\boldsymbol{m}}$ according to (9.119). This establishes the link between the resonant scattering factor in the forward scattering geometry and the XMLD absorption intensity.

Circular Polarization

For incidence along the z quantization axis, circularly polarized X-rays with positive and negative helicity are described by (5.35) and (5.36) or

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$$\boldsymbol{\epsilon}^{\pm} = \mp \frac{1}{\sqrt{2}} \left(\boldsymbol{\epsilon}_x \pm \mathrm{i} \boldsymbol{\epsilon}_y \right), \qquad (9.148)$$

Defining $\boldsymbol{\epsilon}_x \times \boldsymbol{\epsilon}_y = \boldsymbol{\epsilon}_z = \boldsymbol{k}_0$, where \boldsymbol{k}_0 is the unit vector in the direction of X-ray propagation, we have

$$\mathbf{i}\left[(\boldsymbol{\epsilon}^{\pm})^* \times \boldsymbol{\epsilon}^{\pm}\right] = \mp \boldsymbol{k}_0 , \qquad (9.149)$$

meaning that for positive helicity light the cross product gives $-\mathbf{k}_0$ and for negative helicity light $+\mathbf{k}_0$. We obtain from (9.140),

$$f_{2}(E) = \frac{E}{C^{*}} \mathcal{AR}^{2} \rho(E_{b}) \left[\underbrace{\frac{1}{2} \left\{ |C_{+1}|^{2} + |C_{-1}|^{2} \right\}}_{\text{charge}} \underbrace{\mp(\boldsymbol{k}_{0} \cdot \hat{\boldsymbol{m}}) \frac{1}{2} \left\{ |C_{-1}|^{2} - |C_{+1}|^{2} \right\}}_{\text{XMCD}} \right].$$
(9.150)

The charge term is equivalent to the natural linear dichroism intensity given by (9.112) for linear polarization and (9.113) for circular polarization. Since it does not depend on the orientation of the polarization vector ϵ in space it represents the resonant scattering from a *spherical* charge distribution.

If we form the difference between intensities measured with left and right circular polarization according to our XMCD definition (9.95), the charge term drops out and we obtain

$$\Delta f_2(E) = f_2^-(E) - f_2^+(E) = \frac{E}{C^*} \mathcal{AR}^2 \,\rho(E_b) \left\{ |C_{-1}|^2 - |C_{+1}|^2 \right\}.$$
(9.151)

Without the conversion factor E/C^* and after energy integration this result is identical to that derived earlier in (9.102).

In Chap. 10 we shall explore through experiments the theoretical concepts developed earlier.

10.1 Introduction

The goal of the present chapter is to give an overview of experimental X-ray techniques for the determination of the magnetic properties of matter. While it will be advantageous for the reader to have worked through the theoretical concepts developed in Chap. 9, the present chapter is mostly written from an experimentalist's point of view. The chapter may therefore be understood without having mastered the detailed theory of Chap. 9. To facilitate this task, we will present a short summary of the concepts underlying the various X-ray dichroism effects in Sect. 10.2. We will then focus on experimental procedures, data analysis techniques, and the relation of X-ray resonance intensities with magnetic quantities, for example the link between X-ray absorption intensities and magnetic moments. In all cases we illustrate the concepts by experimental results. Our treatment reflects the fact that polarized X-ray techniques have become of considerable importance for the study of magnetic phenomena and materials, owing to their elemental, chemical, and magnetic specificity. We will show here that spectroscopic and microscopic results may be linked to magnetic properties of interest by simple analysis procedures.

We highlight X-ray absorption techniques, both spectroscopy and spectromicroscopy, because of their simplicity and direct link to magnetic properties. We also touch on X-ray scattering, in particular, the use of resonant coherent techniques for magnetic imaging. Absorption and scattering are related as discussed in Sect. 9.8. In practice, the resonantly scattered intensity can always be obtained by the Kramers–Kronig transformations as discussed in Sect. 9.4.4. We shall not specifically discuss reflectivity experiments, which are closely related to scattering experiments and, like the magneto-optical Kerr technique, may conveniently be used for magnetic characterization [358–361]. In contrast to X-ray absorption, however, scattering and reflectivity experiments contain information on both the absorptive and refractive part of the refractive index $n(\omega)$ (see (9.1), (9.6), and (9.7)) and the analysis is there-

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fore more complicated. In particular, care has to be exercised regarding the measured sign of the dichroism signal [358, 361].

Two types of X-ray absorption spectroscopy are often distinguished. The first is concerned with the study of resonances near the absorption edges, often called *near edge X-ray absorption fine structure* (NEXAFS) [189] or X-ray absorption near edge structure (XANES) [413]. The near edge fine structure originates from transitions between a core state and localized valence states. For the transition metals, for example, we are mostly interested in dipole transitions from 2p core to 3d valence states. The intensity of such transitions provides direct information on the magnetic properties of the important d valence electrons and represents the most powerful use of X-ray absorption spectroscopy for the study of magnetic materials.

The second type of spectroscopy deals with nonresonant absorption and is typically called the extended X-ray absorption fine structure (EXAFS) [413]. Magnetic EXAFS, which exists in the region starting tens of eV above the absorption edge, originates from spin-dependent scattering of the excited photoelectron off the magnetic neighbors and may be useful for studies of the local magnetic structure [414, 415]. We shall not treat it here because we believe resonant effects to be more important.

The structure of the chapter is as follows. We first give a quick overview over the four most important dichroism effects and how they manifest themselves in measured spectra. The rest of the chapter consists of two major parts, dealing with spectroscopy and microscopy. We first discuss experimental procedures for polarization dependent X-ray absorption spectroscopy, data analysis methods and present selected results. We concentrate on spectroscopic studies of the 3d transition metals, using their L absorption edges. We then turn to magnetic microscopy with X-rays, better called "spectro-microscopy", because the method combines the principles of spectroscopy such as changes of X-ray energy and polarization with imaging methods. Both real space imaging methods and reciprocal space methods such as holography are discussed and illustrated by examples.

10.2 Overview of Different Types of X-ray Dichroism

The term "dichroism" needs a short explanation. We have learned in Chap. 9 that historically, the term *dichroism* specifically referred to polarization dependent *absorption* of light. On a microscopic level the origin of dichroic behavior of a material originates from the spatial anisotropy of the charge or the spin. In cases where the spins are not aligned and the effect depends on charge, only, one speaks of *charge or "natural" dichroism*.

X-ray "natural" dichroism refers to the absence of spin alignment.

- X-ray natural linear dichroism XNLD is due to an anisotropic charge distribution. The effect is parity even and time even.
- X-ray natural circular dichroism XNCD may be present for anisotropic charge distributions that lack a center of inversion. The effect is parity odd and time even.

If the origin of dichroism is due to preferential spin alignment or magnetic order one speaks of *magnetic dichroism*. We distinguish *directional* spin alignment, as in a ferromagnet or ferrimagnet, from *axial* spin alignment as in a collinear antiferromagnet. The term "directional" is more restrictive since a directional alignment is also axial, but not vice versa. There are two important types of magnetic dichroism.

X-ray "magnetic" dichroism is due to spin alignment and the spin–orbit coupling.

- X-ray magnetic linear dichroism XMLD arises from a charge anisotropy induced by *axial* spin alignment. The effect is parity even and time even.
- X-ray magnetic circular dichroism XMCD arises from *directional* spin alignment. The effect is parity even and time odd.

There are other more complicated types of "magnetic" dichroism where charge and spin effects are both present [88,416]. For example, X-ray *magnetochiral dichroism* arises from axial spin alignment and a chiral charge distribution and the effect is parity odd and time odd [417]. X-ray *nonreciprocal linear dichroism* arises from charge chirality that is induced by an axial spin alignment and the effect is parity odd and time odd [418]. We shall not discuss these cases here. Rather we shall first give a summary of the four kinds of natural and magnetic dichroism highlighted by the boxes above and then specifically treat the three cases of XNLD, XMLD, and XMCD. It turns out that these three types of dichroism are connected and in contrast to XNCD they all arise within the dipole approximation.

The simplest case of dichroism which has been extensively discussed in the book NEXAFS Spectroscopy [189] is X-ray natural linear dichroism, XNLD, due to anisotropic bonding. The most beautiful examples of XNLD are found in covalently bonded systems, such as organic molecules and polymers, where the bonding is directional. Often a simple picture, called the "search light effect", can be used to predict the angle-dependent intensity associated with a transition of a core electron to an empty molecular (valence) orbital. If the \boldsymbol{E} vector points into the direction of maximum density of the empty molecular orbital (one could say "hole" density), the transition is strongest, and it is weakest for \boldsymbol{E} perpendicular to the orbital density. An example is shown in

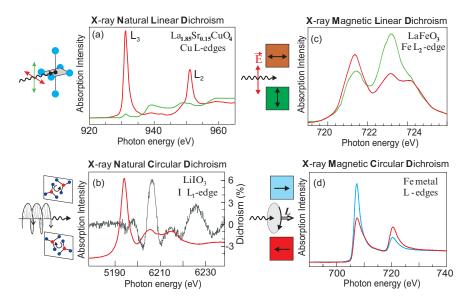


Fig. 10.1. Four important types of dichroism. (a) X-ray natural linear dichroism spectra of La_{1.85}Sr_{0.15}CuO₄ near the Cu L-edge [419]. The resonances are due to transitions to the highest energy unfilled $d_{x^2-y^2}$ orbital. (b) X-ray absorption spectrum (red) of single crystal LiIO₃ and the difference spectrum (gray), the X-ray natural circular dichroism spectrum, obtained from absorption spectra with left and right circularly polarized X-rays, incident along a special crystalline axis [420]. (c) Magnetic linear dichroism spectrum of an epitaxial thin film of antiferromagnetic LaFeO₃ with the E vector aligned parallel and perpendicular to the antiferromagnetic circular dichroism spectrum around the L₃ and L₂ edges of Fe metal. The photon angular momentum was aligned parallel or antiparallel to the magnetization direction of the sample [96]

Fig. 10.1a for the Cu L-edge of $La_{1.85}Sr_{0.15}CuO_4$ [419]. The single crystal sample has a layered structure. The Cu atom shown in black is surrounded by 4 in-plane O atoms and two out-of-plane O atoms. If we define the x, y plane of our coordinate system to lie in the plane of the layers (shown in gray) the in-plane $d_{x^2-y^2}$ orbital is unfilled and when the E lies in the x, y plane a large peak-like transition is observed to this orbital. This resonance is absent when E is oriented perpendicular to the plane, as shown, since there are no empty states in the perpendicular direction. XNLD is used to probe the anisotropy of the valence charge. It is a powerful technique for the determination of the orientation of molecules and functional groups on surfaces and in organic materials [189], the direction and the nature of local bonds in materials [372], and even the orientational order in amorphous materials, that is materials without translational order [388, 421].

X-ray natural circular dichroism, XNCD, may be observed if the bonding around the absorbing atom lacks a center of inversion. The origin of XNCD

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may be visualized by picturing the bonding around the absorbing atom as possessing a handedness in space. When the handed circular light is also pictured in space, as shown in Fig. 5.3, it is then intuitively plausible that the X-ray absorption depends on whether the handedness of the charge and that of the EM wave are the same or opposite. This model also conveys the important fact that the EM wave must contain a k dependence, since only then will it have a "twist" over the atomic volume. This intuitive picture is theoretically reflected by the fact that XNCD vanishes in the dipole approximation.¹ An example of XNCD is shown in Fig. 10.1b for the Iodine L₁-edge X-ray absorption spectrum (red) of single crystal LiIO₃. The XNCD spectrum, defined as the difference of two absorption spectra obtained with left and right circularly polarized X-rays, is shown in gray [420, 422, 423]. It was obtained by aligning the single crystal sample along a special crystalline axis. The effect is seen to be remarkably large of the order of several per cent. Within the context of this book we shall not discuss XNCD any further.

Next we give a brief introduction to X-ray magnetic linear dichroism, XMLD. We have seen above that both *natural* and *magnetic* linear dichroism effects are parity even and time even. They are therefore related and their separation is sometimes tricky. The principal difference is that XMLD only exists in the presence of magnetic alignment and hence it vanishes at temperatures above the Neél or Curie temperature, or for paramagnets in the absence of an external magnetic field. There are two important prerequisites for the existence of XMLD: the existence of atomic magnetic moments and the *spin-orbit interaction*. For example, in ferro- and antiferromagnets, the exchange interaction creates a spin magnetic moment. The spin-orbit interaction creates an orbital magnetic moment which is locked to both the spin moment and the lattice. The result is the creation of a macroscopic "easy" axis along which the spins lie. Ferro- or ferri-magnets are *directional* since there is a net moment direction while collinear antiferromagnets are axial since all spins lie along a particular axis of the crystal but there is no net moment. Both can be studied with XMLD.

$$M = \underbrace{\langle b | \boldsymbol{p} \cdot \boldsymbol{E} | a \rangle}_{\mathcal{A}} + \underbrace{\frac{i}{2} \langle b | (\boldsymbol{r} \times \boldsymbol{p}) \cdot (\boldsymbol{k} \times \boldsymbol{E}) | a \rangle}_{\mathcal{B}} + \underbrace{\frac{i}{2} \langle b | (\boldsymbol{k} \cdot \boldsymbol{r}) (\boldsymbol{p} \cdot \boldsymbol{E}) + (\boldsymbol{k} \cdot \boldsymbol{p}) (\boldsymbol{r} \cdot \boldsymbol{E}) | a \rangle}_{\mathcal{C}}.$$

Term \mathcal{A} is the electric dipole term, \mathcal{B} the electric dipole/magnetic dipole interference term, and \mathcal{C} the electric dipole/electric quadrupole interference term. NCD in the optical range arises from term \mathcal{B} , whereas XNCD is mostly due to term \mathcal{C} . XNCD vanishes for samples without orientational order, and single crystal samples are required. Also, not all samples that lack inversion symmetry exhibit XNCD but only a subgroup, as discussed in more detail by Natoli et al. [422].

¹The dipole approximation neglects the \boldsymbol{k} dependence of the EM wave. It assumes $\boldsymbol{E}e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \boldsymbol{E}(1+i\boldsymbol{k}\cdot\boldsymbol{r}+\cdots) = \boldsymbol{E}$ (see Sect. 9.5.3) and thus neglects the spatial "twist" of the wave over the atomic volume. XNCD arises from keeping the first order term in \boldsymbol{k} in the transition matrix element $M = \langle b | (\boldsymbol{p} \cdot \boldsymbol{E}) (1 + i\boldsymbol{k} \cdot \boldsymbol{r}) | a \rangle$, so that

The existence of a macroscopic magnetic axis leads to a difference in X-ray absorption intensity when the polarization vector is either parallel or perpendicular to the magnetic axis. This can happen in different ways. The most obvious case is when in the presence of magnetic order the lattice lowers its symmetry. For example, a cubic lattice may experience a contraction along the magnetic axis. The charge becomes anisotropic and this causes a nat*ural* linear dichroism effect that is magnetically induced. Another prominent origin of XMLD is the presence of coupled electronic (multiplet) states that are formed under the influence of the exchange and spin–orbit interactions. Such states typically have a nonspherical charge distribution and when transitions between pairs of such states are energetically separated there can be a large polarization dependence of individual transitions. This is the origin of the large XMLD effect in the multiplet-split Fe L₂ resonance in LaFeO₃ shown in Fig. 10.1c. The spectra show the difference in absorption when the E vector is aligned parallel and perpendicular to the antiferromagnetic axis in LaFeO₃ [406]. XMLD is extensively used today for the study of antiferromagnets, in particular, the determination of the orientation of the antiferromagnetic axis in thin films and near surfaces, and the imaging of antiferromagnetic domains.

We conclude the overview of dichroism effects with X-ray magnetic circular dichroism, XMCD. It is used to measure the size and direction of magnetic moments. Both the magnetic moments and the XMCD effect are time odd and parity even. As illustrated in Fig. 10.1d for the Fe L-edge in Fe metal, the XMCD effect is maximum when the X-ray angular momentum is parallel and antiparallel to the magnetic moment of the sample. The effect is seen to be very large at the resonance positions and is opposite at the L_3 and L_2 edges. This directly reflects the opposite sign of the spin component at the two edges, j = l + s at the L_3 edge and j = l - s at the L_2 edge. Like magnetic linear dichroism, XMCD requires the presence of a magnetic alignment, which has to be directional. It is therefore zero for antiferromagnets. It also requires the presence of spin–orbit coupling because the photon angular momentum does not directly couple to the electron spin but only indirectly via the orbital angular momentum. This is because the electronic transition is driven by the electric field which does not act on spin but only on the orbital angular momentum through the charge.

In a simple picture, in the absorption process a handed photon transfers its angular momentum to a core electron. The X-ray energy is tuned so that the created photoelectron is excited into the valence shell. If the valence shell has a preferential angular momentum direction the transition probability will depend on whether the photon and valence shell angular momenta are parallel or antiparallel. The dependence of XMCD on the spin–orbit coupling has the benefit that it allows the separate determination of spin and orbital angular momenta (and therefore moments) from linear combinations of the measured L_3 and L_2 dichroism intensities. This and the ability to determine the size and direction of the moments is a consequence of the famous XMCD sum rules that we shall discuss later in the chapter. XMCD has become an important magnetic tool partly because it allows the study of magnetic properties in combination with submonolayer sensitivity, elemental specificity, and chemical state specificity. When nanoscale magnetic imaging and ultrafast time resolution are added we have a method that is unique for the study of modern magnetic materials.

10.3 Experimental Concepts of X-ray Absorption Spectroscopy

This section gives concepts and experimental details of X-ray absorption spectroscopy. We do not yet discuss *polarization dependent* changes in the spectra, i.e., dichroic effects, but rather concentrate on the basic concepts that determine absorption spectra of magnetic materials spectra. In particular, we outline basic experimental techniques, and by examples of selected X-ray absorption spectra, we discuss important spectral features and aspects of data normalization and analysis. As examples we will predominantly use L-edge spectra of the transition metals since they are best suited to obtain information for the important 3*d* transition metals. We mention that other absorption edges have also been used, like the K-edges of the 3*d* transition metals, first investigated by Schütz in her pioneering XMCD work [95], or the $M_{2,3}$ edges of the 4*d* metals [424, 425] and even the $M_{4,5}$ edges of the actinides [409].

10.3.1 General Concepts

In the last chapter we have seen that the X-ray absorption intensity is attenuated upon transmission through a sample of thickness d according to

$$I = I_0 e^{-\mu_x d} = I_0 e^{-\rho_a \sigma^{abs} d} .$$
(10.1)

Here μ_x is the linear X-ray absorption coefficient with a dimension of [length⁻¹], and σ^{abs} is the X-ray absorption cross-section of dimension [length²/atom]. The two quantities are related according to (9.29) by the atomic number density $\rho_a = N_A \rho_m / A$ with dimension [atoms/length³], where $N_A = 6.02214 \times 10^{23}$ [atoms/mol] is Avogadro's number. We have listed in Table 10.1 the relevant parameters for Fe, Co, and Ni.

Table 10.1. Bulk Properties of 3*d* metals Fe, Co, Ni. Listed are the mass density $\rho_{\rm m}$ at room temperature, the atomic mass number *A*, the atomic number density $\rho_{\rm a}$ and the atomic volume $V_{\rm a}$

Element	$ ho_{ m m}$	A	$ ho_{ m a}$	$V_{\rm a}$
	$[\mathrm{kg/m}^3]$	[g/mol]	$[\mathrm{atoms/nm}^3]$	$[\text{Å}^3]$
Fe (bcc)	7,874	55.845	84.9	11.8
Co (hcp)	8,900	58.933	90.9	11.0
Ni (fcc)	8,908	58.693	91.4	10.9

Historically, X-ray absorption has been measured in a transmission geometry as shown in Fig. 10.2a and the transmitted intensity drops when the X-ray absorption channel is opened up at a threshold (absorption edge), corresponding to loss of photons through core electron excitation to empty states. On the right side of Fig. 10.2a we show a typical measured transmission intensity I_t , normalized to the incident number of photons I_0 . The shown spectrum corresponds to a d = 10 nm Co film, calculated by means of (10.1) from the

X-ray absorption spectroscopy techniques

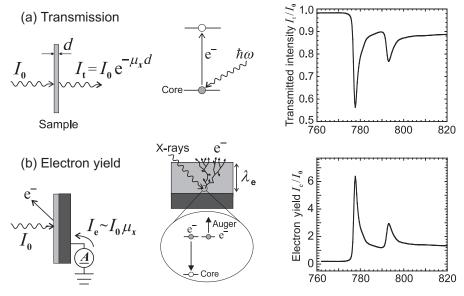


Fig. 10.2. Two common methods for the measurement of X-ray absorption. In the top row (a) we show a typical transmission geometry used for X-ray absorption measurements, the core electron excitation process during an absorption event, and a schematic of the measured transmitted intensity. We have used real data for Co metal, and the plotted transmission intensity I_t/I_0 corresponds to a Co thickness of $10 \,\mathrm{nm}$. In the bottom row (b) we illustrate the method and principles of recording absorption spectra by electron yield (or total electron yield) detection. The absorbed photons create core holes that are filled by Auger electron emission. The primary Auger electrons cause a low energy cascade through inelastic scattering processes on the way to the surface. The total number of emitted electrons is directly proportional to the probability of the Auger electron creation, that is the absorption probability. The emitted electron yield is simply measured with a picoammeter that measures the electrons flowing back to the sample from ground. The electron yield spectrum I_e/I_0 shown on the right is that of Co metal. The numbers on the ordinate actually correspond to the cross-section in Mb since we have simply converted (renormalized) the measured electron yield ratio I_e/I_0 into a cross-section as discussed in conjunction with Fig. 10.9

experimentally measured averaged dichroism spectra shown in Fig. 10.12. It is common to present X-ray absorption spectra "downside-up" by plotting the quantity $\ln(I_0/I)$ which is proportional to μ_x or σ^{abs} and we shall use such plots from now on.

There are two other methods for the measurement of X-ray absorption by solids, X-ray fluorescence and electron yield (EY) detection, as discussed in detail by Stöhr [189]. Of the two methods, EY detection, also called *total elec*tron yield detection, is particularly often used in the soft X-ray region where it offers larger signals due to the dominance of the Auger over the fluorescence decay channel after X-ray excitation [189]. It is also experimentally simple and requires just a picoammeter for the measurement of the photocurrent. It is for these reasons and the important fact that it underlies photoemission electron microscopy (PEEM), discussed later, that we shall discuss EY detection here. The experimental method and the underlying electronic processes are shown in Fig. 10.2b and are explained in the caption. EY detection directly gives a spectrum that is proportional to the X-ray absorption coefficient or the absorption cross-section because the yield is directly proportional to the probability of X-ray absorption. This is seen by writing down the number of absorbed photons according to (10.1) under the assumption of a thin sample $d \ll 1/\mu_x$. We get

$$I_0 - I_t = I_0 (1 - e^{-\mu_x d}) \simeq I_0 d \mu_x = I_0 \rho_a d \sigma^{abs}.$$
 (10.2)

Fortunately, for EY measurements the approximation (10.2) is not only valid for thin samples d but it turns out that it is valid in general since one always measures in the limit of a "thin sample." This is due to the fact that the EY signal originates only from a depth $\lambda_e \sim 2$ nm that is much shorter than the X-ray penetration length or X-ray absorption length λ_x into the sample. This topic has been discussed extensively elsewhere [189, 426] and we shall here only review the important facts.

The X-ray absorption length $\lambda_x = 1/\mu_x$ is the distance in a material over which the intensity has dropped to 1/e of its original value. This length depends strongly on the photon energy and as the absorption coefficient μ_x increases close to an edge, λ_x becomes shorter. For convenience we have listed in Table 10.2 values for σ^{abs} and μ_x for Fe, Co, and Ni at three characteristic

Table 10.2. X-ray absorption cross-sections σ^{abs} [Mb] and linear absorption coefficients $\mu_x[nm^{-1}]$ for Fe, Co, Ni for three energies, 10 eV below the L_3 peak, at the L_3 peak and 40 eV above the L_3 peak. For the conversion between σ^{abs} and μ_x it is convenient to remember that $1 \text{ Mb} = 10^{-4} \text{ nm}^2$

	$10 \mathrm{eV}$ below L_3		at L_3 peak		$40 \mathrm{eV}$ above L_3	
Element	$\sigma^{\rm abs}~[{\rm Mb}]$	$\mu_x [\mathrm{nm}^{-1}]$	$\sigma^{\rm abs} \; [{\rm Mb}]$	$\mu_x [\mathrm{nm}^{-1}]$	$\sigma^{\rm abs}~[{\rm Mb}]$	$\mu_x [\mathrm{nm}^{-1}]$
Fe (bcc)	0.21	1.8×10^{-3}	7.1	6.0×10^{-2}	1.45	1.2×10^{-2}
Co (hcp)	0.195	1.8×10^{-3}	6.4	5.8×10^{-2}	1.34	1.2×10^{-2}
Ni (fcc)	0.18	1.6×10^{-3}	4.6	4.2×10^{-2}	1.28	1.2×10^{-2}

energies, 10 eV below the L₃ peak, at the L₃ peak, and 40 eV above the L₃ peak. We see that the X-ray absorption length $1/\mu_x$ is about 500 nm before the edge, 20 nm at the L₃ peak and 80 nm above the L₃ peak.

We now take a look at the *electron sampling depth* λ_e . As illustrated in Figs. 10.2b and 10.3, the absorption of the incident X-rays leads to the production of Auger electrons that trigger an electron cascade. Only those cascade electrons that have enough energy to overcome the work function of the sample contribute to the measured electron yield. If one thinks of the sample as consisting of atomic layers parallel to the surface, as illustrated on the left side of Fig. 10.3, one can show that the EY contribution from the individual layers falls off exponentially with their perpendicular distance from the surface plane [189].² The depth below the surface of the layer whose contribution is 1/e of that of the first layer is called the *electron sampling depth* $\lambda_{\rm e}$, and experiments show it to be about 2 nm for Fe, Co, and Ni [426]. One may also refer to $\lambda_{\rm e}$ as an effective secondary electron mean free path (see footnote 2). The short value of λ_e causes a high sensitivity to the near surface region or layers, as illustrated on the right side of Fig. 10.3 for a wedge sample. It was grown on a Si substrate (not shown) and consists of a 5 nm-thick Ni film, covered by an Fe wedge of thickness 0-3.5 nm, a constant thickness (1 nm) Cu film and a 1.5 nm Pt cap layer. As the X-ray beam is moved across the wedge toward increasing Fe thickness the EY spectra clearly reveal the increase in the Fe signal and the decrease of the Ni substrate signal, as expected for the short EY sampling depth.

For the L-edge absorption region of Fe, Co, and Ni, the 1/e electron yield sampling depth λ_e from which 63% of the signal originates is about 2 nm. In contrast, the 1/e X-ray absorption length $\lambda_x = 1/\mu_x$ is strongly energy dependent and is about 500 nm before the edge, 20 nm at the L₃-edge, and 80 nm above the edge.

Despite the fact that the X-ray absorption length λ_x is at least 10 times larger than the electron yield sampling depth λ_e one still needs to be careful in the quantitative analysis of EY absorption spectra since the peak intensities are slightly reduced relative to the true X-ray absorption cross-section [426]. This is referred to as the *saturation effect* in the literature. Its origin is easy to understand. Ideally the different layers in the sample contribute to the EY with an exponentially decaying intensity as shown on the left side of Fig. 10.3.

²This can be derived in analogy to the concepts used in photoemission, where the inelastic scattering or attenuation of the elastic electrons along a direction x is described by an exponential decay of the form $I = I_0 \exp(-i\ell_e x)$, where ℓ_e is the *electron mean free path*. This leads to an exponential decay of the elastic photoemission signal from layers below the surface, similar to that shown in Fig. 10.3. In total electron yield measurements one defines an *effective mean free path* λ_e that averages over the various scattering channels [189].

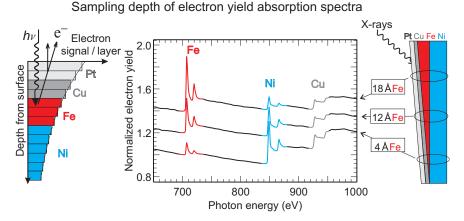


Fig. 10.3. Left: Illustration of layer-by-layer contributions to the electron yield signal from a sample consisting of different layers. We have assumed that the X-ray absorption length is much larger than the electron sampling depth, $\lambda_x \gg \lambda_e$. For simplicity we have also assumed that both λ_x and λ_e are the same for the different layers. Middle and right: X-ray absorption spectra of a wedge sample grown on a Si substrate with the layered structure Ni(5 nm)/Fe(0–3.5 nm)/Cu(1 nm)/Pt(1.5 nm). The spectra reveal the preferential sensitivity to the near-surface layers. As the Fe wedge gets thicker its signal increases relative to that of the underlying Ni. The Cu layer of constant thickness contributes an approximately constant signal, as revealed by the jump at its absorption edge. The Pt cap layer has no absorption edge in the shown spectral region and contributes only a constant background signal. The curves have been vertically shifted relative to each other to facilitate their comparison

If the X-ray absorption length λ_x becomes shorter at the resonance position, say $\lambda_x \approx 10\lambda_{\rm e}$, of the order of 10% of the photons with that energy are absorbed within the electron sampling depth. This means that the X-ray intensity that reaches the deeper layers in the sample is already reduced by several percent at the resonance positions. Therefore the contributions from the deeper layers at the resonance energy is less than the ideal contribution shown in Fig. 10.3, and the relative total EY intensity at the resonance position is reduced relative to that outside the resonance. EY absorption spectra therefore need to be corrected for saturation effects as discussed in the literature [406, 426–431]. We shall come back to this point below (see Fig. 10.9).

10.3.2 Experimental Arrangements

In the soft X-ray region, X-ray absorption experiments on magnetic materials are typically carried out as shown in Fig. 10.4.

A suitable undulator produces X-rays of selectable polarization, and a monochromator selects the photon energy of interest with a typical energy resolution of 0.2 eV. The monochromatic X-rays are then focused to a spot

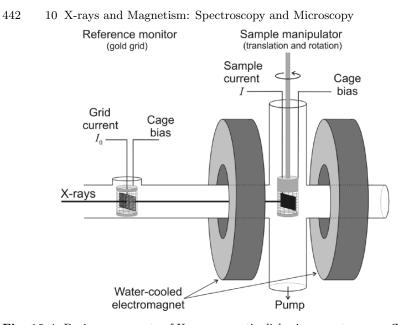


Fig. 10.4. Basic components of X-ray magnetic dichroism spectroscopy. The polarized, monochromatic X-rays are incident on an intensity reference monitor consisting of a high transmission ($\sim 80\%$) metal (e.g., gold) grid that is enclosed by a cage that is positively biased relative to the sample. The electron photocurrent from the grid, I_0 , measured with a picoammeter, serves as a reference of the X-ray beam intensity. For electron yield measurements the sample is also enclosed by a biased nonmagnetic cage which is used to pull the photoelectrons away from the sample. The sample current I is directly measured with a picoammeter. The sample is positioned in the homogeneous field of an electromagnet which is typically parallel to the X-ray propagation direction. The sample can be translated in the beam and rotated about the vertical axis

on the sample that is of the order of a few hundred micrometers in size. On their way to the sample the X-rays pass through a beam intensity monitor which consists of a metal grid surrounded by a wire cage, both made from nonmagnetic materials and coated with a material, often chosen to be Au, that has no prominent absorption edges in the spectral range of interest. The grid inside the cage is chosen to have a large number of fine metal wires within the beam diameter to minimize intensity changes with beam drifts, and typically absorbs about 20% of the incident X-rays. The cage consists of a coarser grid and is positively biased (\sim +20V) to pull off the photoelectrons from the grid inside. The electron current (of order nA) flowing back to the grid from ground is measured with a picoammeter and it serves as the beam intensity signal I_0 .

The sample is positioned in the center of an electromagnet or superconducting magnet, with the field axis typically aligned along the horizontal beam direction. The sample can be rotated in the beam about a vertical axis. If the sample is in the form of a thin film the transmission is measured with a suitable detector like a photodiode that is positioned behind the sample, outside the magnet. It is most common, however, to simply measure the photocurrent of the sample with a picoammeter. Again a biased metal cage around the sample is used to pull of the photoelectrons from the sample. The biased cage has another benefit in that it minimizes the effect of the magnetic field on the measured sample current. When circular dichroism spectra are recorded with fixed photon spin by switching the field direction in the electromagnet, it is best to switch the field at every energy point in the dichroism spectrum. This eliminates effects due to beam instability. The switching typically takes of the order of 1 s and one only counts when the new field has been established. By adjusting the bias voltage of the grid, one can make the signals for the two field directions nearly the same, i.e., minimize the effect of the field on the signal.

A more versatile experimental configuration uses a magnet with variable field directions, as the octopole magnet implemented by Arenholz and Prestemon [432], shown in Fig. 10.5 and described in the caption. The magnetic field with a strength of 0.8 T can be oriented into a random direction, but is

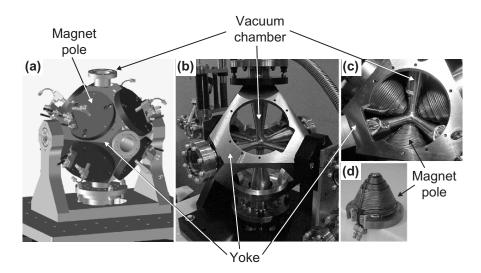


Fig. 10.5. Octopole magnet for the generation of an arbitrary field direction [432]. (a) shows a design drawing with an identification of the main components, the Tialloy vacuum chamber, the steel box yoke, and the magnetic poles with water cooling circuits. The photographs (b)–(d) show the manufactured and partly assembled components in more detail. The vacuum chamber is a six cross with vacuum flanges and a spherical center chamber of about 5 cm diameter. The shared steel yoke holds all eight magnetic poles and provides flux closure. The eight pole design offers better field uniformity in the center (below 1%) and larger fields than a six pole design, which in principle would be sufficient. The pole pieces are surrounded by the magnet coils and on the outside by three parallel water cooling circuits to avoid overheating

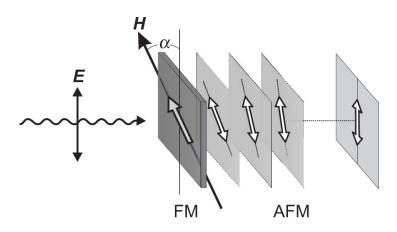


Fig. 10.6. Winding up of an antiferromagnetic exchange spring. An external magnetic field is used to rotate a ferromagnetic (FM) layer that is exchange coupled to an antiferromagnet (AFM). If the antiferromagnet is soft, its antiferromagnetic axis near the FM–AFM interface follows the rotation of the ferromagnetic magnetization. Deep in the bulk the axis remains unchanged. Thus an antiferromagnetic wall is formed that consists of a spring-like twist of the AFM axis by an angle α . This has been observed for Co/NiO by X-ray magnetic linear dichroism spectroscopy [405] using the octopole magnet in Fig. 10.5. The incident X-ray polarization \boldsymbol{E} was fixed and the magnetic field direction \boldsymbol{H} could be rotated relative to \boldsymbol{E} . By use of EY detection only the rotated fraction of the antiferromagnetic domain wall near the interface is observed

typically aligned either along the beam direction or along the horizontal or vertical directions perpendicular to the beam.

An octopole magnet is ideally suited for X-ray magnetic linear dichroism measurements. An example of such an experiment is schematically shown in Fig. 10.6. Without discussing the details of the experiment which can be found elsewhere [405], we only show the concept and the results. The experiment was conducted to prove the conjecture of the Mauri model of exchange bias [433] that an antiferromagnetic wall is formed at the ferromagnet-antiferromagnet interface when the ferromagnet is rotated in an external magnetic field. By fixing the direction E of the incident linearly polarized light, the experiment measured the orientation of both, the ferromagnetic magnetization and the antiferromagnetic axis near the interface, as a function of the orientation of the magnetic field vector H relative to the E-vector. The magnetic linear dichroism effect in NiO revealed that the AFM axis indeed followed the rotation of the ferromagnetic Co magnetization, and therefore an exchange spring is wound up with one end coupled to the FM and the other end anchored deep in the bulk. The use of EY detection assured that only the rotating spin region in the AFM near the FM–AFM was observed.

10.3.3 Quantitative Analysis of Experimental Absorption Spectra

The quantities $\ln(I_0/I_t)$ obtained from a transmission measurement and I_e/I_0 from an EY experiment are called X-ray absorption spectra. Their intensity is directly proportional to the X-ray absorption coefficient or cross-section. In most cases, the sample thickness or the factors that determine the electron yield are not accurately known so that the spectral intensity is in arbitrary units. For the quantitative analysis of the spectra it is usually necessary to convert them into meaningful units. In doing so one uses the fact that, according to (10.1), for a given atom the measured intensity is proportional to $\mu_x d$ and therefore increases linearly with the number of atoms in the beam. Therefore also the edge jump of the absorption spectrum, defined as the difference of the average intensities well above and below the edge, depends linearly on the number of absorbing atoms.

By definition, the edge jump assumes that the absorption intensity changes by a sudden jump from a smooth curve below the edge to a smooth curve above the edge, as observed for the X-ray absorption spectra of atoms [189]. As an example we show in Fig. 10.7 the *atomic cross-sections* around the L-edges of the 3d transition metals taken from the Henke–Gullikson tables [362, 363].

We see that each atom has its characteristic edge jump, whose value is separately shown as circles, connected by a gray line. The cross-sections are simply obtained by extrapolating the ones measured at higher energy, outside the resonance region, into the near edge region and therefore do not account for the "white-line" resonance structure due to bonding. It is therefore common in the analysis of X-ray absorption spectra to proceed as follows.

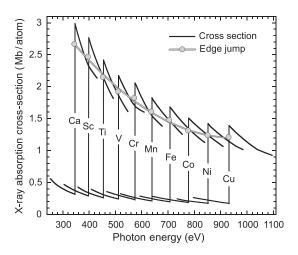


Fig. 10.7. Atomic cross-sections and L-edge jumps (L_3 plus L_2) for the 3*d* transition metals taken from the Henke–Gullikson tables [362,363]. Note that the *atomic* cross-sections simply extrapolate the values determined well above the edge into the near edge region and therefore all resonance effects due to bonding are absent

In the analysis of X-ray absorption spectra one distinguishes the intensities of resonance structures or "white lines" at the absorption thresholds which is sample and bonding-specific from the *atomic-like nonresonant background*. The smooth atomic-like background is independent of the atomic environment and is available as tabulated atomic X-ray absorption cross-sections.

The atomic edge jump picture still holds for bonded atoms if the core electrons are excited to continuum states that lie significantly higher in energy than any bonding (antibonding) orbitals. When the absorption spectrum of a given atom is measured in different environments like the gas phase, in a liquid or in different solids, the fine structure of the absorption edge will greatly change due to the atomic environment, yet for the same number of atoms in the X-ray beam the intensity outside the resonance region will be smooth and its value will be independent of bonding. This is illustrated schematically in Fig. 10.8.

Since the edge jump is proportional to the number of absorbing atoms we can renormalize the measured spectra for a given atom in different samples to a per atom basis by simply scaling and fitting them below the edge and well above the edge to the atomic cross section. We can make the following general statement that underlies different analysis methods of X-ray absorption spectra.

By renormalizing the measured absorption spectra of a given atom in different samples to the same *edge jump* one obtains spectra that correspond to the same number of absorbing atoms.

Absolute X-Ray Absorption Cross Sections

In practice, one rarely determines the *absolute* x-ray absorption cross section of a sample. If needed, one simply fits experimental spectra to the Henke– Gullikson cross-sections [362, 363] outside the resonance region where the cross section is smooth and atomic like. Often, experimental spectra have some background slope which is adjusted to match the slope of the tabulated atomic cross-section. The method is illustrated in Fig. 10.9a for the absorption spectrum of LaFeO₃ [406], which exhibits a large resonance intensity superimposed on a small edge jump. Once the region before and above the edge are properly fitted the resonance intensities are automatically obtained in the proper cross-section units.

For electron yield spectra, which may contain saturation effects in the resonance region, one exploits the fact that saturation effects are generally negligible before and above the edge, because in these regions the X-ray absorption length is much larger than the electron sampling depth (see Table 10.2). The

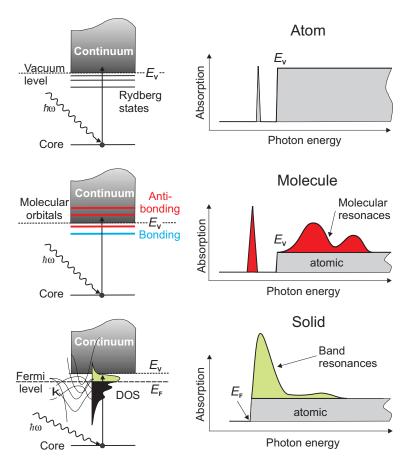


Fig. 10.8. Characteristic X-ray absorption spectra of an atom, the same atom in a molecule and the same atom in a solid, assumed to be a metal. For an atom the lowest energy resonances correspond to transitions to Rydberg states [189], which merge into a step-like structure at the core electron ionization potential (IP), corresponding to transitions from the core shell of interest to states just above the vacuum level $(E_{\rm V})$. For a molecule transitions to unfilled orbitals result in pronounced resonances as shown. For atoms embedded in a metal the lowest energy transition correspond to states just above the Fermi level $(E_{\rm F})$. The X-ray absorption intensity follows the Brillouin zone (k) integrated density of states (DOS). In all cases resonant transitions to specific electronic states are superimposed on smooth atomic-like cross-sections given in the Henke–Gullikson tables [362,363]. In the analysis one assumes that the *atomic* cross-sections well above the "edge" can be simply extrapolated to lower energies, with a step like onset that is positioned either at $E_{\rm V}$ or $E_{\rm F}$ [189] or, for solids, at the position of the first resonance [96]

converted EY spectra do, however, still contain saturation effects in the resonance region. They can be eliminated if the electron sampling depth λ_e is known [406,426–431]. This is illustrated in Fig. 10.9 for LaFeO₃, where $\lambda_e = 20$ Å. The saturation effects are seen to be quite large in this case due to the large resonant cross-section (short λ_x), and the fact that the *effective* X-ray penetration depth perpendicular to the surface is further shortened to $\lambda_x \sin 20^\circ$, since the spectrum was recorded at a 20° grazing X-ray incidence angle from the surface.

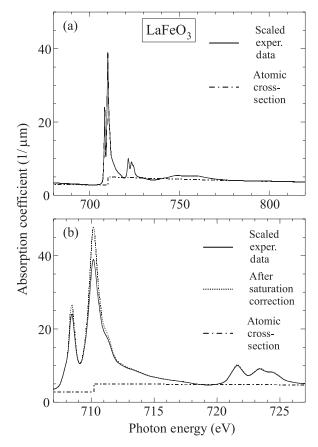


Fig. 10.9. (a) Illustration of converting the measured electron yield spectrum of LaFeO₃ (*solid line*) into an absolute X-ray absorption coefficient. The spectrum is fitted outside of the resonance region to the calculated absolute atomic absorption coefficient (*dashed-dotted line*) taken from the Henke–Gullikson tabulation [362,363]. The experimental spectrum was measured at a grazing X-ray incidence angle of 20° from the surface plane. (b) Enlarged L_{2,3} region of (a). Here we also show the saturation corrected electron yield spectrum as a *dotted line*. Spectra taken from Lüning et al. [406]

Relative Absorption Cross Sections: Edge-Jump Normalization

In many cases one is simply interested in the relative intensities of absorption resonances or dichroic differences. Then the determination of absolute x-ray absorption cross sections can be avoided, and one uses a simple method which goes as follows. One measures two samples, one with known and one with unknown properties, in exactly the same way. If the two spectra have a different average slope with photon energy one approximately matches the slopes. Then a background is subtracted so that the region before the absorption edge has zero intensity. One then simply multiplies the spectra by constants to make the *edge jump* the same in both spectra. They now correspond to the same number of atoms in the beam, without knowing their number. All we know is that the chosen number for the edge jump corresponds to the same number in both spectra. One can now compare the relative intensities of the resonance structures in the spectra.

For example, we shall see below that the L-edge resonance structures in the magnetic 3d transition metals show a large magnetic dichroism effect that is proportional to the magnetic moment per atom. If we wanted to know the size of the magnetic moment in a sample of interest, say one that contains Co, we would take a dichroism spectrum of this sample and compare it to that of Co metal, where we know the magnetic moment per atom. We would normalize both experimental spectra in an identical fashion to the same edge jump, and then compare the size of the resonant dichroism effects in the two samples. This would allow us to determine the unknown magnetic moment per atom by comparison of the two dichroism effects.

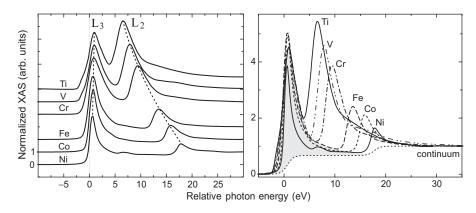


Fig. 10.10. Polarization averaged X-ray absorption spectra for Ti, V, Cr, Fe, Co, and Ni metal [434]. The spectra are normalized to the same unit edge jump for easier comparison. Spectra on the left are vertically offset

10.3.4 Some Important Experimental Absorption Spectra

Fig. 10.10 shows the L-edge X-ray absorption spectra of some important 3d transition metals [434]. The spectra are normalized to the same unit edge jump

for easy comparison of the separation between the L₃ and L₂ resonances. While for the "heavy" 3d metals Fe, Co, and Ni the spin–orbit splitting of the 2p core electrons is significant larger than the width of the associated white line resonances, for the light 3d metals the splitting decreases and the width increases. As illustrated in Fig. 9.26, the comparable size of the spin–orbit coupling and the intraatomic correlation energy will then lead to a mixing of absorption channels leading to the observed resonances. This leads to complications in the determination of spin magnetic moments [435, 436] which is based on the separate analysis of the two $3d \rightarrow 2p_{3/2}$ and $3d \rightarrow 2p_{1/2}$ excitation channels, as illustrated in Fig. 9.16.

Because of the importance of the 3d transitions metals and their oxides we show in Fig. 10.11 the properly normalized X-ray absorption spectra of the magnetic 3d transition metals and their oxides. We have plotted the X-ray absorption coefficient in units of μ m⁻¹ as a function of energy. These spectra form the basis for much of the dichroism work discussed in the rest of the book. Comparison of the spectra in Fig. 10.11 shows the rich resonance fine structure

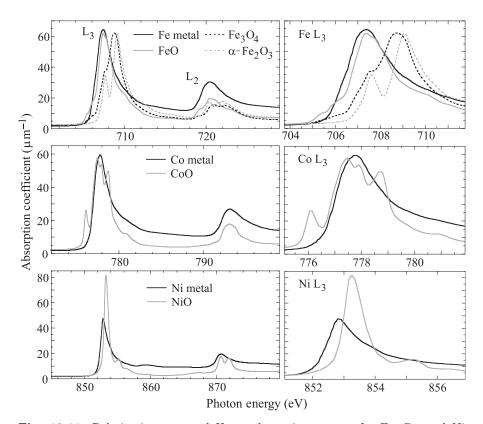


Fig. 10.11. Polarization averaged X-ray absorption spectra for Fe, Co, and Ni metal and their oxides [431]. The spectra are plotted in absolute intensity units of the X-ray absorption coefficient. The rich fine structure of the oxide spectra is due to multiplet effects

in the near edge region. This *chemical sensitivity* allows the identification of different bonding environments for a given atom. Besides the *atomic specificity* of X-ray absorption indicated by the greatly different L-edge positions of Fe, Co, and Ni, the chemical specificity and the later discussed *magnetic specificity* constitute three important cornerstones of the X-ray absorption technique.

Magnetic dichroism spectroscopy offers:

- *Atomic specificity* through the energy separation of characteristic X-ray absorption edges.
- *Chemical sensitivity* through the resonant fine structure at a given atomic absorption edge.
- *Magnetic specificity* through the polarization dependence of the nearedge fine structure.

The rich fine structure in the oxide spectra is due to so-called multiplet splitting. As discussed in more detail in Sect. 9.7.8, the detailed splitting depends on three main quantities, the ligand field symmetry, the valency of the atom, and spin configuration of the electronic ground state.

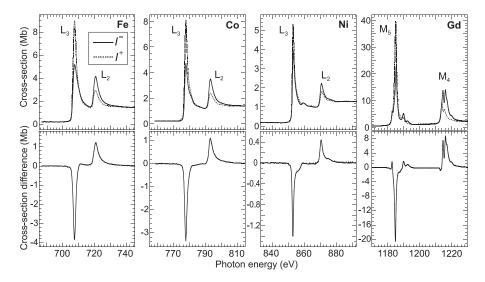


Fig. 10.12. XMCD spectra for the elemental ferromagnetic metals, corrected to correspond to 100% circularly polarized X-rays. The data for Fe, Co, and Ni are from Chen et al. [96, 375], those for Gd are from Prieto et al. [356]. The difference spectra shown underneath correspond to the convention $I^- - I^+$ of (9.95)

10.3.5 XMCD Spectra of Magnetic Atoms: From Thin Films to Isolated Atoms

Data for the four elemental ferromagnets, Fe, Co, Ni [96, 375] and Gd [356], are shown in Fig. 10.12. In all cases, the shown data correspond to maximum

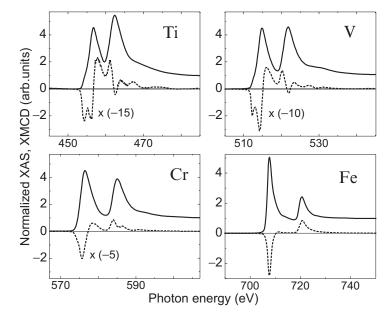


Fig. 10.13. Angle-averaged L-edge X-ray absorption spectra (*solid lines*) for thin metal layers of Ti, V, Cr deposited on Fe and the corresponding dichroism spectra (*dashed*) [434]. The data were corrected for incomplete polarization and saturation effects. The Ti, V, and Cr layers are magnetic through proximity effects, i.e., induced magnetism. Their coupling to Fe is antiparallel as revealed by the sign of the original dichroism spectra. In our plot the dashed XMCD spectra for Ti, V, and Cr have been inverted to avoid overlap of the XAS and XMCD traces. All plotted intensities correspond to a unit edge jump normalization in the original spectra

dichroism effect (100% polarization and alignment of the photon spins and sample magnetization), and we have also plotted the data for the same relative orientations of photon spins and sample magnetization. The more complicated spectrum for Gd is due to multiplet splitting, the origin of which was discussed in Sect. 9.7.8.

The sensitivity of XMCD to small magnetic moments is illustrated in Fig. 10.13. Here we have plotted the absorption and XMCD spectra of Fe and compared it to absorption and dichroism spectra for thin films of Ti, V, and Cr deposited on an Fe substrate. The small dichroism in the Ti, V, and Cr spectra, indicated by the listed multiplicative factors, is due to induced magnetic moments caused by the adjacent Fe layer. Note that we have plotted inverted dichroism (difference) spectra (dashed lines) for the cases of Ti, V, and Cr to avoid overlap of the solid and dashed curves. Since in the original Ti, V, and Cr data the dichroism effects (the dashed spectra) were upside down from those shown in Fig. 10.13, comparison to the spectrum of the Fe standard shows that in all cases the magnetization in the deposited thin films is opposite to that in the Fe substrate.

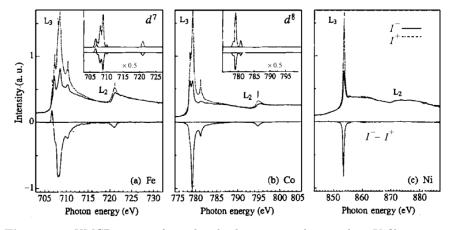


Fig. 10.14. XMCD spectra for isolated 3*d* impurities deposited on K films, corresponding to coverages of 0.015 monolayer for Fe, 0.015 monolayer for Co, and 0.004 monolayer for Ni [437]. The spectra were recorded at 10 K in fields up to ± 7 T. The insets show the spectra calculated for the d^7 and d^8 atomic configurations [438] with the energies renormalized to match the experimental ones

The metal spectra are seen to exhibit rather broad resonances. Only the dichroic difference spectra of the lighter atoms Cr, V, and Ti show significant fine-structure which is associated with multiplet effects. Such effects become pronounced for isolated Fe, Co, and Ni atoms deposited on K films as shown in Fig. 10.14 [437].

The spectra were recorded at 10 K, and fields up to ± 7 T were used to align the atomic moments. The presence of multiplet structure clearly shows the localized character of the 3*d* electrons in the atoms. The multiplet structure serves as a sensitive fingerprint of the electronic ground state configuration which can be determined by comparison of the experimental spectra to those calculated by atomic multiplet theory [438]. The calculated spectra, shown as insets, correspond to $3d^n \rightarrow 2p^53d^{n+1}$ transitions assuming zero ligand field. The comparison of experiment and theory readily allowed the determination of the respective ground states d^7 , ${}^4F_{9/2}$ for Fe, d^8 , 3F_4 for Co and d^9 , ${}^2D_{5/2}$ for Ni (see Table 7.1). These differ from the approximate configurations d^6 for Fe, d^7 for Co and d^8 for Ni in the metals (see Sects. 7.3 and 12.2.2). In fact, prior to the XMCD measurements there had been considerable debate as to the electronic ground state configuration.

The measured XMCD effects are larger than in the bulk metals and show very different ratios of the L₃ and L₂ dichroism intensities and opposite signs. In particular, the L₂ dichroism for Ni is zero. The latter is understood from the ground state configuration d^9 , ${}^2D_{5/2}$, which does not allow L₂-edge transitions, which in a configuration picture correspond to $J = 5/2 \rightarrow J = 1/2$ and thus violate the dipole selection rule.

10.3.6 Sum Rule Analysis of XMCD Spectra: Enhanced Orbital Moments in Small Clusters

In Sect. 10.3.5 we have discussed the XMCD spectra of the ferromagnetic transition metals Fe, Co, and Ni in comparison to those of the isolated atoms, aligned at low temperature in a strong magnetic field. Here we want to take a look at what happens in the transition region between isolated atoms and bulk metals. We shall see that the magnetic properties of small transition metal clusters are quite fascinating, indeed. Because the XMCD studies of interest required a quantitative determination of magnetic moments by application of the sum rules discussed in Sects. 9.6.5 and 9.7.9, we shall use this opportunity to also comment on practical aspects of the sum rule analysis in XMCD.

Today, quantitative analysis of XMCD spectra is often carried out by means of the method suggested by Chen et al. [96]. This method determines the ratios of the spin and orbital moments divided by the number of valence holes. Hence, in order to determine the magnetic moments, the number of valence holes needs to be known. In practice, this is almost never the case for samples of interest. It is for this reason that we discussed in Sect. 9.6.5 the combined use of three sum rules, which all depend on the knowledge of the constant C, which in turn is determined by the radial transition matrix element as expressed by (9.91). The results shown in Fig. 9.17 demonstrate, that for elements with similar atomic number Z, like Fe, Co, and Ni, C is roughly constant. This fact has been utilized, for example, in the determination of the magnetic moment of Cu atoms in Co/Cu and Fe/Cu multilayers [315, 439], where in the analysis of the Cu XMCD spectra the average constant C for Fe, Co, and Ni was used.

The most robust and accurate method of determining magnetic moments is therefore typically the use of a reference sample with known moments, like the elemental ferromagnetic metals, and transfer of the constant C to the analysis of the sample of interest. This method has been successfully used to determine the orbital magnetic moments in small Co clusters and low dimensional structures [440, 441], with the results calibrated by comparison to bulk Co metal.

As shown in Fig. 3.9 small metal clusters in molecular beams show the expected increase in the total magnetic moment toward atomic values. One particularly interesting question is what role the orbital magnetic moment plays in the enhancement of the total moment. In fact, based on our discussion on the quenching effects of the ligand fields in Sect. 7.9 one might expect substantial enhancement of the orbital moment in clusters due to reduced coordination of the surface atoms. This is indeed found [440–442].

As an example we show in Fig. 10.15 the XMCD results for Co atoms on a Pt(997) surface in the form of monatomic chains, a monolayer and a thick Co film. For atoms in low-symmetry environments, the application of the spin sum rule given by (9.133) is complicated by the presence of the anisotropic spin density term $m_{\rm D}^{\alpha}$ [410, 411]. In contrast, the orbital moment can be directly

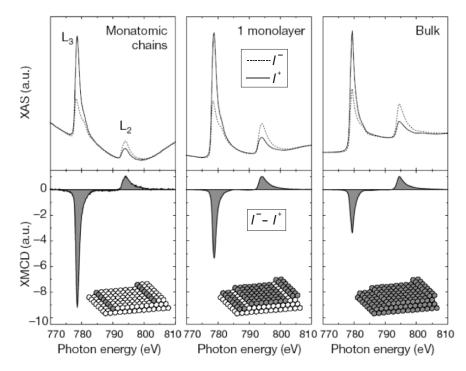


Fig. 10.15. Co L-edge X-ray absorption and dichroism spectra for, from left to right: monatomic chains, a monolayer and a thick Co film, all grown on Pt(997) [440]. Spectra are shown for parallel (I^+) and antiparallel (I^-) directions of X-ray helicity and field-induced magnetization. The dichroism signal $(I^- - I^+)$ is obtained by subtraction of the absorption spectra in each panel and normalization to the intensity of the L₂-edge dichroism peak. Spectra were recorded in the electron-yield mode at T = 10K and B = 7T. Because of the low Co coverage, the edge structures of the monatomic wires are superimposed to a strong background. Changes in the L₃ XMCD intensity indicate that the orbital moment is substantially increased in going from bulk Co to a 2D Co monolayer and to the 1D chains

determined along the applied field direction. The spectra shown in Fig. 10.15 were recorded in the electron-yield mode at T = 10K and B = 7T. According to the orbital moment sum rule (9.134), the orbital magnetic moment is zero if the L₃ and L₂ dichroism intensities A and B have the same size but opposite signs. By normalizing the dichroism spectra to the L₂-edge intensity (peak B in Fig. 9.16), one can therefore conveniently see changes in the orbital moment, as illustrated at the bottom of Fig. 10.15.

We have summarized in Table 10.3 results for various types of Co structures on Pt, taken from work by Gambardella and collaborators [440, 441].

These results clearly show the strong dependence of the orbital magnetic moment on coordination. As expected, the orbital moment increases strongly with decreasing size or dimensionality of the Co structures. For a Co adatom

Table 10.3. Orbital magnetic moments $\langle L_z \rangle$ for various Co/Pt systems, measured by XMCD along the easy axis and values for the magnetocrystalline anisotropy constant K_1 determined from directional magnetization loops. The results were taken from work by Gambardella and collaborators [440,441]

System	$\langle L_z \rangle \; [\mu_{\rm B}]$	$K_1 \; [\mathrm{meV/atom}]$
Co metal (hcp)	0.14	0.053
Co/Pt(997) ML	0.31	0.14 ± 0.01
Co/Pt(111) ML	0.29	
Co/Pt(997) chain	0.68 ± 0.05	2.0 ± 0.2
Co/Pt(111) adatom	1.1 ± 0.1	9.3 ± 1.6

on Pt it has a value of more than 1 $\mu_{\rm B}$ and becomes comparable to the spin moment $(1.7\mu_{\rm B})$ in bulk Co metal. This indicates that the enhancement for the total moment in Fe, Co, and Ni clusters with decreasing cluster size, seen by the Stern–Gerlach experiments on cluster beams [127] shown in Fig. 3.9, must be partly or even largely due to an orbital moment enhancement.

For Co structures on Pt, the increase in orbital moment is accompanied by an increase of the magnetocrystalline anisotropy (MCA) energy K_1 , also listed in Table 10.3. It was derived from angle-dependent XMCD magnetization loop measurements and corresponds to the element specific MCA of Co in the various samples. For the monolayer and isolated adatoms of Co on Pt(111) the easy axis was found to be perpendicular to the surface and for the individual adatoms the MCA had a huge value of $K_1 = 9.1$ meV per Co atom. This should be compared to the values found for the hardest thin film materials, e.g., Co/Pt multilayers with $K_1 \simeq 0.3 \,\mathrm{meV}$ per Co atom or bulk materials such as SmCo₅ with $K_1 = 1.8 \text{ meV}$ per atom [40, 443] or the ordered L1₀ phase of CoPt with $K_1 = 0.8 \text{ meV}$ per Co atom [443]. For Co on Pt(997), the Co monolayer had an out-of-plane easy axis and for the Co chains the easy axis was perpendicular to the chain at an angle of 43° from the sample normal. The observed easy axis orientation perpendicular to the chain axis agrees with earlier tight binding calculations for monoatomic Co chains on Pd [444]. These calculations showed the transition of the easy axis from along the chain axis for free monoatomic Co chains to a perpendicular orientation when the chains were placed on Pd.

The above experiments beautifully demonstrate the dependence of the magnetic properties on the dimensionality of the magnetic materials. For more information on low-dimensional magnetic systems we refer the reader to reviews by Bader [39,445] and Himpsel [250]. One particular strength of XMCD measurements in such systems is clearly the elucidation of the role of orbital magnetism. In addition to the studies reported here many beautiful studies of such systems have been performed by XMCD [325, 328, 442, 446–453]. The experiments also demonstrate the extreme sensitivity of XMCD. For example, the studies of isolated Co adatoms on Pt(111) [441] corresponded to a

coverage of 0.010 monolayers of Co or 1.5×10^{13} Co atoms per cm² or about 10^9 Co atoms in the X-ray beam.

10.3.7 Measurement of Small Spin and Orbital Moments: Pauli Paramagnetism

We conclude the spectroscopy section of this chapter by discussing the use of XMCD spectroscopy to determine truly small magnetic moments. With improvements of the experimental techniques of XMCD spectroscopy, one question that naturally arises is as to the ultimate sensitivity of the technique. How small a magnetic moment can be measured? Of course, the answer to this question depends on the system to be studied. Nevertheless, the following experiment provides a nice demonstration of the capabilities of XMCD in this direction.

We have seen in Sect. 10.3.5 above that we can magnetically align isolated paramagnetic atoms like Fe, Co, and Ni by use of a low temperature and a large magnetic field. This is also possible for paramagnetic metals. When cooled to low temperature and exposed to a large magnetic fields H, they actually

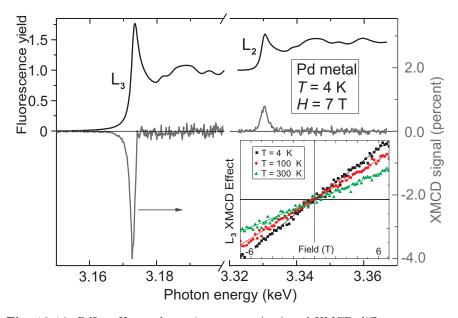


Fig. 10.16. PdL_{2,3} X-ray absorption spectra (*top*) and XMCD difference spectra (*bottom*) of a Pd single crystal, recorded at T = 4K and in an applied field of 7 T. Spectra are corrected for self-absorption and incomplete circular polarization. Inset: Magnetization curves of Pd metal recorded at 4, 100, and 300 K by monitoring the PdL₃ XMCD signal. Figure courtesy of A. Rogalev [88]

acquire an induced magnetization M. The associated small susceptibility $\chi = M/\mu_0 H$ is found to be temperature independent, and this situation is referred to as *Pauli paramagnetism*, as discussed more in Sect. 15.3. Estimates carried out in that sections show that the expected moment is quite small, of order of $10^{-4}\mu_{\rm B}$ per atom.

This small moment has indeed been measured in Pd metal using XMCD spectroscopy by Rogalev and collaborators [454], as shown in Fig. 10.16, despite the rather poor degree of circular polarization of only 12% at the L_3 -edge and 22% at the L_2 -edge available on the used beam line.

After correction of the data for incomplete circular polarization, the XMCD effect is in fact quite large as shown by the right side scale in Fig. 10.16, of order 4% at the L₃-edge and 1% at the L₂-edge. Sum rule analysis of the data gives a spin magnetic moment of $\approx 0.012 \mu_{\rm B}$ and an orbital magnetic moment of $\approx 0.004 \mu_{\rm B}$, under the conditions of the experiment, T = 4 K and in an applied field of 7 T. The presence of an orbital moment shows, that in addition to the Pauli spin paramagnetism the system also exhibits an orbital susceptibility, as suggested by Kubo and Obata [455]. The inset in Fig. 10.16 shows that the measured susceptibility is nearly temperature independent over the 4–300 K range. This confirms that the measured effect is indeed largely due to the Pauli susceptibility. The slope of the curve gives a total paramagnetic susceptibility of the 4d electrons in Pd of $\approx 1.4 \times 10^{-4}$.

10.4 Magnetic Imaging with X-rays

Before we discuss the use of X-rays for magnetic imaging let us briefly take a look at the field of magnetic imaging, in general. One milestone is the 1998 book by Hubert and Schäfer [54] which gives a review of magnetic domains and magnetic imaging. Other valuable resources are the review by Freeman and Choi [456] and the book by Hopster and Oepen [457] which reviews advances in magnetic microscopies up to 2004. The latter book also contains articles by Scholl et al. and Kuch et al. on magnetic imaging by X-rays. The present section should be viewed against the backdrop of all the knowledge that has been accumulated over the years.

It is our goal to provide an overview of the prominent X-ray based imaging methods and to present illustrative examples of their unique power. Like other techniques, X-rays have their specific strength and weaknesses. It will become clear that spatial resolution is only one important asset of magnetic microscopy techniques. In this respect X-rays take second place behind other techniques such a spin-polarized scanning tunneling microscopy [458]. However, they offer capabilities not afforded by other techniques, in particular, elemental and chemical state specificity, variable sampling depth, and the capability to follow ultrafast processes on the picosecond scale.

X-ray magnetic microscopy is based on the dichroism effects already discussed in Sect. 10.3. When the photon energy is tuned to a prominent resonance in the X-ray absorption spectrum, like the L₃ or L₂ edges in the transition metals or the M₅ or M₄ edges for the rare earths, a large dichroism effect exists for magnetic materials. In general, this effect depends on the orientation of the photon polarization relative to the magnetic orientation. For XMCD we have a $\cos\theta$ -dependence of the dichroism intensity on the angle θ between the photon angular momentum and the sample magnetization, expressed by (9.100). For XMLD we have a $\cos^2 \theta$ dependence according to (9.123), where θ is the angle between the **E**-vector and the magnetic axis. It is the X-ray polarization in conjunction with the tunable photon energy that forms the basis for X-ray magnetic imaging. Because of the utilization of these spectroscopy concepts one often speaks of X-ray spectromicroscopy.

It is quite easy to understand the origin of the magnetic contrast. Let us assume that we tune the photon energy to a resonance and fix the photon polarization. If now the sample contains microscopic regions with different magnetic orientations then the signal from these regions will vary because of the dichroic absorption effect. In a transmission experiment, some regions will absorb less and others more, depending on their orientation in the beam. In an electron yield experiment the number of photoelectrons will also be different from the differently oriented regions in the beam. The different signal strength can therefore be used as a contrast mechanism for microscopy. We have seen that we can expect the signal to vary by as much as 20-30% depending on the magnetic orientation. This is indeed a very large contrast considering that Kerr microscopy works with contrasts of less than 1%. All we have to figure out is how to separate the signals from the microscopic areas of the sample by some kind of microscopy technique. We shall first discuss three real space microscopy techniques and then, in Sect. 10.4.1, a technique based on reconstructing a real space image from a coherent X-ray scattering pattern.

10.4.1 X-ray Microscopy Methods

Similar to electron microscopy there are two main approaches, either based on scanning or imaging methods. Three common experimental implementations based on X-rays are illustrated in Fig. 10.17 and we shall now discuss them in turn.

Scanning Transmission X-ray Microscopy – STXM

In scanning X-ray microscopy, illustrated in Fig. 10.17a, a monochromatic Xray beam is focused to the smallest possible spot size and the X-ray intensity transmitted through the sample is monitored as a function of the focused beam position on the sample [459]. In principle, either the sample or the beam position may be scanned but in practice one typically scans the sample. One may also measure the fluorescent X-ray or electron intensity from the sample, as indicated in the figure, but measurement of the transmitted intensity is most

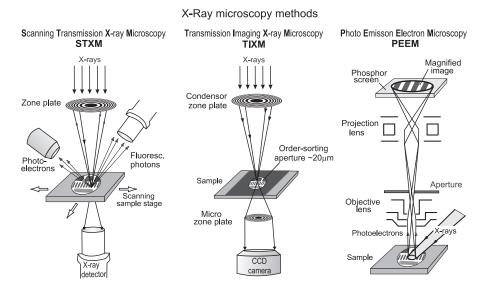


Fig. 10.17. Schematic of three X-ray microscopy methods for imaging of nanoscale magnetic structures. (a) In scanning transmission X-ray microscopy, STXM, a monochromatic X-ray beam is focused to a small X-ray spot by a suitable X-ray optic, e.g., a zone plate as shown, and the sample is scanned relative to the X-ray focal spot. The spatial resolution is determined by the spot size which is determined by the width of the outermost zones in the zone plate. The intensity of the transmitted X-rays or the fluorescence or electron yield from the sample are detected as a function of the sample position and thus determine the contrast in the image. (b) In transmission imaging X-ray microscopy, TIXM, the incident beam may be either monochromatic or not. The beam is focused by a condensor zone plate that in conjunction with a pinhole before the sample produces a monochromatic photon spot on the sample. For an incident polychromatic beam the energy resolution is determined by the zone plate and the pinhole and is typically not very high $(E/\Delta E \approx 200)$. A microzone plate generates a magnified image of the illuminated sample area which can be viewed in real time by a X-ray sensitive CCD camera. The spatial resolution is determined by the width of the outermost zones in the microzone plate. (c) In X-ray photoemission electron microscopy, XPEEM, the X-rays are focused by a shaped mirror to match the field of view of an electron microscope $(1-50 \,\mu\text{m})$. Electrons emitted from the sample are imaged by an assembly of electrostatic or magnetic lenses with magnification onto a phosphor screen, and the image can be viewed in real time at video rates. The spatial resolution is determined by the electron optics within the microscope, the size of the aperture, and the operation voltage. In advanced designs an energy filter is employed to minimize chromatic abberation effects and such effects are further reduced by aberration correcting optics

common. In this approach the energy resolution is given by the monochromator in the beam line (not shown) and the spatial resolution is determined by the size of the X-ray spot. Small X-ray spots can be obtained by using the reflected and focused beam from grazing incidence mirrors or the diffracted and focused beam from either a multilayer mirror or a zone plate. In practice, zone plate focussing, shown in Fig. 10.17a yields the smallest spot sizes. The focal spot size is determined by the width of the outermost zones of the zone plate and today the resolution is typically about 30 nm with resolutions down to 10 nm or less expected in the future [460]. Because the focal length of the zone plate lens changes with photon energy, for spectroscopic studies the sample position also needs to be scannable along the beam direction. X-ray transmission or fluorescence microscopies are well suited for studies in the presence of a magnetic field, contrary to electron based methods. They are "bulk" sensitive, in the sense that the transmitted intensity is determined by the entire thickness of the sample.

Transmission Imaging X-ray Microscopy – TIXM

From an instrumental point of view, transmission imaging X-ray microscopy or TIXM, shown in Fig. 10.17b is closely related to scanning X-ray microscopy since in both cases the spatial resolution is determined by zone plates and both are photon-in/photon-out methods. First generation microscopes used polychromatic beams which were focused and monochromatized by a combination of a condenser zone plate and a pinhole aperture (typically 10–20 µm diameter). In such an arrangement the energy resolution is determined by the zone plate dimensions and the pinhole size and is typically $\Delta E/E \simeq 1/250$. Modern microscopes use a monochromatic incident beam with $\Delta E/E \simeq 1/5,000$ which also allows spectroscopic studies of the detailed near-edge fine structure.

The beam is focused onto the sample by means of a condenser zone plate. The focal spot size then serves as the field of view of the imaging process, accomplished by a microzone plate that generates a magnified image of the illuminated area on the sample onto a phosphor screen or X-ray sensitive CCD camera. The spatial resolution is determined by the width of the outermost zones of the microzone plate [460] and a resolution of 15 nm has been obtained [461]. Spectroscopic studies require movement of both the condensor and microzone plates relative to the sample, and in practice, this has impeded spectroscopic studies with TIXM. Like STXM, TIXM is also well suited for studies in the presence of magnetic fields, and such studies have been performed by Fischer et al. [462, 463].

X-ray Photoemission Electron Microscopy – X-PEEM

The third imaging method is based on X-rays-in/electrons-out and was pioneered by Tonner [464]. It is illustrated in Fig. 10.17c. The sample is illuminated by a monochromatic X-ray beam that is only moderately focused, typically to tens of micrometers, so that it matches the maximum field of view

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of a photoelectron microscope. The energy resolution is determined by the X-ray monochromator in the beam line and the spatial resolution is determined by the electron optics in the X-PEEM. It is limited by three quantities: spherical aberration, chromatic aberration, and diffraction. In practice, for X-ray excitation of electrons, chromatic aberrations dominate [464, 465]. They originate from errors in the focusing of electrons with different kinetic energies.

Most PEEM microscopes do not incorporate an energy analyzer or filter [466] and therefore, in principle, all photoelectrons are detected. In practice, the electron intensity is dominated, by orders of magnitude, by the secondary electron tail in the 0–20 eV kinetic energy range, where zero kinetic energy corresponds to the vacuum level of the sample [467]. The secondary electron intensity which closely follows the X-ray absorption spectrum of the sample [467], determines the X-PEEM intensity, and its large size provides a suitably large signal.

The energy spread of the inelastic tail (about 5 eV for most materials [468]) spoils the spatial resolution through chromatic aberrations. Fortunately, the effective width of the energy spread is reduced by a suitable aperture placed in the backfocal plane of the PEEM. The aperture acts as a filter for high energy electrons which are focused behind the aperture while the low energy portion of the inelastic tail is properly focused at the aperture position and is thus transmitted. Calculations show that a spatial resolution of about 20 nm can be obtained by X-PEEM because of the energy filtering effect of the aperture [469], and this is verified by experiments. Even better spatial resolutions are achieved when the energy spread of the emitted electrons is reduced. This situation is encountered when ultraviolet radiation is used with an energy slightly higher than the workfunction and a spatial resolution of 8 nm has been demonstrated [470]. In this case chromatic aberrations are strongly reduced by the narrow width of the secondary electron distribution. At X-ray energies, a resolution of 22 nm has been achieved by use of an energy filter to reduce the electron energy spread [471]. In the future lateral resolutions below $5 \,\mathrm{nm}$ appear possible [472, 473].

Contrast Mechanisms

The intensity changes with photon energy or X-ray polarization discussed in the earlier spectroscopy section naturally lend themselves as contrast mechanisms for scanning and imaging X-ray microscopy. For example, if the photon energy is tuned to 707 eV, the L₃ resonance of Fe metal, the measured signal from the sample will emphasize Fe over other elements in the sample. If we change the polarization from linear to circular, Fe regions in the sample will be emphasized whose magnetization direction is parallel to the photon spin (see Figs. 9.12 and 10.1d). It is not necessary in many cases to change the photon spin in XMCD microscopy since the contrast is large and can be enhanced by combining images recorded at the L₃ and L₂ edges. For antiferromagnets the photon energy of the linearly polarized light is tuned to a particular multiplet peak, e.g., one of the L₂-edge peaks in Fig. 10.1c. Domains with an orientation of the magnetic axis parallel to \boldsymbol{E} will then show a different intensity than those with the axis perpendicular to \boldsymbol{E} . Again the contrast can be enhanced by combining images taken at different photon (multiplet) energies.

In addition to the spectroscopic contrast, other basic contrast mechanisms exist. In X-PEEM the electron yield from different sample areas is also determined by the local work function and topology. In transmission X-ray microscopy additional contrast arises from differences in the X-ray absorption coefficient at nonresonant photon energies caused by compositional changes or thickness variations of the sample.

10.4.2 Lensless Imaging by Coherent Scattering

We have seen that the resolution of real space X-ray microscopy techniques is determined by optics in the form of X-ray or electron lenses. Here we describe an alternative lensless imaging approach based on X-ray scattering, which in principle is resolution limited only by the X-ray wavelength.

It is well established that, in principle, X-rays may resolve structures down to the size of the X-ray wavelength, the so-called diffraction limit. Diffraction imaging, or crystallography, is a lensless approach where the real space structure is obtained by inversion of a reciprocal space diffraction pattern. This approach has been extensively used for decades to determine the structures of crystalline systems, consisting of repeated identical unit cells. The procedure relies on the remarkable fact that for typical experimental geometries X-ray beams are *coherent* over dimensions that are larger than the unit cell dimensions of the sample, despite the fact that all of today's X-ray sources, including undulators, are characterized by spontaneous emission and are therefore chaotic or incoherent by nature. A coherent beam can be created from the radiation emitted by an incoherent source by spectral and spatial filtering [109].³ When a single crystal is inserted into an X-ray beam, its unit cell is typically so small that across its tiny volume the EM wave has a well defined phase relationship. Therefore the waves that are scattered off the individual atoms within each unit cell can interfere. Because all unit cells are identical, the unit cell interference patterns are identical and add up into intense diffraction spots.⁴ The diffraction spot pattern can then be used to solve the crystal structure.

³ More specifically, one distinguishes *temporal coherence*, which is determined by the bandwidth of the radiation and *lateral coherence* which is determined by the geometry perpendicular to the beam direction.

⁴When the EM field is quantized one finds that for today's X-ray sources all diffraction experiments are based on single photon interference effects because the coherence volume of the radiation contains less than one photon. This will change with the advent of X-ray free electron lasers.

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The diffraction approach breaks down if the sample is nonperiodic since now the interference patterns from small areas in the sample are no longer identical and therefore intense diffraction spots will no longer exist. This situation is encountered in many systems that contain order on the nanoscale without long-range periodicity. A prominent example are magnetic domains which typically consist of irregular nanometer or micrometer sized areas in which the magnetization points in different directions. Despite their disordered arrangement it is still possible, however, to derive their real space arrangement from the scattered intensity as we shall discuss now.

In order to understand how this is possible we first consider the more familiar case of small angle X-ray scattering (SAXS), illustrated in the top half of Fig. 10.18. This well-established technique uses an X-ray beam which at the position of the sample is coherent only over a dimension, called the coherence length, of tens of nanometers. In Fig. 10.18 we have indicated the coherence length as the diameter of the red circles, which are assumed to be larger than the characteristic structures, assumed to be worm domains as shown in the inset. In general, the internal sample structure may correspond to regions of different electron density as in a polymer or areas of different magnetic orientations, i.e., domains, in magnetic materials. The SAXS pattern corresponds to the incoherent superposition of the coherent patterns from different sample regions of the size of the red circles. Owing to the different structural or orientational units in the different sample regions the scattering pattern is somewhat smeared out. For a sample with an average characteristic size d associated with the nanoregions, the scattering pattern consists of a ringlike intensity pattern as shown in Fig. 10.18, located at a momentum transfer $Q = 2\pi/d.$

By moving the sample away from the source, as shown in the bottom half of Fig. 10.18, one reduces the angular opening angle of the beam intercepted by the sample, and therefore the effective path length difference of the used X-rays. This increases the coherent fraction. The associated loss of intensity can be tolerated for modern high-brightness undulator X-ray sources. One may therefore coherently illuminate a sample that has a lateral size of the order of $50\,\mu\text{m}$. Then the scattered waves from all regions of the sample can interfere and the scattered intensity distribution, the "speckle pattern," recorded by an imaging detector contains the complete information on the real space structure of the sample.⁵ The remaining challenge is to invert the reciprocal space pattern into a real space structure.

To obtain a real space image of the sample from the speckle pattern the phases of the scattering amplitudes have to be reconstructed. This is typically attempted by phase retrieval algorithms that rely on oversampling of the speckle pattern [474–477]. The development of such phase retrieval methods remains an active area of research.

 $^{^5}$ The SAXS pattern is an averaged speckle pattern. It contains only statistical information about the sample structure but offers the advantage of higher intensity.

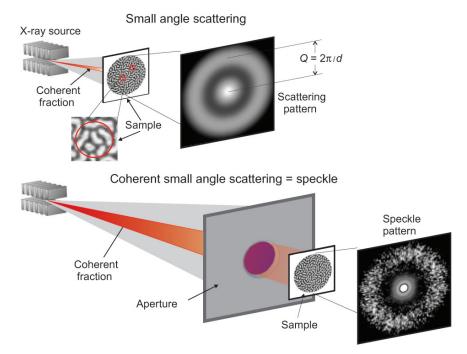


Fig. 10.18. Concepts of X-ray scattering from a sample containing worm domains of nanoscale dimensions. We have assumed a pseudomonochromatic undulator source and record the scattering pattern from the sample with a position sensitive detector. *Top:* The sample is located close to the undulator source and the beam on the sample is coherent (by geometry) only over areas that are of the size of the red circles. These coherently illuminated areas are assumed to be slightly larger than the average separation between the worm domains. The scattering pattern is the incoherent superposition of the coherent patterns from different sample regions of the size of the red circles. *Bottom:* The sample has been moved away from the source so that only a small fraction of the beam, which is coherent by geometry, illuminates the sample. At a great loss in intensity the entire sample is now coherently illuminated and the scattering pattern is a coherent superposition from all regions of the sample. The resulting scattering pattern, called a speckle pattern because of its appearance, now encodes the real space structure of the entire sample

A more robust approach is the real space image reconstruction afforded by holographic methods [478, 479]. One such method is Fourier transform holography [480], which has been successfully used to image magnetic domains with soft X-rays [481], as illustrated in Fig. 10.19.

The key component of the experiment is the introduction of a Au mask before the sample, shown enlarged in the lower left part of the figure. The Au mask contains two holes, a "sample hole" of $1.5\,\mu\text{m}$ through which the sample is illuminated, and a "reference hole" of 100 nm diameters, which is drilled all

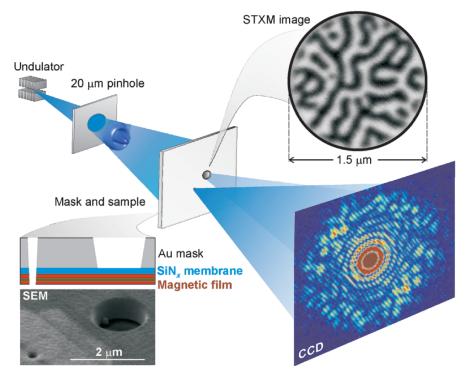


Fig. 10.19. Illustration of an X-ray Fourier transform holography experiment [481]. The X-ray beam from an undulator source with variable polarization is incident on a pinhole that redefines the source. The central part of the Fraunhofer pattern of the pinhole then illuminates a mask that consists of a "sample hole" and a "reference hole." The scanning electron microscopy (SEM) image on the *lower left* shows a close-up of the two holes which were drilled into a Au film by a focused ion beam. In the shown case the mask and sample are integrated, as shown above the SEM image. The magnetic domain structure within the pinhole opening, recorded by a scanning transmission X-ray microscope (STXM) is shown on the *right top*. The experimentally recorded hologram of the sample by a CCD detector is shown in false color on the *lower right*. For magnetic imaging one uses the resonant magnetic dichroism effect near an absorption edge, as illustrated for Fe in Fig. 9.29

the way through the mask/sample sandwich by a focused ion beam (FIB). In the experiment shown, the sample consists of a Co/Pt multilayer film with perpendicular anisotropy which exhibits a magnetic worm domain pattern, revealed in the real space XMCD STXM image on the top right. The two holes are coherently illuminated by circularly polarized photons, tuned to the Co L edge (780 eV) for optimum magnetic contrast. The beam through the larger hole is scattered by the magnetic domains of the sample and interferes on the detector with the beam transmitted through the reference hole. The scattering pattern seen on the detector screen contains speckles like the image in Fig. 10.18 and also fine diagonal stripes which originate from the interference of the beams through the sample and the reference holes. One may think of the scattering pattern as a speckle pattern that has been phase encoded with the reference beam. The real space image of the magnetic domain structure is simply obtained by a single Fourier transformation of the recorded scattering intensities [481]. Its resolution is determined by the encoding reference beam and is therefore limited to the size of the reference hole. The reconstructed image looks identical to the STXM image shown in the top right corner of Fig. 10.18 [481].

In principle, coherent scattering experiments can be performed by means of either nonresonant X-rays or by tuning the photon energy to an absorption edge of the sample. For magnetic systems the contrast is greatly enhanced by using resonant X-rays, that is, taking advantage of the large dichroic effects near an absorption edge, as illustrated in Fig. 9.29 for Fe. In scattering experiments one may use the dichroic effect in either the real (F'(E)) or imaginary (F''(E)) part of the scattering factor as shown in Fig. 9.5. In certain cases it is advantageous to tune to the resonance in the real part F'(E) which occurs below the onset of absorption, i.e., the maximum in the imaginary part F''(E). For example, in experiments with intense free electron laser radiation this will greatly reduce deleterious energy transfer from the beam to the sample.

One of the unique properties of this imaging approach is that no focusing or alignment is required. While this is merely convenient for imaging at a synchrotron radiation storage ring, it is essential for the envisioned single X-ray pulse imaging with future X-ray lasers. It is important to keep in mind that lensless imaging by Fourier transform holography is a true imaging method. No iterative algorithm is required to obtain the real space structure.

The spatial resolution may be further increased by applying additional phase retrieval procedures. Since the recorded X-ray hologram can also be interpreted as a speckle pattern, one may in a second step apply an iterative algorithm to retrieve the scattering phases. This is aided by the fact that iterative phase retrieval algorithms are more effective the closer the initial input is to the real space structure [476]. One can therefore employ a two step analysis. In the first step the Fourier transform provides a resolution that is of the order of the reference hole. In the second analysis step, iterative phase retrieval algorithms are used to obtain higher resolution. The resolution in the second step is typically determined by the angular range (maximum momentum transfer) and signal-to-noise ratio of the measured scattered intensities, and is ultimately limited by the wavelength, which is about 1.5 nm at the transition metal L-edges.

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10.4.3 Overview of Magnetic Imaging Results

Images of Ferromagnetic and Antiferromagnetic Thin Films

We start our discussion of X-ray magnetic imaging by presenting in Fig. 10.20 details about the typical image contrast utilized in imaging of ferromagnetic domains.

The figure shows PEEM images of ferromagnetic domains for a thin film of Co deposited on a cleaved crystal of NiO. We shall see later that the Co FM domain structure has the characteristic striped pattern of the AFM domains in the NiO crystal underneath. There are four Co domains consisting of two

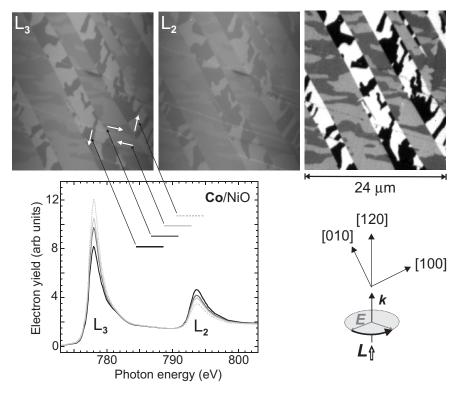


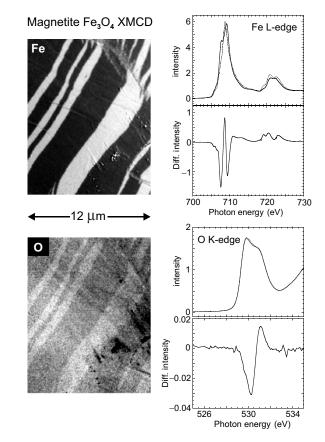
Fig. 10.20. PEEM images of the magnetic domains in a Co film deposited on single crystal NiO recorded with circularly polarized light of fixed photon spin and with the energy tuned to the L_3 -edge (*left top*) and the L_2 edge (*middle top*). The XMCD spectra recorded for different domains whose orientation is indicated in the *left image* are shown underneath. The spectra are shown in different gray shades and the arrows indicate the correspondence to the domains. On the right top we show an image that was obtained by dividing the two images taken at the L_3 and L_2 edges. The orientation of the NiO crystal and the photon polarization is indicated on the right bottom

pairs of orthogonal domains, all with their magnetization in the plane of the film, as indicated by arrows in the left image. Of interest here is not the domain structure itself but how it is revealed in original images recorded with a *given circular polarization* and with the photon energy tuned to either the L_3 or L_2 edges. For this reason we show the raw images recorded at these energies and underneath the original dichroic spectra recorded from the four individual domains. This is accomplished by selecting areas on the sample by a soft-ware-set window and recording the intensity of the pixels in the window as a function of energy.

The figure illustrates the correspondence of the gray scale image contrast to the difference in spectral intensities, indicated by the shading of the spectra and by arrows. In direct analogy to the spectra the image contrast inverts at the L_3 or L_2 resonance energies, and this can be conveniently used to enhance the contrast (without change in X-ray polarization) by dividing the raw images obtained at the two edges. Another method would be to change the circular polarization at a given resonance energy. This is typically not done for microscopes located on bending magnet beam lines because by selecting radiation below and above the orbit plane (see Fig. 4.14) by movement of an aperture one changes the optical path through the beam line and this results in energy shifts. For undulator beam lines the change of polarization is straightforward and one may conveniently use opposite circular polarizations for contrast enhancement.

An example of the unique capabilities of X-rays for imaging ferromagnetic domains is given in Fig. 10.21. The figure shows FM domains in a thin film of magnetite, Fe₃O₄, grown on SrTiO₃(110). As shown in the upper right of the figure, the Fe L-edge spectrum has a characteristic multiplet structure which leads to a complicated XMCD difference spectrum shown underneath. The spectra were recorded independently on an undulator beam line by fixing the circular polarization and saturating the sample into opposite magnetization states. The rich XMCD structure is a consequence of multiplet effects as well as the different Fe sites in magnetite [302] (see Fig. 7.30). The integrated negative and positive XMCD contributions at the L₃-edge have a ratio of about 2 to 1. Antronov et al. have attributed this intensity distribution with the moments on the three different Fe sites in Fig. 7.30, which also have a 2 to 1 spin-up to spin-down ratio. The XMCD domain image shown on the top left was recorded at the Fe L-edge by division of two images taken at energies with opposite dichroism effect.

The tunability of X-rays also allows one to look for a magnetic effect at the site of the O atoms in magnetite. The dichroic O K-edge spectra and the XMCD difference are shown on the lower right of the figure. The O K-edge dichroism effect is about 2% of that at the Fe L-edge and has a characteristic XMCD structure with a negative intensity that is about a factor of 2 larger than the positive intensity, similar to the ratio seen at the Fe L-edge. As for this case, it is tempting to correlate the 2 to 1 intensity distribution with the moments on the three different Fe sites in Fig. 7.30. However, since



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Fig. 10.21. Domain images and XMCD spectra for epitaxially grown magnetite, Fe_3O_4 . On the *right* we show spectra recorded at the Fe L-edge and O K-edge with circular polarized light and magnetically saturated samples and their difference, the XMCD spectra. The O K-edge spectrum agrees with that shown in Fig. 7.32a. The images on the *left* were obtained by dividing two images recorded at two photon energies with opposite dichroism effects

all O atoms in Fe₃O₄ are equivalent, the situation is different, since the O K-shell transitions must reflect different valence orbitals on the same atom. The negative O K-edge XMCD peak would then correspond to transitions to O 2p orbitals involved in the bonding with Fe3d orbitals on the two octahedral Fe^{2+} and Fe^{3+} atoms, with moments coupled parallel by double exchange. The positive peak would correspond to O2p orbitals hybridized with Fe3d orbitals on the *tetrahedral* Fe^{3+} atoms. These Fe atoms have opposite moment orientations than the octahedral Fe atoms because of superexchange. We therefore have the interesting case where we can resolve the 2p-orbital-specific magnetic moments on the same O atom.

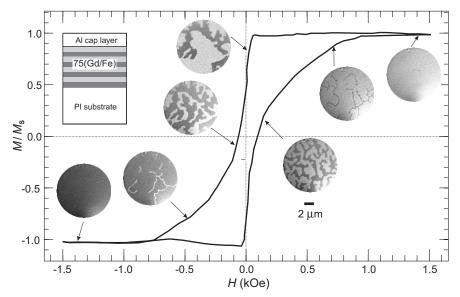


Fig. 10.22. TIXM images recorded at the FeL₃-edge as a function of applied field for a 75 × [Fe(4.1 Å)/Gd(4.5 Å)] multilayer deposited on polyimide and capped for protection with an Al layer [463,482]

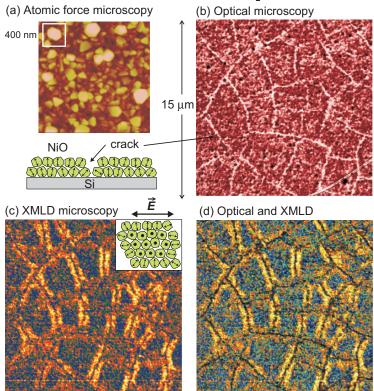
Within each magnetic domain, the dichroism spectrum has the same intensity distribution, and one can therefore use the positive and negative peaks for enhancement of the dichroic image contrast. Doing so yields the magnetic image shown in the lower left corner of Fig. 10.21. We see that it closely resembles the FM image taken at the Fe L-edge.

Our next example, shown in Fig. 10.22, demonstrates the ability of photonin/photon out techniques to record magnetic images in the presence of a magnetic field [463, 482].

Shown here are TIXM images recorded at the FeL₃-edge for a Fe/Gd multilayer with perpendicular magnetic anisotropy at various points around the magnetization loop. The magnetic structure corresponds to domains with opposite magnetization directions along the surface normal.

As another interesting example, we show in Fig. 10.23 various images of a polycrystalline film of NiO. The 400-nm-thick polycrystalline NiO sample was deposited by sputter deposition onto oxidized Si and then annealed for 1 h at 1,100 °C in flowing oxygen at atmospheric pressure, followed by 1 h at 700 °C, and a gradual (4 h) cooldown to room temperature in flowing O₂. The procedure was applied to increase the crystallographic grain size of the film. In Fig. 10.23a we show an atomic force microscopy image of the surface after annealing, revealing an average grain size of about 180 nm, which was significantly larger than the 15–20 nm size before the annealing procedure. Inspection of the film under an optical microscope revealed that the film had

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400 nm NiO on Si annealed in O_2 at 1,100 °C

Fig. 10.23. Structure of a 400 nm thick NiO film sputter deposited on an oxidized Si substrate and annealed in an oxygen atmosphere to increase the grain size. (a) Atomic force microscopy image revealing the grain size, which increased from about 15–20 nm before to about 180 nm after annealing [284]. The schematic underneath illustrates that after annealing the film cracked as revealed by optical microscopy images shown in (b). (c) XMLD images obtained from difference images recorded with linearly polarized X-rays for the shown horizontal \boldsymbol{E} orientation. We used two images recorded on the two L₂ multiplet peaks with opposite XMLD effects, as shown in Fig. 9.27 (also see Fig. 10.25). (d) Direct comparison of the optical image in (b) with the cracks shown in dark, superimposed on the XMLD image in (c)

cracked during the procedure, revealed by the web-like white crack lines in the topographical image in (b). The structure of the film deduced from these results is schematically illustrated at the bottom of Fig. 10.23a.

The sample was also studied by XMLD PEEM microscopy to investigate the antiferromagnetic domain structure. By use of linearly polarized light, images were recorded on the two L_2 NiO peaks shown in Fig. 9.27 (also see Fig. 10.25) and divided for contrast enhancement. The resulting XMLD image in Fig. 10.23c consists of bright double lines which are predominantly oriented vertically. The widths of the bright lines are rather uniform and correspond to the grain size of the film. Direct comparison of the optical image in (b) with the XMLD image in (c), shown in (d), reveals that the crack lines, shown in dark, and the AFM double lines, shown in yellow, can be superimposed and follow the same web-like cracking pattern. However, no significant antiferromagnetic contrast exists along the horizontal or near-horizontal web lines.

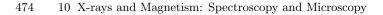
The AFM contrast arises from preferential orientation of the AFM axis relative to the E-vector which for the AFM image in (c) was oriented in the horizontal direction, as indicated. Bright contrast corresponds to regions with their AFM axis oriented parallel to the E-vector. Hence, the bright double stripes in Fig. 10.23c correspond to grains adjacent to the cracks which have a preferred in-plane horizontal orientation of the AFM axis. Dark contrast corresponds to an AFM axis orientation perpendicular to the electric field vector. The image can thus be explained by a preferential orientation of the AFM axis as illustrated in the inset in (c). In the grains at the cracks, the AFM is oriented in-plane, perpendicular to the cracks. Within the islands the AFM is oriented perpendicular to the surface normal.

The results in Fig. 10.23 reveal a correlation between the topographical and AFM structure. The formation of cracks proves the existence of considerable stress and resulting strain in the cooling cycle. The cracking, however, does not fully relieve all film stress and the residual strain profile is expected to be inhomogeneous across the formed islands. We attribute the different orientations of the AFM axes to a magnetostrictive effect with perpendicular strain directions in the center of the island and at the cracked edges [284]. The present case is only one example for the strong correlation between crystallographic structure and strain and the orientation of the AFM axis, as discussed in Sect. 11.3.2.

Images of Coupled Magnetic Thin Films

We now look at another strength of X-rays, the investigations of coupled magnetic layers, where the elemental specificity can be used to investigate the magnetic structure in each layer separately. As an example we take a look at the exchange coupling between a ferromagnet and antiferromagnet, and in Fig. 10.24 we show the first images obtained for such systems [107].

Figure 10.24 shows images of the FM domain structure of a thin Co layer and the AFM domain structure in LaFeO₃ underneath, as schematically illustrated on top of the figure. The magnetic contrast in the right image arises from AFM domains in LaFeO₃ with an in-plane projection of the AFM axis oriented horizontally (light) and vertically (dark). The image was obtained with linear polarization by dividing two images recorded on the two L₂ peaks in Fig. 10.1c with opposite XMLD effects. The FM Co image shown on the left exhibits three distinct grey scales, corresponding to FM domains aligned



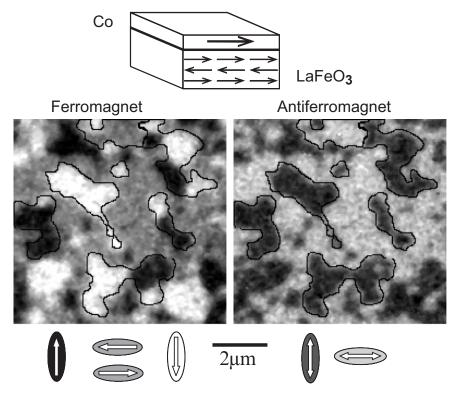


Fig. 10.24. Sample structure and PEEM images of domains in the antiferromagnetic and ferromagnetic layers for 1.2 nm Co on LaFeO₃/SrTiO₃(001) [107]. Left: Co L-edge XMCD image of ferromagnetic domains. Right: Fe L-edge XMLD image of antiferromagnetic domains. The in-plane orientations of the antiferromagnetic axis and ferromagnetic spins are indicated by arrows below the images

vertically up (black) and down (white), and horizontally left or right (gray). For the experimental geometry used for the figure, corresponding to a vertical photon wave vector (angular momentum) direction, we cannot distinguish left from right horizontally oriented FM domains.

Comparison of the in-plane projections of the AFM axis and the FM spin directions, illustrated below the images, reveals that the FM Co spins are aligned parallel or antiparallel to the in-plane projection of the AFM axis. The magnetic alignment of the Co domains, which exhibit an in-plane easy axis, must therefore be caused by a coupling to uncompensated spins at the LaFeO₃ surface with an in-plane component parallel to the in-plane projection of the AFM axis.

Another example of FM–AFM exchange coupling is shown in Fig. 10.25. The right column of the figure shows the AFM domain pattern near the Ni(001) surface and the left column the FM domain patterns of eight mono-

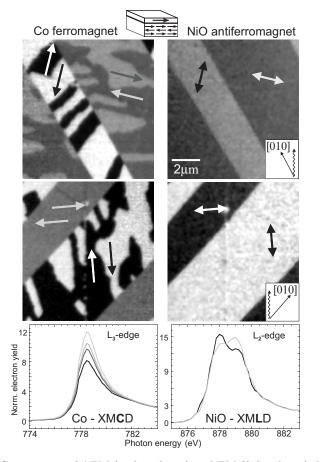


Fig. 10.25. Comparison of AFM (*right column*) and FM (*left column*) domain patterns for eight monolayers of Co on NiO(001) and two different azimuthal geometries, recorded by PEEM [404]. Arrows and wavy lines in the insets indicate the directions of the crystallographic axes and photon wave vectors, respectively. The directions of the magnetic moments in the domains are indicated by arrows. The AFM contrast in NiO was obtained by division of two XMLD images obtained with horizontally polarized light and photon energies corresponding to the two L₂-edge peaks shown in the spectrum on the bottom right. The FM image for Co was obtained by division of XMCD images recorded at the L₃ and L₂ energies. The magnetization direction of the Co film is found to be either parallel or antiparallel to the domains in the AFM, depending on which of the two AFM sublattices are present at the interface to Co. The spectra shown at the *bottom* show the XMCD and XMLD effects responsible for the contrast of the images

layers of Co deposited on top. The top and bottom rows correspond to 45° rotated azimuthal orientations, as indicated in the insets by the orientation of the photon wave vector (wavy lines) and the crystallographic axes. The

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ferromagnetic domains in the Co layer split up into two subgroups with each subgroup spatially following the AFM domains. The observed spatial alignment of AFM and FM domains is caused by exchange coupling and it breaks up upon heating the system above the Néel temperature of NiO. The dichroism contrast of the other subgroup of ferromagnetic domains (black and white in lower left image) is about 30%, while the antiferromagnetic contrast in the lower right image is 14%. Within the near-interface region of NiO the AFM spin directions are found to be completely in plane, parallel to [± 110] and parallel to those in Co [404].

The Spontaneous Magnetization, Anisotropy, Domains

In Chapt. 6 and 7 we have given the *quantum mechanical* origin of the important exchange and spin-orbit interactions, following the historical development which started from the interpretation of atomic spectra in the mid 1920s. This development culminated in Heisenberg's generalization of the atomic exchange interaction which over the years was developed into a powerful description of the magnetic interactions in solids in terms of the Heisenberg Hamiltonian. Here we will take a closer look at these all important magnetic interactions from different points of view.

We start our discussion with the phenomenological *molecular field theory* developed as early as 1907 by Pierre Weiss, before the advent of quantum theory, to explain the observed field and temperature dependence of magnetic materials. This description was later merged with the concept of exchange and Heisenberg's model. The connection between the Weiss and Heisenberg models is straightforward when the Heisenberg Hamiltonian is written in the form of a molecular field or mean field model. However, while the concepts of the "molecular field" and "exchange" are related, their difference is the basis of our modern understanding of finite temperature magnetism. The distinction between the concepts of the Weiss field and the Heisenberg exchange lies at the very heart of magnetism. It is the origin of many historical arguments between great thinkers in the field of magnetism like Slater and Van Vleck, captured in as simple a question as: do the exchange splitting and/or the atomic moments vanish at the Curie temperature? For this reason we also give here an account of the temperature dependence of the spontaneous magnetization.

We will take another look at the spin-orbit interaction as well, this time again from a solid state approach. We shall see that this rather small interaction is of great importance in that it is the origin of the magnetocrystalline anisotropy. The origin of magnetic anisotropy will be discussed in terms of historically used phenomenological treatments and a quantum theory based treatment of the anisotropy of the spin-orbit interaction. We then discuss the origin of the magnetic domain structure and the related topic of magnetization loops. Finally, we address the topic of magnetism in small particles. This

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is important from a science and technology point of view in that advanced magnetic recording media consist of such particles. Furthermore it has become possible lately to produce mass selected small clusters on solid state substrates and initial measurements have revealed fascinating magnetic properties.

11.1 The Spontaneous Magnetization

Pierre Weiss recognized in 1907 that the properties of some materials with a strong response to a magnetic field, such as iron, require the existence of a *spontaneous magnetization*, that is a magnetization that exists even when no external magnetic field is applied.

The *spontaneous magnetization* is defined as the magnetization that exists in individual regions or domains even when no external magnetic field is applied. The magnetization directions of the domains may be macroscopically aligned by an external magnetic field.

For a long time it was difficult to directly measure the *spontaneous magnetization* since one had to apply a magnetic field to macroscopically magnetize the sample and then measure the *saturation magnetization*. Today the spontaneous magnetization can be directly observed with microscopy techniques which can resolve the individual spontaneously magnetized domains. This point will become particularly important in the discussion of critical fluctuations in Sect. 11.1.6 later.

Weiss also understood that the atoms must carry magnetic moments in order to sustain the spontaneous magnetization. The problem was then how these atomic magnetic moments could be aligned against thermal motion. One might first think that the alignment is due to the fields generated by the atomic dipoles. A quick calculation shows that the dipolar fields are too weak. The magnetic dipole generates a magnetic field at a distance r. According to (3.2), we may estimate the strength of this field within a factor of 2 that depends on the orientation of the dipole, from the expression $\mu_0 H_D = B_D =$ $|\mathbf{m}|/2\pi r$. At typical distances of atoms in a crystal lattice of r = 0.15 nm and assuming $|\mathbf{m}| = 1\mu_B$, we find $B_D \sim 1$ T. In Sect. 3.4 we learned that the dipolar interaction of atomic moments of $1\mu_B$ then leads to magnetic order at temperatures of ~ 1 K. This small value is at odds with the Curie temperature of the common ferromagnetic metals Fe, Co, and Ni and their alloys which is of order $\sim 1,000$ K. Clearly, the magnetic field generated by the atomic dipoles themselves is too weak to explain ferromagnetism.

In order to account for the large Curie temperature, Weiss postulated that a molecular field of unknown origin with an enormous value of $\sim 1,000$ T must exist in the ferromagnetic materials. Such a molecular field or Weiss

field would then be able to generate the spontaneous magnetization by aligning the atomic dipoles against thermal agitation. Weiss further recognized that the magnetostatic field generated outside a homogeneously magnetized macroscopic piece of material requires sizeable energy. This led him to assume that the spontaneous magnetization is split up into domains which are magnetized in different directions in order to minimize the stray magnetic fields. With these assumptions, Weiss was able to explain the dependence of the magnetization of ferromagnetic materials on the applied magnetic field, and he was also able to understand the main features of the magnetic phase transition from a spontaneously magnetized to a paramagnetic material that takes place at the Curie-temperature $T_{\rm C}$.

The Weiss domains are nowadays imaged and studied with numerous imaging techniques, and their response to a magnetic field finds many applications. The electric transformer is one example. Without transformers our present civilization relying on the distribution of electric energy could not exist. The molecular field postulated by Weiss is the basis of the so-called mean field theory, which has become a cornerstone in the understanding of any phase transition. The term "mean field" refers to the assumption that the entire entity of electron spins creates a temperature dependent effective magnetic field to which every moment is exposed. We shall now discuss the temperature dependence in such a mean field model.

11.1.1 Temperature Dependence of the Magnetization in the Molecular Field Approximation

According to the ingenious assumption of Weiss, the molecular field $H_{\rm W}$ is proportional to the magnetization,

$$H_{\rm W} = \beta M , \qquad (11.1)$$

where β is the molecular field constant. From this follows the spontaneous magnetic saturation at low temperatures and the "phase"-transition to a paramagnetic material at the temperature $T_{\rm C}$. The concept of the Weiss molecular field, also referred to as *mean field theory*, remains a cornerstone of contemporary magnetism. The Weiss field is responsible for the *long-range interatomic magnetic ordering* and its value therefore determines the Curie temperature. The relevant energy is given by that of a magnetic moment m in the field which according to (3.15) is given by,

$$E_{\rm W} = -\boldsymbol{m} \cdot \boldsymbol{H}_{\rm W} \tag{11.2}$$

with units of [V A s], where 1 VAs = 1 Joule [J] = $0.624 \times 10^{19} \text{ eV}$.

The Weiss molecular field is responsible for the long-range interatomic magnetic order and its magnitude determines the Curie temperature.

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The basic idea of the mean field theory is best explained by considering the case where the atomic moments are generated by a single unpaired electron of spin s = 1/2, following the discussion in Sect. 3.4 for a paramagnet. In a ferromagnet, the magnetic moments are exposed to a field that is the sum of the external field H and the molecular field βM . We can then follow Sect. 3.4 for the description of the temperature dependence. The parameter $x = \mu_{\rm B} H/k_{\rm B}T$ for a paramagnet can simply be replaced by $x = \mu_{\rm B}(H + \beta M)/k_{\rm B}T$ and the two equations (3.19) and (3.20), describing the temperature dependence for a paramagnet, now take the following forms for a ferromagnet

$$M^* = \frac{M(T)}{M(0)} = \tanh x = \tanh \left[\frac{\mu_{\rm B}(H + \beta M(T))}{k_{\rm B}T}\right],$$
 (11.3)

and

$$M^* = \frac{M(T)}{M(0)} = x = \frac{\mu_{\rm B}(H + \beta M(T))}{k_{\rm B}T} .$$
(11.4)

Here the saturation magnetization corresponding to zero temperature is given as before by $M(0) = N \mu_{\rm B}$, where N is the volume density of the spins, and we have introduced the relative magnetization or magnetic order parameter M^* with values $0 \leq M^* \leq 1$. It eliminates the variation of the magnitude of the spontaneous magnetization for different materials and makes the theory "universal", that is independent of specific material properties.

To calculate the spontaneous magnetization we now consider the limit $H \to 0$ and require that both functions (11.3) and (11.4) are satisfied simultaneously. The solutions may be obtained graphically by plotting both functions at various T and determining the points of intersection or today they are readily obtained by computer. The solution for s = 1/2 is plotted in Fig. 11.1. We see that a temperature $T_{\rm C}$ exists where M^* disappears abruptly and that M^* converges to 1 with a derivative $dM^*/dT = 0$ for $T \to 0$.

It is straight forward to derive an expression for $T_{\rm C}$ by considering the intercept of the two expressions for M^* given by (11.3) and (11.4) with H = 0 in the limit $x \to 0$. The condition for interception in this limit is that the slopes of the straight line $M^* = k_{\rm B}Tx/(N\mu_{\rm B}^2\beta)$ and of the function $M^* = \tanh(\mu_{\rm B}\beta M(T)/k_{\rm B}T)$ are equal at the origin. With $\tanh(x) = x$ for $x \ll 1$ one obtains the expression for $T_{\rm C}$ for s = 1/2

$$T_{\rm C} = \frac{N\mu_{\rm B}^2\beta}{k_{\rm B}} = \frac{\mu_{\rm B}}{k_{\rm B}}\,\beta M(0) \ . \tag{11.5}$$

Equation (11.5) allows one to estimate the magnitude of the molecular field constant β from the observed values of $T_{\rm C}$ and M(0) and the Weiss field from the simple expression $H_{\rm W} = k_{\rm B}T_{\rm C}/\mu_{\rm B}$. With the caveat that the expression (11.5) is only valid for systems with atomic spins s = 1/2, we can nevertheless get an estimate of the Weiss fields in the elementary transition metals by use of their measured Curie temperatures. The results are given in Table 11.1.

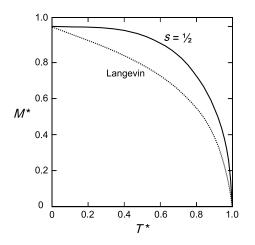


Fig. 11.1. The relative magnetization $M^* = M(T)/M(0)$ for a spin 1/2 magnetic moment and for a macrospin with no direction quantization as derived from the Langevin function versus the reduced temperature $T^* = T/T_{\rm C}$. The ferromagnetic metals Fe, Co, and Ni follow closely the spin 1/2 curve while magnetic materials with large magnetic moments such as Gd (S = 7/2) or complex moments such as magnetite Fe₃O₄ are between the spin 1/2 curve and the Langevin curve.

Table 11.1. Measured Curie temperatures $T_{\rm C}$ for the elemental transition metals and Weiss fields $H_{\rm W}$ calculated from the molecular field expression for spin s = 1/2, $H_{\rm W} = k_{\rm B}T_{\rm C}/\mu_{\rm B}$

element	$T_{\rm C}$ [K]	$\mu_0 H_{\rm W} [{\rm T}]$
Fe	1043	1553
Co^*	1388	2067
Ni	631	949

*Note that Co is hcp at room temperature but is fcc at $T_{\rm C}$.

We see that the Weiss molecular fields are huge. They cannot be produced by currents in wires or coils. The Weiss field, generated by the quantum mechanical exchange interaction discussed in Sect. 6.3, comes free of charge with the appropriate materials. One goal in contemporary magnetism research is to utilize the exchange fields that exist at interfaces (see Chap. 13) and accompany spin polarized currents as discussed in Chap. 14.

The case s = 1/2 is a special case of the general expression for a system with atomic angular momenta J and magnetic moments along the field direction z given by $m_z = g_J \mu_B J_z$ with $-J \leq J_z \leq +J$ (see Sect. 3.2.2). We shall simply state the well-known result for the Curie temperature in this general case [229, 281].

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For a system of atomic angular momenta J with magnetic moments along the field direction z given by $m_z = g_J \mu_B J_z$, the Curie temperature is directly related to the size of the Weiss molecular field $H_W = \beta M(0)$ at T = 0 by the mean field expression

$$T_{\rm C} = \frac{\mu_{\rm B} g_J (J+1)}{3k_{\rm B}} H_{\rm W} . \qquad (11.6)$$

For J = s = 1/2 and $g_J = g = 2$ this expression reduces to (11.5). We shall come back to this expression when we discuss the origin of the Weiss field in the Heisenberg model in Sect. 11.1.2 later.

By introducing the universal temperature scale $T^* = T/T_{\rm C}$, as done in Fig. 11.1, the phase transition occurs at $T^* = 1$. The quantity $M^*(T^*)$ is a universal function valid for any magnetic material irrespective of its specific material properties. From the universal curve one can derive the so-called critical exponent with which the magnetization M^* disappears at $T_{\rm C}$. At small x and s = 1/2 one has $M^* = \tanh(x) = (x - x^3/3)$ and $M^* = T^*x$. Eliminating x yields,

$$M^* = [3(1 - T^*)]^{1/2} . (11.7)$$

The critical exponent in the mean field theory for s = 1/2 is thus 1/2.

It turns out that the general trend of M^* for the atomic magnetic moments of Fe, Co, and Ni is well reproduced by the mean field theory shown in Fig. 11.1, and is actually closest to the s = 1/2 line. However, deviations exist from the s = 1/2 curve at the lowest and highest T^* values. In particular, the critical exponent is found to differ significantly from 1/2 depending on the dimensionality of the sample and on the detailed symmetry of the magnetic interactions. These deviations from the mean field theory are due to spinwaves and critical fluctuations of the spontaneous magnetization as we shall discuss later.

11.1.2 Curie Temperature in the Weiss-Heisenberg Model

In Sect. 6.3.5 we have encountered the Heisenberg Hamiltonian (6.59) which describes the interactions between a pair of spins (i, j) by means of an exchange parameter J_{ij} . In the case of a ferromagnet the strong parallel spin alignment is a cooperative phenomenon that can only be broken by a large thermal energy. It is therefore possible to use the Heisenberg model for the description of the temperature dependence of the magnetization. We get a particularly simple theory if we establish a connection between the Weiss field $H_{\rm W}$ and the Heisenberg model since we can then simply substitute the expression for $H_{\rm W}$ into our general equation (11.6) and we have an analytical expression for $T_{\rm C}$. The connection of J_{ij} to the Weiss field is seen by considering the energy of an atomic moment, corresponding to a *composite atomic spin* s, under the influence of the mean value of all other composite atomic spins. From (6.59) we can write for the energy of a given magnetic moment $\mathbf{m}_i = -g\mu_{\rm B}\mathbf{s}_i$ (where we have defined s to be dimensionless, rather than in units of \hbar)

$$E_i = -2\boldsymbol{s}_i \cdot \sum_j J_{ij} \, \boldsymbol{s}_j = -\, \boldsymbol{m}_i \cdot \boldsymbol{H}_{\mathrm{W}} \,, \qquad (11.8)$$

where the factor of 2 takes care of the double counting over atomic pairs as discussed in conjunction with (6.59). Note that we do not consider individual spins but group them into composite atomic entities, so that the exchange constant J_{ij} reflects the *inter-atomic exchange* between atomic moments. H_W corresponds to the Weiss field

$$\boldsymbol{H}_{\rm W} = -\frac{2}{g\mu_{\rm B}} \sum_{j} J_{ij} \, \boldsymbol{s}_j \; . \tag{11.9}$$

In using the molecular field approximation of the Heisenberg Hamiltonian we have abandoned the coupled two-spin scheme that gives rise to the singlet– triplet splitting in Fig. 6.6 in favor of an independent spin scheme. For example, for a material consisting of identical atomic spins s with an exchange constant J_{ij} per pair (single counting), the energy expressed by (11.8) for a single atomic spin in the Weiss field has the value

$$E_i = -2s \cdot s \sum_j J_{ij} = -2s(s+1) \sum_j J_{ij} .$$
 (11.10)

We can now use expression (11.9) to derive the Curie temperature of a material consisting of identical atomic spins s with an exchange constant J_{ij} per pair. If we abbreviate the sum over the neighbors around the selected atomic spin as $J_0 = \sum_j J_{ij}$ we get for the field magnitude

$$H_{\rm W} = \frac{2\,s}{g\mu_{\rm B}} J_0 \ . \tag{11.11}$$

In deriving an expression for the Curie temperature we then substitute the classical vector product $\mathbf{s} \cdot \mathbf{s}$ in (11.10) by its quantum mechanical expectation value $\mathbf{s} \cdot \mathbf{s} = s(s+1)$. In analogy to expression (11.6) we obtain with J = s and $g_J = g = 2$

$$T_{\rm C} = \frac{2\,(s+1)s\,J_0}{3k_{\rm B}} \ . \tag{11.12}$$

Mapping onto Density Functional Theory: Weiss–Heisenberg–DFT Model

Today, information on the interatomic exchange in materials and its temperature dependence may be obtained by mapping the results of (spin) density functional band theory, discussed in Sect. 7.4.4, onto an effective Heisenberg Hamiltonian [483]. The idea behind such an approach is to use the proven capability of spin density band theory to account for the magnetic ground state at T = 0, and to use the Heisenberg model for the description of the magnetic properties at finite temperature. This is done through spin-wave-like excitations of the magnetization as discussed in Sect. 11.1.5 later. Such an approach is able to theoretically describe not only the low temperature spin wave excitations but can also account for the Curie temperature by an expression similar to (11.12) [222, 483, 484].

In deriving the relevant expression we express the Heisenberg Hamiltonian in a suitable mean field form that separates out fluctuations responsible for temperature dependent effects [281]. In short, one assumes that the atomic spins s_k consist of a mean constant component $\langle s_k \rangle$ and a fluctuating component $s_k - \langle s_k \rangle$, according to

$$s_k = \langle s_k \rangle + \underbrace{(s_k - \langle s_k \rangle)}_{\text{fluctuations}}$$
 (11.13)

When this expression is substituted into the Heisenberg Hamiltonian (6.59)

$$\mathcal{H}_{\text{eff}} = -\sum_{i,j} J_{ij} \, \boldsymbol{s}_i \cdot \boldsymbol{s}_j \,\,, \qquad (11.14)$$

one obtains a new expression that contains a mean field term, which for a given atomic test spin s_i has the form of (11.8) [281]

$$-2\boldsymbol{s}_i \sum_j J_{ij} \langle \boldsymbol{s}_j \rangle . \tag{11.15}$$

From this expression it becomes clear that the mean field energy of an atomic moment with expectation value $\langle s \rangle$ in the field of identical atomic spins with the same expectation value contains a term $\langle s \rangle^2$ instead of the semiclassical $\langle s^2 \rangle = s(s+1)$ term that appeared in the derivation of (11.12). Therefore all we have to do is make the substitution $s(s+1) \rightarrow \langle s \rangle^2$ in (11.12) to obtain an expression that maps onto band theory. We get [222, 483, 484]

$$T_{\rm C} = \frac{2 \, \langle s \rangle^2 \, J_0}{3k_{\rm B}} \,. \tag{11.16}$$

We see that in mean field theory, the thermal energy at the Curie temperature, $k_{\rm B}T_{\rm C}$, becomes equal to one third of the energy of a single spin in the molecular field, given by $E_{\rm W} = 2 \langle s \rangle^2 J_0$. The factor of 1/3 arises from the assumption of

Table 11.2. Heisenberg exchange constants calculated for Fe, Co, Ni by Pajda et al. [484]. Listed are the values $\langle s \rangle^2 J_{01}$ for a nearest neighbor pair, the number of nearest neighbors N, the sum over nearest neighbors $N \langle s \rangle^2 J_{01}$, the total sum over all neighbors $\langle s \rangle^2 J_0$, the Curie temperatures according to (11.16), and the Weiss fields $B_{\rm W} = \mu_0 H_{\rm W}$ calculated from (11.19) with the magnetic moments $m = 2.2 \mu_{\rm B}$ for Fe, $1.7 \mu_{\rm B}$ for Co, and $0.6 \mu_{\rm B}$ for Ni (from Table 12.5)

element	$\langle s \rangle^2 J_{01}$	N	$N\langle s \rangle^2 J_{01}$	$\langle s \rangle^2 J_0$	$T_{\rm C}$	$B_{\rm W}$
	[meV]		[meV]	[meV]	[K]	$[10^3 \mathrm{T}]$
Fe (bcc)	19.5	8	156	183	1414	2.9
Co (fcc)	14.8	12	178	212	1645	4.3
Ni (fcc)	2.8	12	34	51	397	2.9

a continuous spin distribution described by the Langevin function¹, and $T_{\rm C}$, given by (11.16), is therefore also called the Langevin temperature [222].

In Weiss-Heisenberg-DFT mean field theory the Curie temperature is directly proportional to the exchange coupling constant and the square of the expectation value of the atomic spin moments.

Let us take a look at the results from such a model for the elemental ferromagnets Fe, Co, and Ni, calculated by Pajda et al. [484], given in Table 11.2. In the table we list the individual values $\langle s \rangle^2 J_{01}$ for a neighbor pair, the values $N\langle s \rangle^2 J_{01}$, assuming N identical nearest neighbors appropriate for Fe, Co, and Ni metal, and the values $\langle s \rangle^2 \sum_j J_{0j} = \langle s \rangle^2 J_0$ summed over all neighbors, where the sum may contain ferromagnetic (positive J_{ij}) and antiferromagnetic (negative J_{ij}) pair contributions [484]. The last columns in Table 11.2 list the related Curie temperatures and Weiss fields. The latter are given in terms of the atomic magnetic moments m by the expression

$$H_{\rm W} = -\frac{\langle s \rangle J_0}{\mu_{\rm B}} = \frac{2 \langle s \rangle^2 J_0}{m} , \qquad (11.19)$$

and we have taken the magnetic moments from Table 12.5. We see that the calculated Curie temperatures differ somewhat from the experimental values 1043 K (Fe), 1388 K (hcp Co), and 631 K (Ni), listed in Table 12.5.

$$L(x) = \coth x - \frac{1}{x} \approx \frac{x}{3} \tag{11.17}$$

so that

$$\frac{\bar{m}}{m} = \frac{1}{3} \frac{mH}{k_{\rm B}T}.$$
(11.18)

¹In the derivation of (11.16) one considers a magnetic moment m that can assume continuous directions in an external magnetic field H. The average moment along the field direction \bar{m} is given in terms of the Langevin function $\bar{m} = m L(x)$ with $x = mH/k_{\rm B}T$. For small arguments (fields) the Langevin function is given by

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In summary, we have the following approximate values.

For Fe and Co, the Weiss field exchange energy between a pair of atomic spins is of order 20 meV.

• The *total Weiss field exchange energies* are larger by the approximate number of nearest neighbors, i.e. by about 10.

• The Weiss molecular exchange fields are huge with a value of a few thousand Tesla.

11.1.3 Curie Temperature in the Stoner Model

The mean field concept discussed above to account for the Curie temperature is a classical or semiclassical concept based on the interactions of atomic moments. In the original model of Weiss these atomic moments were just little dipoles whose origin was unknown. After the discovery of the spin and the development of quantum mechanics the model was extended by assuming the atomic moments to be composed of quantum mechanical spins, or more generally angular momenta J, with the quantum mechanical expectation value $\langle J^2 \rangle = J(J+1)$. This is the basis of equations (11.6) and (11.12). We have also seen that today we go a step further and map the Heisenberg Hamiltonian onto band structure results. With the expectation values for the atomic spins $\langle s \rangle^2 =$ $(m/g\mu_{\rm B})^2$ replacing the semiclassical expression for the eigenvalues s(s+1)we obtain an equation like (11.12) where the molecular field is expressed in terms of an exchange coupling constant J_0 . This expression tacitly assumes that the atomic moments are dominated by the electron spin and that the orbital moments are negligible. This is indeed a reasonable approximation as discussed in Sect. 12.2.2.

In the mid 1930s when the concept of band theory emerged, Stoner [30,31] developed a new theory of ferromagnetism. His model became very famous at the time because it readily explained the observed noninteger atomic moments in the elemental ferromagnetic metals in terms of their band structure. When temperature dependent effects were included in the model it also made predictions about the low temperature behavior of the magnetization and the Curie temperature. We now appreciate that Stoner attempted to solve an extremely difficult problem, the first principles solution for the temperature dependent magnetization. This problem still remains unsolved today [222]. In retrospect it is therefore no surprise that the Stoner model fails in the description of the temperature dependence and especially the Curie temperature. This recognition did not come easy and it took more than 50 years of heated discussions about the validity of the Stoner model for the description of finite temperature magnetism [281, 485]. Today the shortcomings of the Stoner model are well recognized and it is common in practise to treat the temperature dependence

of the magnetization, for lack of a better theory², by means of the mean-field Weiss-Heisenberg model. We shall therefore not go into mathematical details of the temperature dependence of the Stoner model but just state the important points for completeness. The interested reader is referred to the book by Mohn [281] for more details.

The essence of the *Stoner model* are three basic assumptions:

- The magnetic moments in Fe, Co, and Ni are due to the d shell, which through the formation of periodic bonds takes the form of energy bands.
- The energy of the bands containing different spins, labelled "up" and "down", are shifted relative to each other under the influence of a molecular exchange field.
- The up and down bands are filled according to Fermi statistics and the Fermi function describes the temperature dependence.

As discussed in Sect. 7.4.2 the Stoner picture consists of spin-up and spindown bands that are shifted relative to each other by the so-called exchange splitting $\Delta \simeq 1$ eV, whose origin is assumed to be the molecular field. For the case of a "strong ferromagnet", as shown in Fig. 7.7, one spin band, called the *majority band*, is completely filled and the highest states in this band have a separation from the Fermi level called the *Stoner gap* $\Delta_{\rm S}$ (see Fig. 7.7). The electrons are filled into the bands up to the Fermi energy. The difference between the number of electrons in the majority and the less-filled *minority band* is the magnetic moment in units of $\mu_{\rm B}$. The success of this model is the prediction of noninteger values of the magnetic moments in the transition metals Fe, Co, and Ni, as discussed in detail in Sect. 12.2.2. In general, an approximate relationship indeed exists between the exchange splitting and the size of the atomic moments as shown in Fig. 11.2.

The model is far less successful in predicting the temperature dependence of the magnetization. It was worked out by Stoner assuming, most importantly that the temperature dependence is determined by changes in the Fermi distribution function, which leads to changes in the DOS at the Fermi level. At a temperature below $T_{\rm C}$ the number of spin-up (N^+) and spindown (N^-) d electrons in the two bands, which give the magnetic moment $m = \mu_{\rm B}(N^- - N^+)$, is given in terms of the T = 0 DOS D(E) by the famous Stoner equation [281]

$$N^{\pm} = \int_0^\infty D(E) \left[e^{(E - \eta^{\pm})/k_{\rm B}T} + 1 \right]^{-1} \mathrm{d}E, \qquad (11.20)$$

where $\eta^{\pm} = \mu \pm \mu_{\rm B} H_{\rm mol} \pm \mu_{\rm B} H_{\rm ext}$ is given in terms of the chemical potential μ , the molecular field $H_{\rm mol}$, and external magnetic field $H_{\rm ext}$. This leads to the *Stoner criterion* for spontaneous magnetic order

 $^{^{2}}$ A generalization of density functional theory to finite temperature was derived by Mermin in 1965 [486] but we presently do not know a physical meaningful approximation to the finite temperature exchange correlation potential.

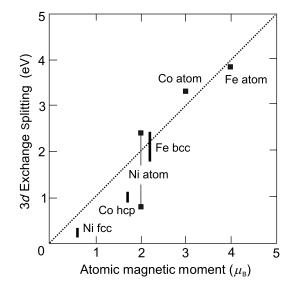


Fig. 11.2. Correlation between size of atomic moments for Fe, Co, and Ni and the 3d exchange splitting, determined from experimental data, taken from Himpsel [487]. The dashed line corresponds to an approximate correlation of 1 eV/ $\mu_{\rm B}$

$$\frac{2\mu_{\rm B}H_{\rm mol}^0}{N} D(E_{\rm F}) \ge 1 , \qquad (11.21)$$

where H^0_{mol} is the molecular field at T = 0 and $N = N^+ + N^-$ is the number of d electrons per atom. The criterion predicts the existence of magnetic order if either the molecular field or the density of states at the Fermi level $D(E_{\text{F}})$ is large. It suggests that only systems with d or f electrons that have potentially large values of $D(E_{\text{F}})$ can be magnetic.

The Curie temperature is determined by the temperature dependent Stoner criterion which can be written as,

$$\frac{2\mu_{\rm B}H_{\rm mol}^0}{N} \int_0^\infty D(E) \left| \frac{\partial f(T_{\rm C})}{\partial E} \right| dE = 1 .$$
(11.22)

The Fermi function is given by

$$f(T) = \frac{1}{\mathrm{e}^{(E-\mu)/k_{\mathrm{B}}T} + 1} \ . \tag{11.23}$$

As the temperature increases the convolution of the DOS with the function $\partial f(T_{\rm C})/\partial E$ leads to a decrease of the DOS at the Fermi level until the left side in (11.22) becomes equal to 1. Because the exchange splitting Δ is found to be of the order of 1 eV from detailed density functional band structure calculations, corresponding to a temperature of about 10,000 K, one easily sees that the Stoner model has significant problems explaining the observed Curie temperatures around 1,000 K.

The Stoner theory makes certain predictions which have proven problematic and in some cases do not agree with experiment. The most important predictions are:

- The Curie temperature scales linearly with the magnetic moment.
- At the Curie temperature the magnetic moment of each individual atom vanishes.
- The susceptibility above $T_{\rm C}$ follows roughly a quadratic temperature dependence instead of the experimentally observed Curie–Weiss law.
- The predicted Curie temperatures are of order 5,000–10,000 K.

The last point, in particular has caused considerable debate. It is resolved by understanding the meaning of the "exchange splitting" $\Delta \approx 1-2$ eV in the Stoner model and the meaning of "exchange energy" $E_{\rm W} \simeq 300$ meV in conjunction with the Weiss–Heisenberg model. Let us take a closer look at the meaning of "exchange".

11.1.4 The Meaning of "Exchange" in the Weiss–Heisenberg and Stoner Models

The meaning of "exchange" in solids goes to the very heart of the origin of magnetic order. It has a long history of controversy and some confusion exists to this day. At the root of all this is the historical mystery that the Stoner model, despite all its success to account for the fractional magnetic moments, predicts a Curie temperature that is nearly an order of magnitude too large [485,488]. Related to this problem are general questions about the temperature dependence of local moments and the exchange splitting, particularly the question whether the exchange splitting and the atomic magnetic moments vanish at the Curie temperature.

The resolution to these problems lies in the distinction of the meaning of "exchange" with respect to the Weiss molecular field model and the Stoner band model. For the following discussion we refer to Fig. 11.3, where we have illustrated in simple terms the meaning of "exchange" in different situations.

As discussed in Chap. 6 the concept of exchange emerged in the late 1920s through Heisenberg's calculation for the He atom and the Heitler-London calculation for the H₂ molecule, leading to the phenomenological Heisenberg Hamiltonian, given by (6.59). Today we closely associate the term "exchange" with the coupling constant J and energy of the Heisenberg Hamiltonian. At the top of Fig. 11.3 we have reviewed the meaning of exchange in a two-electron atom. It corresponds to the singlet-triplet splitting of the coupled two-electron system which has the value 2J, as discussed in Sect. 6.3.5.

In the middle of Fig. 11.3 we illustrate the meaning of exchange in the Weiss model, cast in terms of the mean-field Heisenberg Hamiltonian, as discussed in Sect. 11.1.2. Today we map this effective field model onto the band model, calculated within density functional theory, so that the values

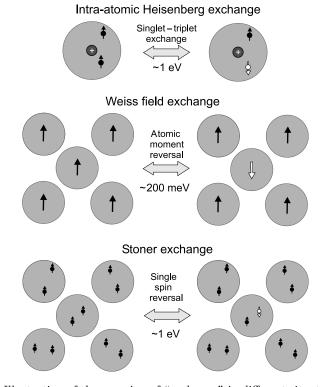


Fig. 11.3. Illustration of the meaning of "exchange" in different situations and pictures. On top we illustrate the original idea of exchange in two-electron atoms. This is captured by Heisenberg's Hamiltonian for the two electron case, giving rise to a singlet–triplet splitting of order 1 eV. In the middle the molecular field concept of Weiss is illustrated. When cast into the formalism of a mean field Heisenberg model the exchange energy corresponds to the reversal of an atomic spin, composed of all unpaired intra-atomic spins, in the Weiss field of all other atoms. At the bottom the origin of the Stoner exchange energy, sometimes called spin-flip energy, corresponds to the reversal of a single electron spin in the sea of all other electrons in the sample. In energy it is close to the intra-atomic exchange value, about a factor of 5 larger than the inter-atomic exchange in the Weiss model

of the atomic moments and the ground state energy matches at zero temperature. In this Weiss–Heisenberg–DFT model the "exchange energy" is given by $E_{\rm W} = 2\langle s \rangle^2 \sum_j J_{0j}$, where the sum is over all neighbors j of the central atom i = 0 characterized by pairwise (single counting) "exchange constants" J_{0j} . It reflects the energy of a central spin i = 0 with expectation value $\langle s \rangle$ in the field of all other spins j with the same expectation values $\langle s \rangle$. We have seen that in practice a good estimate of the total "exchange energy" is simply obtained by multiplying that of a nearest neighbor pair $2\langle s \rangle^2 J_{01} \approx 30$ meV by the number of nearest neighbors (≈ 10) giving a value of about 300 meV. The Weiss–Heisenberg–DFT model therefore describes the temperature dependence of the magnetization through the concept of a molecular field, established through interatomic interactions between atomic moments, which vanishes at the Curie temperature. Thus for $E_{\rm W} \simeq 300$ meV we have a Curie temperature $T_{\rm C} = E_{\rm W}/3k_{\rm B} \approx 1,000$ K, in reasonable accord with observations.

The bottom of Fig. 11.3 illustrates the meaning of "exchange" in the band model of Stoner. This is the case that has caused so much headache. In the Stoner band model, discussed in Sect. 11.1.3, there exists a splitting between the centers of gravity of the spin-up and spin-down bands, the "Stoner exchange splitting", which from density functional band calculations is found to be about $\Delta \approx 1-2$ eV, as discussed in Sect. 12.2.1 later. When it is assumed that the Stoner exchange splitting vanishes at the Curie temperature one is led to values of $T_{\rm C}$ that are several thousand K [488], in gross contradiction to measured values of about 1,000 K.

In Fig. 11.4 we have summarized the correlation between experimentally observed atomic moments in Fe, Co, and Ni and the exchange splitting determined by photoemission and band theory (left) and the experimental Curie temperatures (right). The difference in the associated energies clearly illustrates the difference of the "exchange energies" associated with the Stoner and Weiss–Heisenberg models. Note that for the transition metals the linear relationship between experimental exchange splitting and atomic moments (also see Fig. 11.2) only holds approximately, while theory predicts a linear relationship.

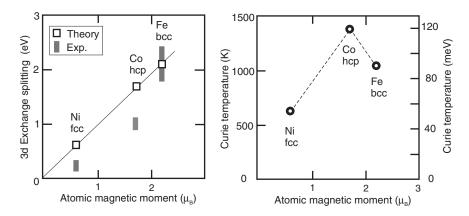


Fig. 11.4. Relationship between size of atomic moments for the transition metals Fe, Co, and Ni and the 3d exchange splitting (*left*) and the Curie temperature (*right*). The magnetic moments are from magnetization measurements (from Table 12.5), the experimental exchange splitting is from photoemission spectroscopy [487], the theoretical splitting is from Fig. 12.1, and the Curie temperatures are from Table 12.5

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The reason for the different energies associated with the Stoner exchange splitting Δ and $T_{\rm C}$ is as follows. The Stoner exchange splitting corresponds to the energy required to reverse a single electron spin in the sea of all other unpaired electrons in the crystal, as shown schematically at the bottom of Fig. 11.3. A Stoner excitation is therefore also called a *spin-flip* excitation of a single electron spin. The large difference between the Stoner exchange energy and the Weiss exchange energy arises from the fact that starting with a given single electron spin the intra-atomic Coulomb interactions are large and they are responsible for most of the energy that it takes to reverse a single spin in an atom. As the distance from the central single spin increases the interatomic Coulomb interactions are rapidly screened by the s-p conduction electrons in a metal and do not contribute significantly to the Stoner exchange energy. One may thus say that the Stoner energy characterizes the intra-atomic moment formation while the Weiss-Heisenberg energy reflects the inter-atomic exchange responsible for long range ordering and hence $T_{\rm C}$. This explains why local moments survive far above $T_{\rm C}$ as attested by the Curie–Weiss behavior of the susceptibility. Local moments should eventually cease to exist at very high temperatures but to our knowledge this has not been verified experimentally.

We can summarize as follows.

The *Stoner exchange splitting* is the energy needed to reverse the spin of *one electron* in an itinerant ferromagnet. It is the relevant energy for local moment formation.

The Weiss-Heisenberg exchange interaction is the energy needed to reverse the magnetic moment of one atom, composed of all uncompensated spins in the atomic volume, in the mean field of all other atomic moments. It is the relevant energy for long range interatomic ordering and determines $T_{\rm C}$.

11.1.5 Thermal Excitations: Spin Waves

We have seen above that the Curie temperature cannot be accounted for by considering Stoner or spin-flip excitations associated with the reversal of single electron spins because the energy associated with such spin flips is too large. Therefore Stoner excitations cannot be responsible for changes in the magnetization below $T_{\rm C}$ associated with small energies. We have discussed in Sect. 11.1.1 that in Fe, Co, Ni, and other magnetic materials the low temperature dependence of M^* lies somewhere between the two curves shown in Fig. 11.1. The decrease in magnetization at temperatures $T \ll T_{\rm C}$ therefore needs to be caused by a new excitation mechanism.

Such an excitation mechanism was first proposed by Felix Bloch in 1930 [141]. The excitations are called *spin waves* or *magnons* and involve many lattice sites. To understand spin waves, one again uses the mean field Weiss–Heisenberg model. In particular, we are interested in small excitations of the

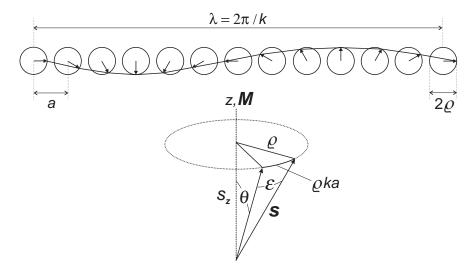


Fig. 11.5. The upper part describes the motion of a classical spin s in a plane perpendicular to the magnetization when a spin wave or magnon is excited. The amplitude of the spin wave is ρ . If the wavelength of the spin wave is λ , then $\lambda = Na$ where a is the lattice parameter and N the number of involved sites. The lower part of the figure shows the angle ε between neighboring spins and its connection to the amplitude ρ

spins about their equilibrium orientation. With the knowledge of Sect. 11.1.2 it is easy to calculate the excitation energy for a pair of spins. It is given by the difference in energy between a state where the spins are parallel and where they include a small angle ε . For the case of the two identical spins s the excitation energy over the parallel spin configuration ($\varepsilon = 0$) in the ground state is given by

$$\Delta E = 2Js^2[1 - \cos \varepsilon] \cong Js^2\varepsilon^2 . \tag{11.24}$$

This shows that we can have a whole range of small excitation energies and that the excitation vanishes with ε^2 .

Next we consider a chain of spins as illustrated in Fig. 11.5, producing a *spin wave*. The spins on adjacent sites precess with a well defined phaseshift and the magnon wavelength is defined by the distance between sites over which a 360° precession occurs. The spin wave amplitude ρ is defined as the radius of spin precession about M. If N spins are involved, the spin wave excitation energy is simply given by N times that of the two spin system, i.e.,

$$\Delta E = N J s^2 \varepsilon^2 , \qquad (11.25)$$

Spin waves or magnons consist of a number of spins that coherently precess about the magnetization direction M.

We can express the energy given by (11.25) also as a function of different quantities defined in Fig. 11.5. We assume that ε is small which is the case

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when many spins are involved and hence N is large. For the length of the arc between two neighboring spins we have $2\pi \rho/N = 2\pi \rho a/\lambda = \rho ka$, where $k = 2\pi/\lambda$ is the wave vector of the spin wave and a the lattice constant. We then obtain $\varepsilon \sim \sin \varepsilon = \rho ka/s$, where we have made the "classical" approximation |s| = s for the spin moment.³

In order to go further we need to combine the classical model shown in Fig. 11.5 with the quantum theoretical concept for the spin, derived in Sect. 8.4. We would like to map a Stoner excitation, consisting of a single spin that is flipped in the down direction as illustrated in Fig. 11.3, onto the situation where a chain of N spins, distributed over N different lattice sites contains one spin that is in the spin down direction. Then all N individual electrons participating in the spin wave have a small but nonvanishing probability to be in the down spin state, and the phase of the down spin state is related to the phase of the wave-function of the neighboring electrons. We know from Sect. 8.4.3 that the total spin polarization P_z of an ensemble of N electrons is given by $P_z = (N^{\uparrow} - N^{\downarrow})/(N^{\uparrow} + N^{\downarrow})$, where in our case $N^{\uparrow} = N - 1$ and $N^{\downarrow} = 1$, so that $P_z = (N-2)/N$. By use of (8.15) we then obtain for the component s_z of the individual spins $s_z = P_z/2 = (1/2) - (1/N) = s - (1/N)$. This allows us to obtain the precession radius of the individual spins $\rho = \sqrt{1/N}$ in Fig. 11.5 by use of the triangulation relation $\rho^2 = s^2 - s_z^2$ and neglecting a quadratic term $1/N^2$ which is small for large N.

Combining the two results $\varepsilon = \rho ka/s$ and $\rho = \sqrt{1/N}$ we can then rewrite the total energy contained in a spin wave, given by (11.25), in terms of a dispersion relation of the spin wave energy with wavevector k, according to

$$\Delta E = \hbar \omega = Ja^2 k^2 = Dk^2, \qquad (11.26)$$

where D is often called the *spin wave stiffness*. The energy of a spin wave thus tends to zero with decreasing k or increasing wavelength λ so that excitations of the magnetization with arbitrarily small energy are possible.

The spin wave model distributes the spin-flip of a single electron, a Stoner excitation, over many lattice sites.

The spin wave angular momentum corresponds to a single electron spin flip $|\Delta s_z| = \hbar$.

The spin wave *energy* depends on the wavelength λ . It ranges from the Stoner spin flip energy for short λ to nearly zero for large λ .

Spin waves or magnons may be considered as particles with an energy $\hbar\omega$, a linear momentum $\hbar k$ and an angular momentum $\pm\hbar$. The even angular momentum tells us that spin waves are Bosons, obeying Bose-Einstein statistics.

³In quantum mechanics $\langle s \rangle = \sqrt{S(S+1)}$. We note that the full quantum mechanical derivation yields the same final result given by (11.26), but our semiclassical derivation is shorter.

Spin waves have an even angular momentum and are therefore Bosons.

This is important for the stability of magnetism. Bosons can accumulate in one and the same state. Hence when the temperature is raised above zero, all the thermal energy could go into the generation of very long wavelength spin waves, destroying magnetic order right away. Such excitations, however, cannot occur if there is an energy gap that inhibits low energy excitations of the magnetization. This is the basis of the famous *Mermin-Wagner theorem*, stating that a 2-dimensional thin film cannot be magnetic unless it possesses a magnetic anisotropy that generates an energy gap for the long wavelength spin waves. Magnetic anisotropy generates an easy direction of the magnetization in the solid and will be discussed in detail later.

The most important fact to know about spin waves is that they explain the temperature dependence of the magnetization for 3-dimensional ferromagnetic materials in the range $T^* \leq 0.3$. The temperature dependence follows the $T^{3/2}$ -law,

$$M(T) = M(0) \left[1 - \kappa C T^{3/2}\right], \qquad (11.27)$$

where C is a constant that contains the spin wave stiffness, and the factor $\kappa = 1$ in the bulk but $\kappa \neq 1$ at the surface, as we shall see. To derive this equation, one must integrate over all the spin waves excited at the temperature T. The average number n_k of spin waves with a given wave vector k, corresponding to an average number of reversed spins, at a certain temperature T, is just given by Planck's distribution formula,

$$n_k = \frac{1}{\mathrm{e}^{E_k/k_{\mathrm{B}}T} - 1} \tag{11.28}$$

Integrating this over the number of k-states between k and k + dk yields the famous $T^{3/2}$ -law (11.27).

The probability to find a spin wave is different at the surface compared to the bulk. In most cases, the surface is a free end for the spin waves. If this applies, the surface must be the location of an antinode. The probability to find a spin wave is proportional to the square of the amplitude of the spin wave which is $\cos^2 kx$. Hence in the hypothetical case that the exchange constant J is the same at the surface as in the bulk, one expects that the probability of a spin wave is just twice as high at the surface compared to the bulk. This arises because in the bulk we have the average value of $\cos^2 kx = 1/2$ while at the surface with x = 0, $\cos^2 kx = 1$ [489]. If however the exchange is weakened on a path perpendicular to the surface compared to the spherically averaged exchange in the bulk, the probability to find a spin wave at the surface will increase. Yet it has also been observed that J^{\perp} increases which leads to a reduction of the spin wave probability accurs when it generates a large demagnetization field at the surface as in Sect. 15.5.2. Hence generally

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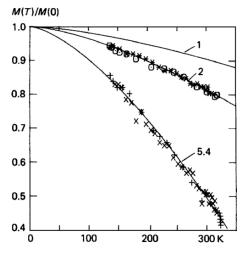


Fig. 11.6. Temperature dependence of the relative magnetization M^* in the amorphous ferromagnet FeNiB_{0.5} with $T_{\rm C} = 700$ K [491]. The lines are calculated from (11.27) with the factor κ as indicated. The measurement of M^* in the bulk ($\kappa = 1$) is done with a Josephson magnetometer, while the magnetization of the clean surface ($\kappa = 2$) and the surface with 1/2 monolayer or Ta ($\kappa = 5.4$) is determined from the measurement of the spin polarization of the low energy cascade electrons, excited with a primary unpolarized electron beam of 3 keV energy

one expects that the magnetization at a free surface or at an interface to a nonmagnetic material decreases according to the $T^{3/2}$ -law (11.27), but with a constant $\kappa \neq 1$. This is illustrated in Fig. 11.6.

The temperature dependence of the surface magnetization has been measured by elastic scattering of polarized electrons from the surface [492]. The exchange interaction makes this scattering dependent on the relative orientation of the magnetization and the spin of the scattering electrons as discussed in Sect. 13.3.1. The elastic scattering at an energy of 100 eV has the lowest possible magnetic probing depth of about 3 atomic layers from the surface. It shows the $T^{3/2}$ law as predicted. However, fractions of a monolayer of a nonmagnetic metal may cause a dramatic decrease of the spinwave stiffness and lead to a much larger constant in front of $T^{3/2}$. Therefore, one has to be aware that interfaces might exhibit a drastically reduced magnetization at finite temperature [491], as illustrated in Fig. 11.6.

Spin wave spectra are obtained from inelastic neutron scattering and inelastic scattering of light, called *Brillouin scattering*. The experimental spectra are of course more complex than suggested by (11.26). Spin waves can also be excited with electron beams, but the cross-section for spin wave excitation with electron beams is smaller compared to the cross-section for single electron excitations [493].

11.1.6 Critical Fluctuations

Theory predicts critical fluctuations of the order parameter near the ordering temperature $T_{\rm C}$ [494]. This means that the magnetization does not vanish as postulated by the mean field theory and as shown in Fig. 11.1. Rather, correlated regions, so-called "spin blocks" of spontaneously magnetized material form and dissolve at temperatures close to $T_{\rm C}$, as illustrated in Fig. 11.7.

The experimental investigation of the temperature dependence of the spontaneous magnetization has been a challenge for a long time. To appreciate the difficulties arising in the early experiments and the progress made with recent techniques, one must realize the difference between the spontaneous magnetization and the saturation magnetization in an external field. The measurement of the spontaneous magnetization is not possible directly with the classical methods of magnetization measurement because it requires a magnetically saturated macroscopic piece of material. This means that the Weiss domain structure has to be removed which can only be done by applying an external magnetic field until M reaches saturation. Extrapolation of M to $H \to 0$ then yields the spontaneous magnetization. M^* determined with this method invariably shows a tail extending to $T > T_{\rm C}$ instead of disappearing abruptly at $T \to T_{\rm C}$. It was never quite clear whether this tail was due to impurities generating crystallites with different Curie temperatures or whether it was a genuine property of the clean material.

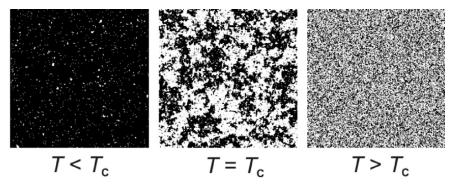


Fig. 11.7. Instantaneous images of the magnetization calculated by means of Monte Carlo simulations for a 2D Ising system with periodic boundary conditions. Regions of opposite magnetization directions are shown as black and white. In the simulation, carried out for a 250×250 lattice, the ordering temperature is $T_{\rm C} = 2.42 J/k_{\rm B}$, slightly higher than the Onsager solution $T_{\rm C} = 2.269 J/k_{\rm B}$ for an infinite lattice. At $T_{\rm C}$ the domain structure, at an instantaneous point in time, is shown in the middle image. The other two simulations are for $T = 2.0 J/k_{\rm B}$ (ferromagnetic regime), shown on the left, and for $T = 3.0 J/k_{\rm B}$ (paramagnetic regime), shown on the right

A further related problem is that at temperatures close to $T_{\rm C}$, M(H) approaches saturation only gradually making the extrapolation of M to zero field uncertain. In fact, the M(H) curves in a neighborhood of $T_{\rm C}$ look as if huge magnetic moments would be aligned in an external field against thermal motion, that is the M(H) curves look like Langevin-functions at T = const. The lower half of Fig. 11.8, later, shows such a magnetization curve observed at $T = T_{\rm C}$ with a very thin film of Fe.

Néel was the first to propose that the appearance of large clusters of spontaneously magnetized material on approaching $T_{\rm C}$ must be the cause of this phenomenon. Such clusters behave like paramagnetic uncoupled macrospins. The important difference to fluctuating superparamagnetic particles (see Sect. 11.5.2) is that the spin "blocks" are not anchored to one specific location, they will appear and dissolve in varying places. Figure 11.7 also illustrates that the "blocks" have a rather fractal like appearance. The magnetization curves close to $T_{\rm C}$ provide in fact the most direct evidence that spontaneously magnetized spin-blocks are present at $T^* \sim 1$. Further evidence for the existence of critical fluctuations is now abundant but it remains a challenge to this day to image the elusive spin blocks directly since their lifetime is short and their size is small.

Figure 11.8 shows the remarkable results for the temperature dependence of M^* with an ultrathin magnetic Fe film. Pescia and collaborators [495] grew epitaxial Fe films on top of a single crystal W(110) surface. These films order ferromagnetically and have an easy axis of magnetization along the in-plane [110] direction. Films of thickness 1–2 atomic layers consist of one complete atomic layer of Fe followed by a two dimensional (2D) network of irregular patches with a $T_{\rm C}$ around room temperature. By applying an external fieldpulse along the easy direction, the films can be brought into a state which is homogeneously magnetized in the easy direction. The magneto-optic Kerr effect provides then a signal that is proportional to the spontaneous magnetization without applying a magnetic field. In fact, the susceptibility of M^* to external magnetic fields is so large that the magnetic field of the earth has to be compensated to detect the intrinsic $M^*(T)$.

At $T_{\rm C} = 316.77 \,\mathrm{K}$, M^* shows an extremely sharp transition to zero. The magnetization $M^*(T)$ drops to zero for $T \to T_{\rm C}$ with a critical exponent close to 1/8, as predicted in the 2D *Ising model*. In this model, appropriate for the present uniaxial system, the spin on each site can only be up or down, and neighboring sites have an energetic preference of aligning along the same direction, mediated by the exchange interaction. The temperature dependence is consistent with a magnetic correlation length of $\ell \simeq 1 \,\mu$ m. Evidently, the existing morphological defects such as monoatomic steps and the steps due to patch formation during growth are not able to interrupt the correlation. The large lateral correlation length, which is much larger than the film thickness, is the key to observing the true 2D phase transition. The correlation length can be estimated from the graph in the lower part of Fig. 11.8 showing that the spin

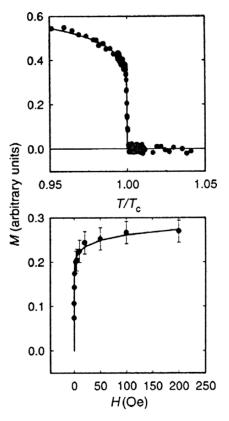


Fig. 11.8. Top: temperature dependence of the relative magnetization $M^*(T)$ observed with the magneto-optic Kerr-effect in 1.7 ± 0.1 monolayers of Fe on a W(110) substrate [495]. The temperature dependence of $M^*(T)$ for $T \to T_{\rm C}$ is close to that predicted in the 2D *Ising model. Bottom*: $M^*(H)$ at $T = T_{\rm C} = 316.77$ K yielding evidence for very large spin blocks that can be aligned against thermal agitation by applying only 0.2 Oe. The number N of spins in a spin block is estimated from $N\mu_{\rm B}H/k_{\rm B}T_{\rm C} = 1$, where $H \sim 0.3$ Oe = 24 A/m

blocks are aligned in an external field of $H \simeq 0.2$ Oe. From $N\mu_{\rm B}H = k_{\rm B}T_{\rm C}$, where N is the number of spins in a spin block, one obtains $N = 2.4 \times 10^7$ spins/block. Associating each Fe atom in a bcc lattice with a moment of $\sim 2\mu_{\rm B}$, we see that a spin block indeed covers an area of $\sim 1\,\mu\,{\rm m}^2$ that is $\ell \simeq 1\,\mu\,{\rm m}$. The field dependence of M^* at $T = T_{\rm C}$ also makes it evident that the initial susceptibility defined by $\partial M/\partial H$ for $H \to 0$ is enhanced by 4 orders of magnitude compared to the values observed in the bulk of Fe. Theoretically, the initial susceptibility should diverge at $T \to T_{\rm C}$ like $\chi = {\rm const.}(T - T_{\rm C})^{-1}$ but this is not quite observed since spins are pinned at defects and the temperature cannot be stabilized sufficiently.

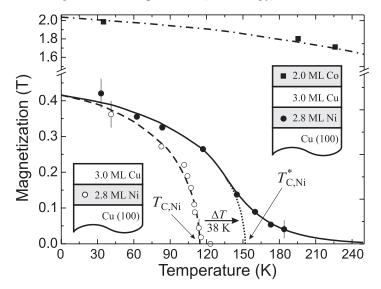


Fig. 11.9. Temperature dependence M(T) of the magnetization observed with XMCD in an isolated Ni film (*circles*), and same Ni-film coupled to a ferromagnetic 2D Co-film (*squares*) over a very thin Cu spacer layer as indicated. The proximity of the FM Co-film produces a large shift $\Delta T^*_{C,Ni} = 38 K$ of the pseudo-phase transition in Ni as well as long tails of M(T) extending far above $T_{C,Ni}$. The solid and dot dashed lines are guides to the eye. Courtesy of Andreas Scherz [496]

Today, the theory of continuous phase transitions has gone far beyond mean field theory. We understand where and why the mean field theory fails, and how the magnetic phase transition depends on the symmetry of the magnetic interactions and on the dimensionality of the sample, be it the surface or the bulk of a 3-dimensional body, a 2-dimensional magnetic thin film, or a quasi 1-dimensional wire. Contemporary spectroscopic techniques have added already substantially to the understanding of the continuous phase transition. In particular, the ability to measure the magnetization or at least the temperature dependence of the magnetization without applying a magnetic field has resulted in a much clearer picture of the magnetic phase transition.

As an example for the progress being made, we show the phase transition of a coupled magnetic system consisting of two ferromagnetic 2D-films F1 and F2 separated by a nonmagnetic spacer layer. With XMCD, the magnetization $M_1(T)$ and $M_2(T)$ can be observed independently for each film since the measurement of M(T) with X-rays is atom specific. Figure 11.9 shows that an ultrathin Ni-film of 2.8 monolayers (ML), taken by itself, orders at $T_C \approx 120$ K. But if a 2D-Co-film of 2 ML with a much higher T_C is placed on top of the 3 ML nonmagnetic Cu-spacer layer, $M_{\rm Ni}(T)$ changes dramatically. First of all, M(T) vanishes much more gradually with a large tail extending to higher temperatures. Secondly a turning point of M(T) exists with a susceptibility maximum, suggesting a pseudo-phase transition at a much increased $T_{\rm C,Ni}^*$. A pseudo-phase transition is expected to take place in coupled systems which can, according to theory, have only one single true phase transition. Hence the tail of $M_{\rm Ni}(T)$ will extend up to the Curie-point of the Co-film. The large shift of the critical pseudo-phase transition temperature upon proximity of a ferromagnet with high $T_{\rm C}$, does not exist in 3D systems but only in systems with reduced dimensionality.

One intriguing point of these studies is the existence of the interlayer exchange coupling (IEC) discussed in Sect. 13.4.5 later. IEC can be positive or negative or zero depending on the thickness of the Cu-spacer layer. By adjusting the thickness of this spacer layer, the effective exchange coupling between the films and thus the Curie temperature can be manipulated. In fact, two groups have studied the Co/Cu/Ni system with XMCD [496, 497]. The result is that the experiment and the theory based on a Heisenberg-model give evidence that the transfer of a static exchange field from the Co-film into the Ni-film is not sufficient to understand the large tail of M(T) or the large change of the pseudo- $T^*_{C,Ni}$. Rather, higher order spin-spin correlations appear to be important to quantitatively understand the observed M(T) [496].

Great progress is expected in the future. This expectation is based on the fact that, in particular, X-ray based spectroscopies and microscopies are able to determine the spontaneous magnetization without applying a magnetic field, an important prerequisite when testing the theory of continuous phase transitions. X-rays offer the ultrafast measurement capabilities of lasers yet overcome their Achilles' heel, the diffraction limit set by the relatively long laser wavelength (of order of 200 nm or longer). Speed and spatial resolution are important assets when trying to investigate the fluctuations predicted by theory.

It may even be possible to directly image the elusive spin blocks in a time resolved experiment. In principle, a temporal snapshot of the magnetization M^* can be recorded at a time resolution solely determined by the length of the X-ray pulse, provided that there are enough photons in a single pulse to yield a low noise image. This appears possible with the advent of an X-ray free electron laser where a single X-ray pulse of femtoseconds duration contains about 10^{13} photons, a number presently available at advanced synchrotron facilities by integrating over 1 s. The lifetime of a spin block is proportional to the initial susceptibility, but the actual lifetime cannot be predicted with confidence as the dynamic scaling arguments are not as well founded as the static ones [494]. Direct imaging could prove that the spin blocks appear at arbitrary locations and are not pinned to fixed sites. Magnetization fluctuations of ferromagnetic particles of a somewhat higher $T_{\rm C}$ anchored at impurities could be mimicking critical fluctuations.

11.2 The Magnetic Anisotropy

Experimentally it is found that the magnetization M tends to lie along one or several axes in the magnetic solid. It costs energy to turn it into any direction different from the preferred axes, called the *easy axes*. As mentioned in Sect. 7.9 in the context of the spin–orbit interaction we can define the magnetic anisotropy as follows.

The *magnetic anisotropy* is defined as the energy that it takes to rotate the magnetization direction from the easy into the hard direction.

Magnetic anisotropies may be generated by the electric field of the solid or crystal, by the shape of the magnetic body, or by mechanical strain or stress, all of which are characterized by *polar* vectors. Hence they cannot define a unique direction of the magnetization which is an *axial* vector. This is why no unique anisotropy direction can exist but only a unique axis. The energy density E_{ani} connected with the magnetic anisotropy must therefore be constant when the magnetization is inverted, which requires that it be an even function of the angle γ enclosed by M and the magnetic axes,

$$E_{\rm ani} = K_1 \sin^2 \gamma + K_2 \sin^4 \gamma + K_3 \sin^6 \gamma + \cdots, \qquad (11.29)$$

where K_i (i = 1, 2, 3, ...) are the anisotropy constants with dimensions [energy/volume] and units $[J m^{-3}]$. This is only a series expansion. Depending on the magnetic material and on the specific experiment, one might have to add more higher order terms.

We note that without the existence of magnetic anisotropy, 2D objects such as thin films could not order magnetically as already mentioned, and even in 3D samples, the magnetization would twist itself into interwoven curls and be hardly observable [124]. This happens because the exchange interaction is short range and the magnetization can thus be rotated over a distance called the magnetic coherence length into a new direction at a very low expense of energy.

Very often one encounters the need to represent the magnetic anisotropy by an effective magnetic field $H_{\rm ani}$ constructed to simulate the effect of the magnetic anisotropy. $H_{\rm ani}$ is called the anisotropy field. It must be parallel to the easy axis to keep M there, but it must change sign when M changes sign. If M deviates from the easy axis, $H_{\rm ani}$ induces a precession of M around the easy axis until the damping of the precession forces M back into the easy direction. We derive $H_{\rm ani}$ for the simplest, but most important case of uniaxial anisotropy where only $K_1 \neq 0$ (with higher anisotropies, $H_{\rm ani}$ is derived analogously, but can have more than one direction.) According to (11.29), the effective torque acting on the magnetization is given by $\partial E_{\rm ani}/\partial \gamma = 2K_1 \sin \gamma \cos \gamma$.

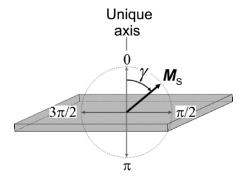


Fig. 11.10. In general, the angle γ in (11.29) is defined as the direction of the saturation magnetization $M_{\rm S}$ with respect to a *unique axis* of the sample. For a thin film, the unique axis is often chosen to lie along the normal of the film, as shown. Note however, that in case of a strong in-plane uniaxial anisotropy the unique axis is sometimes defined as the in-plane easy axis

We postulate that this torque is equal to the torque $\mathbf{M} \times \mathbf{H}_{ani} = M H_{ani} \sin \gamma$ that the effective anisotropy field exercises on \mathbf{M} . This yields

$$H_{\rm ani} = \frac{2K_1}{M} \cos \gamma. \tag{11.30}$$

We see that $H_{\rm ani}$ indeed simulates a preferred axis since it changes sign when γ goes through $\pi/2$. The anisotropy field can be added vectorially to the other axial magnetic fields, exchange and applied, in order to calculate quantities like the precession frequency of M in magnetization dynamics or in magnetic resonance.

The first order term K_1 is usually much larger than the other terms and we discuss it for the example of a thin film. Because in thin films the surface normal defines a characteristic axis, one often defines γ in (11.29) as the angle of the magnetization with this axis, as shown in Fig. 11.10. With the definition of Fig. 11.10 and defining the magneto-crystalline anisotropy energy $\Delta E_{\rm so}$ according to (7.50) as the difference between the energies along the hard direction minus that along the easy direction, we have $\Delta E_{\rm so} = K_1 > 0$ if the easy axis is perpendicular to the surface and $K_1 < 0$ for an in-plane easy axis.

We can write the anisotropy constant K_1 in (11.29) as a sum of two contributions $K_1 = K_u + K_s$. The first term K_u is the magnetocrystalline anisotropy (MCA) generated by the atomic structure and bonding in the film, discussed previously in Sect. 7.9 and also in Sect. 11.2.2 later. The second term $K_s = -M^2/2\mu_0$ is the shape anisotropy, discussed in Sect. 2.6 and 11.2.1 below. The first order term of the anisotropy energy density in a thin film is then given by,

$$E_{\rm ani} = (K_{\rm u} + K_{\rm s})\sin^2\gamma + \cdots \tag{11.31}$$

According to Sect. 7.9, in multilayers $K_{\rm u}$ may be positive and large. If $(K_{\rm u} + K_{\rm s}) > 0$, the thin film prefers to be magnetized perpendicular to its plane,

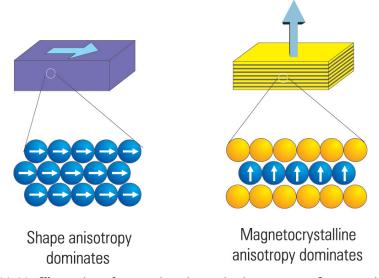


Fig. 11.11. Illustration of magnetic anisotropies in two cases. In magnetic films with a thickness of several nanometers the easy magnetization direction is typically in-plane due to the dominance of the magneto-static or shape anisotropy. In multilayer systems, consisting of alternating magnetic and nonmagnetic layers of subnanometer thickness, such as Co and Au, the easy axis may be out-of-plane due to the dominance of the spin–orbit derived magneto-crystalline anisotropy

but for $(K_{\rm u} + K_{\rm s}) < 0$, the easy direction will be in plane. The balance between $K_{\rm u}$ and $K_{\rm s}$ is delicate in thin films and mulitlayers and can change with temperature. In the system Fe/Cu(001) for instance, one observes that the magnetization turns from its perpendicular direction at low temperatures into the plane of the film at ~300 K. This reorientation transition has been studied in detail [498–500].

In applied magnetism, it is of great interest that thin films that are embedded in layered structures (and also some ordered alloys) may exhibit an easy axis that is perpendicular to the sample surface. As illustrated in Fig. 11.11, for an isolated thin film the magnetization is typically in plane due to the effect of the shape anisotropy, while in certain sandwich structures, like Au/Co/Au or Pt/Co/Pt, the magnetization prefers to be out-of-plane. Such a perpendicular magnetic anisotropy (PMA), is of great technological importance and it is also a beautiful example of the competition between the two anisotropy mechanism to determine the easy axis. We can summarize as follows.

The *easy magnetization axis* of a sample is determined by a competition between the *magneto-crystalline anisotropy* and the *shape anisotropy*.

In the following we shall briefly review the two main anisotropy contributions.

11.2.1 The Shape Anisotropy

In general, the magnetization distribution in the atomic cells contains spin and orbital contributions and it is not spherical but involves various multipoles. In the multipole expansion of the spin density, the largest term, after integration over the atomic volume, corresponds to the magnetic spin moment. Since it arises from the exchange interaction, the spin moment is intrinsically isotropic and magnetic anisotropy arises only from the preferred dipolar coupling between the atomic moments. The spin density term therefore gives rise to the conventional dipole–dipole interaction between magnetic moments \mathbf{m}_s , located at the atomic positions in the lattice,

$$E_{\rm dip-dip} = -\frac{1}{2\pi\mu_0} \sum_{i\neq j} \frac{1}{r_{ij}^3} \left[\mathbf{m}_i \cdot \mathbf{m}_j - 3\frac{(\mathbf{r}_{ij} \cdot \mathbf{m}_i)(\mathbf{r}_{ij} \cdot \mathbf{m}_j)}{r_{ij}^2} \right].$$
(11.32)

The summation is over all atomic dipoles \mathbf{m}_i and \mathbf{m}_j whose absolute values are given by the spin moment m_s . Every pair of dipoles is only counted once, and \mathbf{r}_{ij} is the vector connecting two moments. The next higher (quadrupole) term in the multipole expansion of the spin density reflects the lowest-order anisotropic spin distribution in the atomic cell and it gives rise to the intraatomic magnetic dipole moment \mathbf{m}_D . The orbital moment also contributes to the magnetization density in the atomic volume and its anisotropy m_o^{α} is typically comparable to that of the intra-atomic magnetic dipole moment \mathbf{m}_D . In practice, however, both contributions are much smaller than the lowestorder magnetic dipole-dipole interaction given by (11.32).

Remembering that all moments are parallel because of the dominant exchange interaction, the dipole–dipole energy between two magnetic dipoles, for example, is smallest when both atomic moments align parallel along the internuclear axis, as illustrated in Fig. 11.12.

For a thin film the internuclear axes are preferentially oriented in the plane of the sample and the dipole energy is therefore minimized for an in-plane direction of the magnetic moment. For bulk materials the dipolar field may be decomposed into three contributions, a "microscopic" component consisting of the contributions from the atomic dipoles on the actual lattice sites within a spherical volume, $E_{\rm S}$, that arising from pseudo-charges on the surface of the sphere, $E_{\rm L}$, and a "macroscopic" component due to the demagnetizing field from pseudo-charges on the external sample surface, $E_{\rm D}$, according to

$$E_{\rm dip-dip} = E_{\rm S} + E_{\rm L} + E_{\rm D}$$
 . (11.33)

The dominant term, $E_{\rm D}$, arising entirely from the demagnetizing field, is the shape anisotropy, already discussed in conjunction with (11.31). It is given by

$$E_{\rm D} = K_{\rm s} = -\frac{1}{2\mu_0}M^2 \quad . \tag{11.34}$$

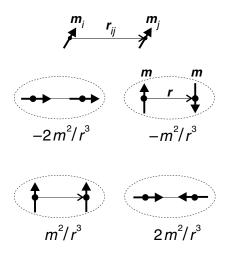


Fig. 11.12. Physical basis of shape anisotropy. On top we give the definition of vector relationships corresponding to (11.32), where r_{ij} is the distance between two magnetic moments m_i and m_j . Note that the exchange coupling ensures that the moments are collinear. The bottom two rows show four relative alignments of two collinear dipoles with the same moments m = |m|, separated by a distance r. Below each drawing we give the dipole–dipole interaction energy. In the lowest energy state the dipoles are aligned along the internuclear axis. These results may already be derived from (3.2)

This result is obtained from (2.21) with $H_i = -M/(2\mu_0)$, where M is the volume magnetization. The other two terms depend on the crystallographic arrangement of the atoms in the sphere and therefore constitute a dipolar magneto-crystalline anisotropy. For Co, for example, the microscopic component is found to be negligible in size $(E_{\rm S} + E_{\rm L} \approx 4 \times 10^{-7} \, {\rm eV}/{\rm atom})$ relative to the shape anisotropy $(E_{\rm D} = 9.3 \times 10^{-5} \, {\rm eV}/{\rm atom})$, see Table 11.3) [123].

For surfaces and ultrathin films the anisotropy may be calculated by a two dimensional lattice sum [501]. Typical calculated anisotropy energies are $\leq 5 \times 10^{-5} \,\mathrm{eV}/\mathrm{atom}$ for a single ferromagnetic layer, smaller than those observed experimentally [123]. Therefore the important PMA, in particular, cannot be accounted for by a dipolar anisotropy. Instead, it arises from the dominance of the MCA, as illustrated in Fig. 11.11.

11.2.2 The Magneto-Crystalline Anisotropy

Uniaxial anisotropies may be induced by a anisotropic crystal structure, by stress, or in thin films by epitaxial growth on a substrate such as W(110) with a preferred direction as we have already discussed in conjunction with

Table 11.3. Bulk anisotropy energies for the 3*d* metals Fe, Co, Ni at 4.2 K [123]. Listed are values for the atomic volumes $V_{\rm a}$, the shape anisotropies $E_{\rm D} = -M^2/2\mu_0$ calculated from the values in Table 2.2, the magnetocrystalline anisotropies $K_{\rm u}$ and the bulk easy axes.

metal	$V_{\rm a}$ [Å ³]	$E_{\rm D} \ [{\rm eV/atom}]$	$K_{\rm u} \ [{\rm eV/atom}]$	easy axis
Fe (bcc)	11.8	-1.4×10^{-4}	4.0×10^{-6}	[100]
Co (hcp)	11.0	-9.3×10^{-5}	5.3×10^{-5}	c-axis
Ni (fcc)	10.9	-1.2×10^{-5}	8.6×10^{-6}	[111]

Fig. 11.8. In practice, $K_{\rm u}$ is often treated as an empirical constant derived mostly from ferromagnetic resonance or from the magnetization curve measured in the hard direction, at right angle to the easy direction as explained later. Historically the MCA and the magneto-elastic anisotropy are distinguished from each other. On a microscopic level, however, they both arise from the same mechanism, the anisotropy of atomic structure and bonding in conjunction with the spin-orbit interaction as discussed in Sect. 7.9. We therefore discuss both of them under the general name MCA.

Van Vleck [319] first proposed the MCA to arise from the spin–orbit interaction which couples the isotropic spin moment to an anisotropic lattice. In today's electronic structure calculations the magnetocrystalline anisotropy energy corresponds to the largest difference of the spin–orbit energy when the sample is magnetized along two different crystallographic directions. In the absence of shape anisotropy effects, the two directions then define the "hard" versus the "easy" magnetization directions.

It has been difficult to obtain a clear picture of the origin of the MCA because the complexity of electronic bandstructure calculations impedes simple physical insight [332,335,502–504]. Also, for the bulk transition metals Fe, Co, and Ni the crystal symmetries are high and the MCA's are extremely small of order 10^{-5} eV as listed in Table 11.3. Although models have been suggested to account for the approximate size of the MCA [505], even today it is still very difficult to calculate K_u reliably, even in an ideal crystal. Reliable results sometimes require calculation with a huge number of k-points in the Brillouin zone. For example, the easy [111] magnetization direction of bulk fcc Ni and its change to [110] at elevated temperatures could not be accounted for by means of electronic structure calculations [504] that used a typical number of about 25,000 k-points. Halilov et al. [506] later showed that the correct answer could indeed be obtained by brute force, using about 370,000 k-points.

In contrast to the elemental metals Fe, Co, and Ni in bulk form, the situation is different for layered thin films, which have an inherent in-plane/outof-plane asymmetry and the resulting MCA is larger by up to two orders of magnitude $(10^{-4} \text{ eV}/\text{atom})$ [320, 325, 336, 507–511]. This opens the door for an interpretation of the MCA based on a chemical bonding concept, based on ligand field theory as previously done in Sect. 7.9. The strength of this con-

cept, although possibly oversimplified, is its intuitive nature [332, 333, 503]. In the following we shall give a brief account of the history of the surface or interface induced magnetic anisotropy which can cause the magnetization to be oriented perpendicular to the plane of the magnetic film.

11.2.3 The Discovery of the Surface Induced Magnetic Anisotropy

It is known that the bulk anisotropy of single crystals can be strong enough to sustain a perpendicular magnetization down to rather thin films. Examples are Gd-garnets of interest for "bubble memories" and 3d - 4f alloys like FeTb used in magneto-optical recording. This fact can be qualitatively understood by means of Van Vleck's idea [319] that the magnetic anisotropy is due to spin–orbit coupling and that the bulk lattice creates a preferred "easy" axis. Néel [512] first predicted that the magnetic anisotropy is substantially different at the surface of a ferromagnet compared to the bulk, owing to missing bonds and an incompletely quenched orbital moment. For a long time it was unclear whether a few-layer-thick film of a material like Fe, with only weak bulk anisotropies, could have a perpendicular anisotropy at the surface that was sufficiently strong to overcome the shape anisotropy and produce a perpendicular magnetization.

Today we know that surface or interface induced perpendicular magnetic anisotropy (PMA) can indeed occur. It took the art of making atomically clean epitaxial metallic films on a single crystal metallic substrate to verify this effect. Many thought this to be impossible because metals interdiffuse much more readily relative to insulators and semiconductors.

In 1969 Gradmann [513] produced mainly crystalline layers of $Ni_{48}Fe_{52}(111)$ on Cu(111) and first reported that ultrathin films, a few atomic layers thick, could be spontaneously magnetized perpendicular to the surface due to Néel's surface anisotropy. This work was continued many years later by several groups. In 1986 Chappert et al. [514] evaporated thin Co-films onto polycrystalline Au with a preferential orientation of the Co hcp axis perpendicular to the surface and saw that the magnetization turned perpendicular to the surface if the Co-film thickness was reduced to about 1 nm. Simultaneously, Jonker et al. [515] grew epitaxial Fe films on Ag(111). At 2.5 monolayers of Fe, spin splitting of the bands appeared, but the spin polarization of the photoelectrons along a quantization axis in the plane of the films remained zero. The authors concluded that the films must be magnetized perpendicular to the surface. This was confirmed by the first serious theoretical calculation of surface magnetic anisotropies by Gay and Richter [516], published shortly afterward. Pescia and coworkers [498] then showed that a few Fe layers grown on Cu(001) exhibit spin polarization along a quantization axis perpendicular to the surface. Stampanoni et al. [517] proved that 3–4 bcc Fe-layers on Ag(001) are indeed remanently magnetized perpendicular to the surface at 30 K as proposed [515], but the magnetization turns in-plane when the temperature is increased to $T > 100 \,\mathrm{K}$. This was of interest in the light of the

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Mermin–Wagner theorem [518] according to which a 2-dimensional specimen can not order magnetically unless it possesses magnetic anisotropy.

At the transition of the magnetization from in-plane to perpendicular, the shape anisotropy is exactly compensated and thus at this temperature, there should be no magnetic order. A loss of magnetization was indeed reported [519]. Later, Kashuba and Pokrosvsky [499] found that the spin reorientation transition produces stripe domains susceptible to thermal meandering. The latter have been imaged directly with spin resolved low energy microscopy (SPLEEM) [74] and PEEM [500]. Pescia and coworkers [520] then showed that the stripe domains become a labyrinthine domain structure and then again a stripe domain structure as the temperature is raised. Finally, Qiu and collaborators [500] investigated the stripe domains in a transferred exchange field and established a universal dependence of their width on the effective magnetic field. At present, the time dependence of the spin reorientation transition is of interest, as well [521].

11.3 The Magnetic Microstructure: Magnetic Domains and Domain Walls

The macroscopic properties of a magnetic material are explained by the magnetic microstructure. Magnetic domains and the transition regions between the domains called magnetic domain walls are the elements of the magnetic microstructure. We will outline here the most important physical principles indispensable to understanding the very basic features, but we cannot give a full description of this very rich field. For an extensive treatment of ferromagnetic domains and the analysis of the magnetic microstructure, the reader is referred to the book by Hubert and Schaefer [54]. We shall separately discuss ferromagnetic and antiferromagnetic domains.

11.3.1 Ferromagnetic Domains

If the magnetic anisotropy were the only energy determining the direction of the magnetization, a magnetic sample would tend to be homogeneously magnetized along one of its easy directions. However, depending on its physical shape, a homogeneously magnetized sample will generate a magnetic stray field. The generation of a magnetic field outside the sample costs energy according to (2.20). To reduce this energy, the magnetization will split up into domains, that is it will prefer to lie in multiple directions in order to minimize the stray magnetic field. The most favorable magnetic configuration is a magnetic ring as we have already seen in Sect. 2.6, and the magnetization will thus tend to approximate this most favorable configuration. In the presence of domains there have to be transitions from one direction of the spontaneous magnetization into another one. These transitions occur in "domain walls", but the formation of the domain walls costs some energy as well. The internal

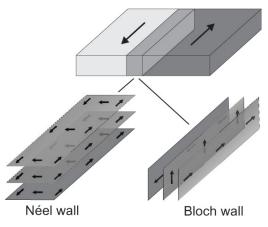
structure of domain walls is a fascinating topic of magnetic microscopy. It is different at the surface compared to the bulk, and it also changes with 2D samples compared to 3D samples.

Ferromagnetic domains arise from the minimization of the stray field energy. If the stray field energy is larger than the energy it takes to form domain walls, the ferromagnet will break up into domains.

The thickness and energy of magnetic domain walls are important to the world of nanomagnetism. First, magnetic films in the nanometer range of thickness turn out to be too thin to support a domain wall parallel to their surface. This reduces the magnetic microstructure to tractable simplicity. In the case that the easy direction lies in the plane of an atomically thin film, a homogeneously single domain state for the whole film is lowest in energy like in the example of Fe on W(110) of Fig. 11.8. This arises from the fact that the demagnetizing field (2.20) is only large for a lateral extension of the order of the film thickness, but a domain wall is much thicker than a few atomic layers, hence it is not favorable to change the magnetization direction. Secondly, small magnetic particles cannot support a domain wall if the wall energy is larger than the stray field energy, hence such nanomagnets have to be single domain, that is they are always fully magnetized, possibly with the exception of some spins at the edges of the magnetic particle. Such particles then do not exhibit a magnetic microstructure at all. In summary, we need to know the thickness and energy of a domain wall in order to know over what distances the macrospin approximation might be reasonable.

Two prominent types of domain walls are illustrated in Fig. 11.13, named after the scientists who first conceived them. In both cases two regions with oppositely oriented magnetization directions are separated by a planar transition region, called a wall. In a *Bloch wall* a continuous 180-degree transition of the magnetization occurs with the moments in the wall oriented parallel to the plane of the wall. In a *Néel wall* the moments in the transition region are aligned perpendicular to the plane of the wall. Bloch walls are more common in bulk-like thick films, while Néel walls often occur in thin films, where a surface stray field is avoided by rotation of the moments within the surface plane, as shown on the left of Fig. 11.13.

In the following we shall briefly discuss the characteristics of Bloch walls. Such walls occur in an infinite uniaxial medium with negligible magnetostriction, separating two domains of opposite magnetization. To rotate the magnetization by $\gamma = \pi$ it has to enclose an angle $0 < \gamma < \pi$ with the easy direction over some distance d. When the magnetic anisotropy energy is large, the moments are strongly held along the easy direction. The wall width d will be small to minimize the length of the rotation from the easy direction, i.e., the wall energy. When the exchange energy between the moments is large the moments will form a stiff chain that resists bending, so the wall thickness



180° domain walls

Fig. 11.13. Illustration of two types of 180° domain walls. In a Bloch wall, common in thick films, the magnetization rotates in a plane parallel to the plane of the domain wall. In a Néel wall, favorable in very thin films, the magnetization rotates in a plane perpendicular to the wall, i.e., within the surface plane, thus avoiding the creation of a stray field

d will be large to minimize the wall energy. Hence the competition between the exchange and anisotropy energies determines the wall thickness and the wall energy. In the case of the Bloch wall, the demagnetization field energy vanishes, $K_s = 0$, so that one only needs to consider the magnetocrystalline anisotropy (MCA) energy. This facilitates our calculation.

For a Bloch wall with a gradual change of the magnetization direction by 180° over a row of N atoms, with equal angles $\varepsilon = \pi/N$ between adjacent spins, the exchange energy is given by $JS^2(\pi^2/N^2)$ according to (11.25). For one row of N atoms, the energy is $JS^2(\pi^2/N)$. The number of rows of atoms per unit area of wall depends on the crystal structure, but it is certainly of the order of $1/a^2$, where a is the lattice parameter. Now with a wall thickness d = Na one has for the exchange energy per unit wall surface $JS^2\pi^2/Na^2 = JS^2\pi^2/da$. The crystalline anisotropy energy per unit area is $E_{\rm K} = K_{\rm u}d$, where $K_{\rm u}$ is the magnetocrystalline anisotropy or MCA, given by (11.31). The total energy per unit area, $E = K_{\rm u}d + JS^2\pi^2/da$, is at a minimum when the derivative of E with respect to d is zero.

This gives the following important expressions for the domain wall energy and thickness. For a 180° wall, the *wall energy* per unit area of the wall surface, $E_{\rm w}$, with dimension [energy/area] is given by

$$E_{\rm w} = 2\pi \sqrt{AK_{\rm u}} , \qquad (11.35)$$

where $A = J S^2/a$ is called the exchange stiffness with dimension [energy/length] and K_u is the MCA with dimension [energy/vol]. It is minimum when the wall thickness d has the value

$$d = \pi \sqrt{A/K_{\rm u}} \ . \tag{11.36}$$

The exchange stiffness A decreases with temperature. Its zero-temperature value may be estimated from $A(0) \simeq k_{\rm B}T_{\rm C}/a$. MCA energies are generally large when the spin-orbit coupling is large such as in the rare earth ferromagnets or when the orbital moment is anisotropic at interfaces and surfaces, as illustrated in Fig. 7.35. In the bulk of Fe, $K_{\rm u} \simeq 0.46 \times 10^5 \text{ J/m}^3$. Equation (11.36) then yields a wall thickness in Fe due to crystalline anisotropy of ~50 nm corresponding to about 200 lattice spacings at a wall energy $\sim 5 \times 10^{-3} \text{ J/m}^2$. For detailed calculation of wall energies and thicknesses the reader is referred to the book by Hubert and Schaefer [54].

In contrast to a model based entirely on the MCA energy, the shape anisotropy energy may also be important, particularly with materials of high magnetization $M \simeq 2T$ such as Fe, yielding $K_{\rm s} \simeq 10^6 \,{\rm J/m^3}$. The shape anisotropy comes into play when the magnetization is directed perpendicular to a surface and may lead to a smaller wall thickness and/or a transition from the Bloch wall structure to the Néel wall structure as the thickness of a film is reduced.

In general, we can make the following statements.

The properties of a domain wall are determined by the competition between the exchange energy and the magnetic anisotropy energy. The domain wall energy increases with both the exchange energy and the anisotropy energy, because both favor a collinear moment alignment. The domain wall width increases with the exchange energy but decreases with increasing magnetic anisotropy energy.

A wide range of scales appear generally in magnetic problems. The correlation length ℓ is relevant for magnetic phase transitions, discussed in Sect. 11.1.6. Equation (11.36) defines yet another length, the so called "exchange length" which is the distance over which the magnetization is expected to change direction in the presence of magnetic anisotropies. In the bulk of Fe, the crystalline anisotropy is dominant and the exchange length is defined as $l = \sqrt{A/K_u}$. It is of the order of the thickness of a Bloch wall of 50 nm. However, when the shape anisotropy is dominant, the exchange length in the same material is given by $l = \sqrt{A/K_s} = \sqrt{2\mu_0 A}/M$. This might be much shorter and comes into play for instance in the core of a magnetization vortex where the magnetization is perpendicular to the surface. The vortex structure is schematically depicted in Fig. 15.18. In Fe, the diameter of the vortex is believed to be of the order of 10 nm [522]. We see that a careful analysis is necessary before one applies the macrospin approximation in which all spins are parallel.

11.3.2 Antiferromagnetic Domains

In an antiferromagnet, there is no stray field and one might expect that the thermodynamically stable configuration is a single domain. In practice, antiferromagnets usually adopt multidomain configurations for a variety of reasons. A common reason for AFM domain formation is the existence of crystalline imperfections. In epitaxial thin films, imperfections or boundaries resulting from twinned crystallographic regions interrupt the long-range magnetic ordering, allowing a change of the spin axis. This has been studied in detail for NiO since the 1960s [523–528]. Some domain configurations, while not representing global free-energy minima, may be stable because of kinetic considerations [529]. A T-domain wall in NiO (see Fig. 7.25) [284, 285] is such a configuration [530]. Once formed, it is essentially stable.

In a perfect crystal, the lowering of free energy that accompanies an increase in entropy can lead to an equilibrium multidomain structure. For an S-domain wall (see Fig. 7.25), the absence of demagnetization energies allows the wall some flexibility of configuration, with a consequent increase in entropy. This entropy increase can be greater than the energy cost of forming the domain wall, in which case the multidomain configuration is thermodynamically favored [531]. Domain formation is favored for NiO over a wide temperature range, $100 \text{ K} < T < T_{\text{N}} = 523 \text{ K}$ [532]. The equilibrium domain configuration can also be modified by external forces such as stresses and/or applied fields [523,528]. We have already encountered an example in conjunction with Fig. 10.23.

Antiferromagnetic domain formation has also been investigated theoretically in conjunction with the topic of exchange bias [533]. These studies were based on prior extensive model studies of diluted Ising antiferromagnets [534]. Such Monte Carlo simulations also provide convincing theoretical evidence on the seeding and pinning of AFM domains by defects.

11.4 Magnetization Curves and Hysteresis Loops

The magnetization curve (MC) is the response of a magnetic material to the application of a magnetic field. It is essential to all applications of magnetic materials, the most important ones include the electric transformer, powerful permanent magnets, and magnetic data recording. We will outline the physical principles for some important cases later but do not intend to give an exhaustive treatment of MCs. For this, the reader is referred to the specialized literature [54].

If an external field is applied, a torque $T = M \times H$ acts on the magnetization and the magnetic microstructure changes in order to reduce the energy. Regions in which the magnetization lies in a favorable direction will grow at the expense of unfavorable ones by a movement of the domain walls

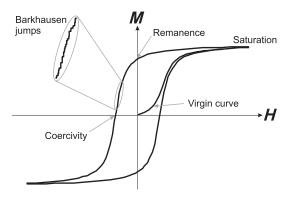


Fig. 11.14. Definition of the main features of the magnetization curve (MC), that is the dependence of the sample magnetization M on the applied field H. The discontinuous changes near the coercive field (Barkhausen jumps) are not observed with all magnetic samples.

(see Fig. 15.17). Also, it can happen that the magnetization of a whole region "jumps" more or less suddenly into a new direction. Eventually, the magnetization rotates into the direction of the external field. MCs usually depend on the initial distribution of the magnetization over the sample volume. In other words, MCs depend on the history of the sample. The microscopic elementary processes are mostly not reversible [535]. They also depend on the speed with which the external field is changed. With magnetic field pulses shorter than $\sim 10^{-10}$ s, the precessional motion of the magnetization is dominant and the MCs change character entirely. The following discussion is focused on the quasistatic MCs occurring with slowly changing magnetic fields.

Figure 11.14 defines some frequently used terms to describe the MC. The saturation field is the applied magnetic field at which the domain structure is removed. M points then entirely into the direction of the applied field. The magnetic remanence is the magnetization that remains if the applied field is decreased to zero. The *coercive field* is the field that must be applied in the direction opposite to the saturation field in order to reduce the magnetization to zero. The virgin curve is the MC of a sample that has never been exposed to a magnetic field. It is obtained by first heating the sample to $T > T_{\rm C}$ and subsequently cooling it in a field free region. The MC obtained after this procedure is the virgin MC. Demagnetizing a sample in a slowly decreasing alternating field may lead to a different MC. At very small fields and with soft-magnetic materials having the highest magnetic permeabilities, the virgin MC often starts with a smaller slope but then at somewhat higher field strength, the slope increases steeply. The initial lesser slope is due to reversible motion or bulging of domain walls. In the steep part of the virgin MC as well as at field strength close to the coercive field, the magnetization often seems to change in a discontinuous way. This was first observed in 1919 by Barkhausen with the help of the new cathode tube amplifier. Since then

the jumps are called Barkhausen noise and can be heard when a pick up coil is placed close to the sample. Today one knows that these jumps are caused by the irreversible motion of a domain wall between two regions of opposite magnetization. Finally, when M changes only slowly, it rotates from its own local easy direction in a crystallite into the direction of the applied field.

Only in very simple cases is it possible to uniquely interpret MCs in terms of elementary processes such as domain wall motion and coherent rotation of M. Therefore, magnetism has become a rich field for magnetic microscopy. Some 50 years ago it was only feasible to image the surface of static magnetic domains at a lateral resolution of micrometers by means of the Bitter technique [536]. Great progress has been made through magneto-optical techniques as discussed by Hubert and Schaefer [54], and at higher resolution through electron and X-ray based microscopies as discussed by Hopster and Oepen [457] and Freeman and Choi [456]. It is even possible today to obtain magnetic images with atomic resolution through spin polarized magnetic scanning tunneling microscopy as reviewed by Bode [458].

Today, the dynamics of magnetic domains can be watched at video rates, and for periodically repeatable processes, pump-probe techniques offer a time resolution in the tens of picosecond range at tens of nanometer resolution [456, 537, 538]. In addition, X-ray based techniques can image the magnetic moments with atomic specificity and can also image antiferromagnetic domains. Typically, with modern microscopy techniques the magnetic domains are visible only within a certain probing depth below the surface.

11.5 Magnetism in Small Particles

11.5.1 Néel and Stoner–Wohlfarth Models

Magnetic samples that are too small for the formation of a magnetic domain wall behave like a single magnetic domain, i.e., a macrospin. Equation (11.36) tells us that this occurs for nanoparticles containing typically 10^4-10^6 Bohr magnetons. Magnetization changes are then expected to occur solely by uniform rotation of M. The theory of MCs in such single domain particles was developed by Néel in 1947 [539] and Stoner and Wohlfarth in 1948 [540]. However, a rigorous experimental test of the "Stoner–Wohlfarth (SW) model", that is of the magnetization reversal by uniform rotation had to wait until well characterized single particles could be made whose small magnetization could be measured with high sensitivity techniques. Wernsdorfer [541] gives an excellent description of how such experiments can be done on particles containing down to 10^3 spins using microscopic superconducting quantum interference devices (SQUIDS). He shows that with good single crystalline particles, the SW-model seems to describe the hysteresis loops satisfactorily.

For the simplest case of a sample with uniaxial anisotropy constant K which includes shape and crystalline contributions (see (11.31)), the energy of

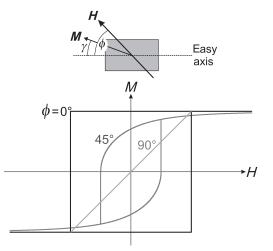


Fig. 11.15. Dependence of the component of M along the direction of the applied field H on the field strength according to the Stoner–Wohlfarth model. It is assumed that the sample consists of one single domain or a "macrospin" and has one easy magnetization axis. The angles γ and ϕ specify the directions of the magnetization M and the external field H relative to the easy axis as illustrated on top

a single domain particle with magnetization M and volume V, in a magnetic field H, is given by

$$E = KV \sin^2 \gamma - MVH \cos(\phi - \gamma) , \qquad (11.37)$$

where γ and ϕ are the angles enclosed by M and H, respectively, with the easy axis of magnetization as shown in Fig. 11.15. The energy (11.37) has two minima, separated by a potential barrier.

The hysteresis loop is the magnetization component $M \cos(\phi - \gamma)$ along the direction of the applied field specified by H and ϕ . It is obtained by solving (11.37) numerically.

The magnetization loop depends on the orientation ϕ of the external field relative to the easy axis. For a given ϕ it is a plot of the magnetization component along the direction of the applied field as a function f of the applied field according to

$$M\cos(\phi - \gamma) = f[H(\phi)] . \tag{11.38}$$

Here the angles γ and ϕ are defined in Fig. 11.15 and the loop is obtained by solving (11.37) numerically.

Three examples of SW-loops are shown in Fig. 11.15. There is a characteristic dependence of the loops on the angle ϕ . In particular, if \boldsymbol{H} is applied under 45° to the easy axis, the particle switches at 1/2 of the field strength required for reversal along the easy ($\phi = 0$) or in the hard direction ($\phi = 90^{\circ}$). There is no hysteresis when \boldsymbol{H} is applied in the hard direction ($\phi = 90^{\circ}$) since \boldsymbol{M} turns gradually into the field direction with increasing field strength. For \boldsymbol{H} applied in the easy direction ($\phi = 0$), the magnetization jumps abruptly into the opposite direction when \boldsymbol{H} reaches the coercive field.

We see from Fig. 11.15 that in the SW model the *coercive field* H_{coer} and *anisotropy field* H_{ani} are the same, since the loop jump in the easy direction is the same as the saturation field needed to move M into the hard direction, compensating H_{ani} .

In the *Stoner–Wohlfarth model* the coercive field H_{coer} and anisotropy field H_{ani} are the same.

The hard axis saturation field is often used to determine the strength of the magnetic anisotropy constant K_1 according to (11.30). But in practice, it turns out that the field H_{coer} is usually lower than H_{ani} . This can be due to the formation of domain walls at imperfections or to curling and buckling modes of M in the process of reversal. Furthermore, H_{coer} depends critically on the time span over which the field is applied at a given temperature. Therefore, the coercive field H_{coer} is not suitable to determine the magnetic anisotropy reliably.

The potential energy (11.37) has two minima separated by an energy barrier. The extreme points are found from $\partial E/\partial \phi = 0$. If H increases, one minimum loses depth relative to the other until, at the switching field $H_{\rm SW}^o$, it disappears completely. The strength of $H_{\rm SW}^o(\phi)$ can thus be determined from the simultaneous occurrence of the two conditions $\partial E/\partial \phi = 0$ and $\partial^2 E/\partial \phi^2 = 0$. A short calculation yields the angular dependence of $H_{\rm SW}^o(\phi)$ in the SW-model. Quoting $H_{\rm SW}^o$ in units of the anisotropy field $H_{\rm ani} = 2K/M$ yields the dimensionless switching field,

$$h_{\rm SW}^o = \frac{H_{\rm SW}^o}{H_{\rm ani}} = \frac{1}{\left[\sin^{2/3}\phi + \cos^{2/3}\phi\right]^{3/2}} \ . \tag{11.39}$$

Since $h_{\rm SW}^o$ does not depend on specific material properties, (11.39) should be universal, that is valid for any material. Plotting $h_{\rm SW}^o$ in polar coordinates thus yields the universal SW-astroid. The switching field $h_{\rm SW}^o$ is highest at $\phi \pm 90^\circ$, 0° and 180° , and 2 times lower for $\phi = \pm 45^\circ$ and $\phi = \pm 135^\circ$. We note here that there is a different astroid for precessional reversal, the dynamic SW-astroid [542]. In precessional reversal, the switching field may be lower compared to the quasistatic case for $\phi = \pm 90^\circ$, depending on the damping of the precessional motion.

11.5.2 Thermal Stability

The direction as well as the magnitude of the spontaneous magnetization in small particles fluctuates as a result of thermal excitations. Two types of excitations have to be distinguished: The uniform precession in the anisotropy field and the spin wave excitations which are driven by the exchange interaction. The uniform precession mode can switch the magnetization into the other direction if the temperature is high enough. The spin wave excitations reduce the absolute value of M, with M vanishing in the limit $T \to T_{\rm C}$.

The potential barrier between the two magnetization directions determines the energy involved in the excitation of the uniform precession mode. The anisotropy barrier is essential for the thermal stability of the magnetic moment direction \boldsymbol{m} in small particles. If the thermal energy $k_{\rm B}T$ approaches the lowest height of the barrier $\frac{1}{2}H_{\rm A}m$, then the particle switches erratically between the two magnetization directions. Such thermally unstable particles are called superparamagnetic. They behave magnetically like giant paramagnetic moments, but should not be confused with the fluctuating spin blocks appearing at the magnetic phase transition, illustrated in Fig. 11.7. The stability of the magnetization is given by the Boltzmann factor e^x , where $x = N\mu_{\rm B}H_{\rm A}/2k_{\rm B}T$ [443] and N is the number of Bohr magnetons of a particle. The average lifetime τ of the magnetization is then given by

$$\tau = \tau_0 \,\mathrm{e}^{N\mu_{\rm B}H_{\rm A}/2k_{\rm B}T}.\tag{11.40}$$

The attempt frequency of $1/\tau_0$ is estimated to be $\sim 10^{10}$ from the magnetization precession in the anisotropy field [541]. If one requires that the data stored in magnetic recording media last for a few years, the exponent $N\mu_{\rm B}H_{\rm A}/2k_{\rm B}T$ must be of the order of ~ 40 . Hence a particle in a particulate magnetic recording media must contain at least 2×10^4 spins in order to be stable at room temperature with a magnetic anisotropy field of $H_{\rm A} = 10^4$ Oe. If $H_{\rm A}$ is increased, the data last longer but the writing of the data becomes increasingly difficult.

Magnetism of Metals

12.1 Overview

In all of solid state physics the understanding of the properties of metals has played a special role. The basis for our present understanding emerged shortly after the discovery of the electron in 1897. It builds on the theory of Drude which is based on a kinetic theory borrowed from gases with a Maxwell-Boltzmann distribution for the electron velocities. This theory was extended by Sommerfeld after it became clear that electrons obey the exclusion principle, and that the Maxwell-Boltzmann distribution had to be replaced by a Fermi-Dirac one. The understanding of the magnetic properties of metals was developed in the time frame 1935–1938 by Mott [27], Slater [28,29], and Stoner [30, 31] who realized the important role of the d electrons and band structure effects.

In this chapter we discuss the basic physical models used to explain the properties of the four ferromagnetic elementary metals Fe, Co, Ni and Gd. In the history of magnetism and still today the magnetic properties of the transition metals Fe, Co, and Ni and their alloys have constituted the core of the whole field of magnetism. The reason is that for these metals the electronic structure is just right to give sizeable magnetic moments at room temperature. While the rare earths or 4f elements have also been important in magnetism, especially when alloyed with the transition metals, the pure metals are all paramagnetic at room temperature. Therefore the scientific understanding and technological applications of the 3d-transition metals have dominated the field.

The difficulties and fascination with the transition metals are mainly due to their "split personality", the duality between localized and delocalized, socalled *itinerant*, behavior. One may draw a comparison between the localized– delocalized duality of electron behavior in solids to the particle-wave duality of light and state as follows.

12

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For *delocalized electrons* the kinetic energy dominates and the electrons move through the crystal like propagating Bloch waves – the electrons behave wave-like.

For *localized electrons* the Coulomb repulsion between the electrons dominates so that electrons stay apart from each other by remaining localized on different sites - the electrons behave particle like.

This duality forms the core of the electronic many-body problem and it the essence of magnetism. Very basic challenges remain to this day in its theoretical description. We shall discuss the concept and consequences of "localization" in detail later in conjunction with the magnetic properties of the transition metals and rare earths.

With our conceptual understanding of the band model of ferromagnetism discussed in Sect. 7.4 we begin this chapter by presenting band theoretical results for the elemental 3d and 4f ferromagnetic metals, Fe, Co, Ni, and Gd. The following section then discusses spectroscopic tests of the predictions of band theory by means of spin resolved photoemission and inverse photoemission. In this discussion it will become clear that the major challenges today lie in the unified description of the itinerant and localized properties and of the dynamic properties which determine finite temperature magnetism.

The following two sections are devoted to a discussion of magnetic excitations in metals. We start with a discussion of electrical and spin transport and introduce the "two-current model" which is the foundation of modern spintronics. We then discuss the anisotropic magneto-resistance effect which needs to be distinguished from the giant magneto-resistance effect in multilayers, discussed in Sect. 14.1.4 later.

The following section explores in more detail the probability of excitations that lead to changes of the spin relative to excitations that conserve the spin. We discuss the transport of spin polarized electrons through a magnetic material both in the *ballistic regime*, and in the *diffusive regime*. Ballistic transport of the spin is produced by injecting electrons from a spin polarized gun, or a magnetic tunnel junction. Diffusive transport of the spin occurs through a transparent contact between a ferromagnetic and a nonmagnetic metal. We shall see that the development of the spin polarization in the ballistic regime at energies relevant for solid state applications, as it depends on distance from the point of injection.

The chapter concludes with a critical assessment of our state-of-the-art understanding, pointing to significant challenges ahead.

12.2 Band Theoretical Results for the Transition Metals

In the following we shall take a closer look at the results of band structure calculations. Instead of discussing the details of the k dependent band structure, as shown in Fig. 7.8 and taken up later in Sect. 12.4.2, we shall concentrate on k-integrated properties which determine important parameters such as the magnetic moment. Key to this discussion is the understanding of the density of states (DOS).

12.2.1 Basic Results for the Density of States

As illustrated in Fig. 7.8 the magnetic moment is defined as the number of band states (summed over the Brillouin zone) per atom, per unit energy and per spin. The Stoner model in Fig. 7.6 relies on a particularly simple density of states that is assumed to have the shape of a semicircle with no structure. More realistic DOSs, calculated for Fe, Co, Ni, and nonmagnetic Cu with the same band structure code [543] are shown in Fig. 12.1. It is evident that the shapes of the density of states in all four metals are quite similar but Cu, as expected, shows no exchange splitting. The exchange splitting Δ , defined as the relative shift of spin-up and down bands is of the order of 1 eV from Fig. 12.1. If we use the relative shift of the largest peak in the DOS we get about 2.2 eV in Fe, 1.7 eV in Co, and 0.6 eV in Ni, in remarkable agreement with the trend in the d shell spin moments which from Table 12.1 later are about 2.2, 1.7, and 0.7 $\mu_{\rm B}$ for Fe, Co, and Ni, respectively. As discussed later in Sect. 12.4.2 the theoretical results for Δ are larger than those obtained with spin resolved photoemission spectroscopy. Himpsel et al. [249, 250] give a range of values for Δ found at different points in the Brillouin zone. They find 1.8-2.4 eV for Fe, 0.93-1.05 eV for Co, and 0.17-0.33 eV for Ni.

The structures in the density of states are due to the overlap interactions of the *d*-states on neighboring atoms, with the atoms located on lattice points of well-defined symmetry. The most important difference in the four DOSs is the different position of the dashed line, which indicates the position of the Fermi energy $E_{\rm F}$. It separates the occupied from the unoccupied states, accounting for the increasing number of *d*-electrons on going from Fe to Cu.

Figure 12.1 also shows the density of states generated by the s-p-electrons which is much smaller and more or less flat and becomes clearly visible at energies above the d bands. At lower energies it underlies the 3d DOS. While the number of s-p-electrons is of the order of 1 per atom only, the bandwidth of the s-p-electron states is much larger compared to the one of the 3d electrons. This is due to the fact that the s-p-electrons are delocalized and thus move quite freely in the crystal lattice. The s-p band width is approximately given by the Fermi energy and is about 10 eV. We can summarize as follows.

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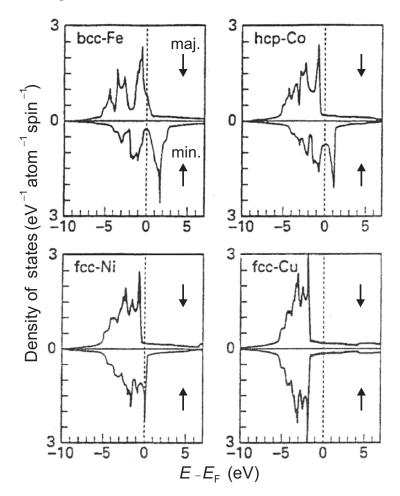


Fig. 12.1. Density of states of Fe, Co, Ni, and Cu for the majority and minority spins [543], labeled "down" and "up", respectively, according to the convention in 7.6. The Fermi energy $E_{\rm F}$ is set to zero. Ni and Co are called strong ferromagnets because the majority spin bands are fully occupied, Fe is called a weak ferromagnet, and Cu is seen to be nonmagnetic

The band width of the d electrons is about 3 eV. The exchange splitting of the d band is of order 1 eV. The band width of the s-p-electrons is large, about 10 eV.

The exchange splitting of the s-p-states is believed to be much smaller compared to the one of the 3d states, and may even have the opposite sign thus providing a negative contribution to the magnetic moment (see Fig. 12.4, later).

Table 12.1. 3*d* valence shell properties for the metals Fe, Co, and Ni, calculated by means of local density functional theory by Wu [545] and Eriksson [544]. Listed are the number of *d* electrons, $N_{\rm e}^d$, the spin magnetic moments m_s^d and orbital magnetic moments m_o^d

	$N_{\rm e}^{d\ a}$	$N_{\rm e}^{d\ b}$	$N^{d\ c}_{ m e}$	$m_s^{d\ a}$	$m_s^{d\ b}$	$m_s^{d\ c}$	$m_o^{d\ a}$	$m_o^{d\ b}$	$m_o^{d c}$
				$[\mu_{ m B}]$	$[\mu_{\rm B}]$				
Fe (bcc)	6.07	6.11	6.11	2.23	2.25	2.31	0.09	0.05	0.05
Co (hcp)	7.20	7.20	7.20	1.67	1.69	1.77	0.14	0.08	0.08
Ni (fcc)	8.22	8.25	8.25	0.65	0.68	0.71	0.07	0.05	0.05

^a Calculated by Eriksson [544] using the linear-muffin-tin-orbital method in the Barth-Hedin parametrization of the local density approximation. Experimental lattice constants were used. The orbital moment was calculated by inclusion of orbital polarization [385, 546].

^b Calculated by Wu [545] with the full-potential-linearized augmented plane wave method in the Hedin-Lundqvist local density approximation. Experimental lattice constants were used.

 c Calculated by Wu [545] with the full-potential-linearized augmented plane wave method in the generalized gradient approximation. Experimental lattice constants were used.

12.2.2 Prediction of Magnetic Properties

Figure 12.1 shows that band theory for the ferromagnets predicts a more or less rigid shift of the "spin-down" DOS $D^{\uparrow}(E)$ relative to the "spin-up" DOS $D^{\downarrow}(E)$. Furthermore, it apparently predicts two types of ferromagnetic metals. In bcc Fe the degree of spin polarization

$$P(E_{\rm F}) = \frac{D^{\uparrow}(E_{\rm F}) - D^{\downarrow}(E_{\rm F})}{D^{\uparrow}(E_{\rm F}) + D^{\downarrow}(E_{\rm F})}$$
(12.1)

at the Fermi energy $E_{\rm F}$ is positive, and in Co and Ni it is negative. The positive sign for Fe is due to a minimum in the spin-down DOS at $E_{\rm F}$. The sign of the spin polarization at $E_{\rm F}$ is a critical property important for a number of experiments, for example, those that determine the sign of the spin polarization of electrons emitted from states near $E_{\rm F}$, as discussed in Sect. 13.2. While $P(E_{\rm F})$ clearly contributes to the sign of the spin polarization of the electric current density j, it is not the only factor determining the sign of the spin polarization of the electric current because $\mathbf{j} = \sigma \mathbf{E}$, and the conductivity σ is largely determined by the s-d scattering as we shall see in Sect. 12.5. This scattering is spin selective, hence affects the spin polarization.

Another basic feature revealed by the band model is that in Ni and Co there are to first order no spin-up d holes. The notion that magnetism in Ni and Co is mainly due to electrons in one spin band has led to the name "strong" ferromagnets. In contrast, Fe is called a "weak" ferromagnet because

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there are sizeable d band contributions in both spin channels. This historical nomenclature is somewhat misleading because the magnetization in Fe is considerably larger than that of Ni and Co. Modern band structure calculations also show that this simple "black and white" picture needs to be revised because of hybridization effects between the s, p, and d partial wave channels. Let us take a closer look at this phenomenon.

We start our analysis of the band theoretical results by comparison of the magnetic moments in the transition metals calculated with density functional theory at T = 0 for Fe, Co, and Ni in Table 12.1. In particular, we compare calculations done by Eriksson et al. [544] and Wu et al. [545] by use of different basis functions and approximations for the exchange correlation potential as indicated in the table. In all cases the spin dependent number of electron states were calculated by integrating the respective majority and minority density of states over all filled states up to the Fermi level. By projecting out the angular momentum components for $\ell = 2$ and $\ell = 0, 1$, respectively, the d and s-p contributions to the spin moments can be obtained separately.

The orbital magnetic moments $m_o = -\mu_B \langle l_z \rangle$ arise from an imbalance in the occupation of $+m_l$ and $-m_l$ states. The listed orbital moments are calculated by Wu et al. with the standard band functions, those calculated by Eriksson et al. include an orbital polarization term that specifically accounts for Hund's rule of maximum orbital moment [385, 546].

Except for the orbital moments, the results in Table 12.1 show good agreement between different approximations within DFT calculations and the differences can be regarded as typical. The orbital moment m_o is entirely due to the *d* electrons and is of the order of 5–10% of the spin moment.

The results for the integrated d band properties are shown in more detail in Fig. 12.2, plotted from the calculated values by Wu [545]. In the left column, Fig. 12.2a, c, we show the results for the d states, only, while in the right column, Fig. 12.2b, d, the plotted data correspond to the summed contributions of the 3d, 4s, and 4p states. In all cases we show the integrated number of states and the integrated magnetic spin moments as a function of energy E relative to $E_{\rm F} = 0$. For the number of valence states plotted in 12.2a, b we start our integration below the bottom of the valence band at $-10 \,\text{eV}$ and integrate to an energy $E - E_{\rm F} \leq 10 \,\text{eV}$. For the d states one would therefore expect that the integral converges to a value of 10 states. For the summed s-p-d states a convergence to the total number of states 10 + 2 + 6 = 18 is not expected because of empty s-p states at higher energies.

For the magnetic moments we have chosen to integrate separately over electron and hole states to facilitate a direct comparison of the integrated electron and hole moments. For the electron states we integrate from $E - E_{\rm F} =$ $-10 \,\text{eV}$ to an energy $E - E_{\rm F} \leq 0$, for the hole states we start our integration at $E - E_{\rm F} = 0$ and integrate to an energy $E - E_{\rm F} \leq 10 \,\text{eV}$. In a simple localized *d*-states model, expressed by (7.18), we would expect the integrated values of the electron and hole moments to be identical.

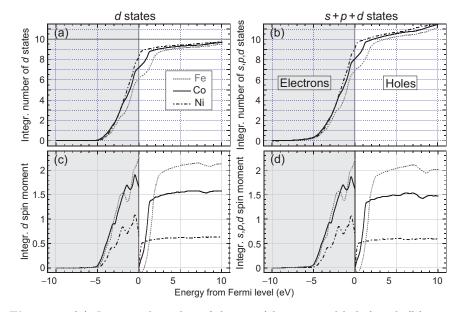
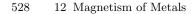


Fig. 12.2. (a): Integrated number of d states (electrons and holes) and, (b), integrated number of s + p + d states in Fe, Co, and Ni. The integration is from below the bottom of the bands, $E - E_{\rm F} = -10 \,\mathrm{eV}$, to an energy $E - E_{\rm F} \leq 10 \,\mathrm{eV}$. (c) and (d) Integrated electron and hole moments for d and s + p + d states. The integration for the electron moments extends from $E - E_{\rm F} = -10 \,\mathrm{eV}$ to $E - E_{\rm F} \leq 0$, and from $E - E_{\rm F} = 0$ to $E - E_{\rm F} \leq 10 \,\mathrm{eV}$ for the hole moments. The data were provided by Wu [545]

The results in Fig. 12.2 provide important information. First, we see that the magnetic moments in the transition metals are almost entirely due to the d electrons. Comparison of panels c) and d) reveals very similar values with and without the s-p electrons. Close inspection actually reveals that the s-p contribution has opposite sign from the d contribution and is of order $-0.04\mu_{\rm B} \le m_s^{sp} \le -0.07\mu_{\rm B}$ for Fe and Co and $-0.02\mu_{\rm B} \le m_s^{sp} \le -0.04\mu_{\rm B}$ for Ni. Second, we see that the hole moments are slightly reduced relative to the electron moments. The origin of this effect is revealed by Fig. 12.2a. Here we see that even at 10 eV above the Fermi level the number of d states has still not converged to the expected value of 10. Up to 0.5 d states or 5% is missing. Therefore, while the sum and the difference of spin polarized electron states is well defined because of the Fermi energy cutoff, the number of unfilled dstates depends on energy and still has not converged to the expected value, even at $10 \,\mathrm{eV}$ above E_{F} . This was first pointed out by Wu et al. in conjunction with the X-ray dichroism sum rules [240, 241] and arises from hybridization of the d states with the more delocalized s-p states. Some of these hybridized d states lie at higher energies above $E_{\rm F}$.



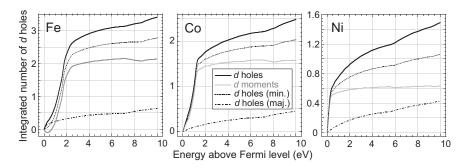


Fig. 12.3. Integrated number of d holes in Fe, Co, and Ni. Plotted curves correspond to the d holes in the minority and majority bands, the total number of holes (sum) and the magnetic moments (difference) in units of $\mu_{\rm B}$, calculated by Wu [545]

Table 12.2. Experimental values for the total magnetic moments m_{sat} and the orbital moments m_o (which are included in m_{sat}) for the metals Fe, Co, and Ni

	$m_{\rm sat}{}^a[\mu_{\rm B}]$	$m_o{}^b[\mu_{\rm B}]$
Fe (bcc)	2.216	0.0918
Co (hcp)	1.715	0.1472
Ni (fcc)	0.616	0.0507

 a From saturation magnetization [485].

 b From a combination of Einstein-de Haas magnetomechanical and ferromagnetic resonance data, evaluated by Wohlfahrt [485].

This point is better illustrated by Fig. 12.3, where we have separately plotted the d states in the majority and minority bands, integrated to an energy $E \leq 10 \text{ eV}$ above E_{F} . At the highest energies we obtain the number of holes 3.4 for Fe, 2.5 for Co, and 1.5 for Ni, in comparison to the numbers 3.93 for Fe, 2.80 for Co, and 1.78 for Ni determined from the filled states in Table 12.1. The lack of convergence of the integrated number of spin polarized empty d states as a function of energy is clearly seen and the individual majority and minority curves as well as their sum, the total number of holes, exhibit a significant positive slope with energy. The difference of the majority and minority curves, the magnetic moment, shows a smaller slope and better convergence yet the missing hybridized d states, that are shifted to higher energy, lead to a reduced value relative to that obtained for the filled electron states, as seen in Fig. 12.2.

The calculated values for the magnetic moments should be compared to the available experimental data listed in Table 12.2. We can summarize as follows: The magnetic moments of the transition metals are nearly entirely due to the d electrons. They are dominated by the spin moment. The orbital moment contributes only about 5–10%. The hole moment is reduced by about 5% relative to the electron mo-

ment because of hybridization of d states with s-p states that extends to energies to more than 10 eV above the Fermi level.

The distribution of the magnetic density in real space can also be calculated. Freeman and coworkers [547] have shown that one can obtain the spin density distribution in the bulk and at surfaces using the full potential linearized augmented plane wave (FLAPW) method. In the bulk, the distribution of the magnetic moment density in real space can be determined by analysis of neutron diffraction data. But for surfaces or thin films one needs to resort to techniques with a short sampling depth. Examples are experiments with spin polarized electrons which are typically sensitive to the last three layers from the surface, as will be discussed in Sect. 12.4 later. As an example of a calculation we show in Fig. 12.4 the distribution of the magnetization $m(\mathbf{r})$ in

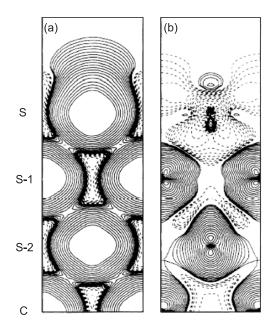


Fig. 12.4. (a) The total spin density $m(\mathbf{r})$ and (b) the spin density from states at $E_{\rm F}$, $m(\mathbf{r}, E_{\rm F})$, for the Fe(110) surface, from [547]. The solid line indicates positive and the broken line negative spin density. S is the surface layer, S-1, S-2, and C are subsequent layers toward the bulk

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real space near the bcc Fe(110) surface [547]. Around the atomic positions we observe large positive contributions to the total magnetic moment, consistent with the notion that the centrifugal barrier confines the 3d electrons to a close neighborhood of the atoms. At the surface, an enhancement of the magnetic moment occurs. This is typical and agrees with experimental observations for various surfaces and ultrathin films [447]. But between the atoms, there is a negative contribution to the magnetization due to the itinerant s-p electrons.

Part (b) of Fig. 12.4 examines specifically the spin density at the Fermi energy $E_{\rm F}$. The polarization of these electrons which can be measured by angle and spin resolved photoemission is important for the interpretation of transport measurements. In this context, Fe is particularly interesting because according to Fig. 12.1 it is expected to yield a positive contribution at $E_{\rm F}$. Yet we see from Fig. 12.4 that the Fe-atoms located in the surface layer clearly contribute minority spins at $E_{\rm F}$. The most important message from Fig. 12.4 relevant for the dynamics of ferromagnetic spins is that there must be a reversed sign of the molecular field in the regions with negative spin density. Hence the exchange fields are strongly variable in real (and reciprocal) space as opposed to the notion of a rigid exchange splitting. The s-p electrons are sampling these varying exchange fields to a much larger extent than the 3delectrons. Furthermore, it is clear that we cannot expect a priori to find bulk like magnetic properties at surfaces. This is of great practical importance since the properties of modern magnetic materials are increasingly determined by surfaces and interfaces [250, 445].

12.3 The Rare Earth Metals: Band Theory versus Atomic Behavior

In addition to the metals Fe, Co, and Ni, the rare earth metal Gd is the fourth elementary ferromagnetic metal in nature. Its Curie point ($T_{\rm C} = 289$ K) is just below room temperature. We have already discussed the different localization of the 3d and 4f electrons in Sect. 7.2 and this is one of the reasons for the extensive studies of Gd by theory [280, 548] and experiment [549, 550]. Of particular interest is the electronic density of states because it is bound to reflect the role of the "localized" 4f electrons and the other more band-like valence electrons in the outer 5d, 6s, and 6p shells. In the following we shall start with a brief discussion of the magnetic configurations and interactions in the rare earths and then explore the electronic structure of Gd in more detail.

The term rare earths is sometimes used to include both the lanthanides and actinides in the periodic table. We shall here use a more restricted definition and speak of "rare earths" synonymously with "lanthanides" [551]. For the neutral atoms their electronic structure consists of a Xe atom core with a partially filled 4f shell and outer valence electrons in the 5d and 6s shells, i.e., [Xe] $4f^N 5d^1 6s^2$. The 4f shell is increasingly filled across the series from La (N = 0) to Lu (N = 14), while the 5d and 6s shells remain quite similar Table 12.3. Occupation of 4f orbitals with quantum numbers m_{ℓ} for Gd metal with a $4f^7$ configuration and for neighboring configurations f^6 and f^8 . We use the convention $s_z = -1/2 = \downarrow$. We also list the angular momenta S, L, J and terms ${}^{2S+1}L_J$ from Hund's rules, and the magnetic moments m_{J_z} expected from a Hund's rule ground state, which we assume to be split by the exchange field with only the lowest J_z state occupied. Note that J = |L - S| for a less than half filled shell and J = L + S for a more than half filled shell. The last column gives the magnetic moment for the 4f shell in ferromagnetic Gd metal, determined by subtracting the moment $0.63\mu_{\rm B}$ due to the 5d shell [548] (see Table 12.5)

$m_\ell \rightarrow$	+3	+2	+1	0	-1	-2	-3	S	L	J	$^{2S+1}L_J$	$m_{J_z}{}^a$	$m_{\exp}{}^{a}$
f^6	↓	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow		3	3	0	${}^{7}F_{0}$	0	
f^7	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	$\frac{7}{2}$	0	$\frac{7}{2}$	${}^{8}S_{7/2}$	7	7.0
f^8	$\downarrow\uparrow$	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	3	3	6	${}^{7}F_{6}$	12	

^{*a*}Moments are in units of $[\mu_{\rm B}]$.

resulting in mostly identical chemical properties of the metals. In compounds such as oxides or fluorides the rare earths typically come in a 3+ state. In the neutral metals the three outer electrons constitute the conduction band composed of 5d, 6s, and 6p orbitals. The 4f occupation of the elements in the 3+ ionic or metallic form is the same. Gd (Z = 64) metal has the special property of a half filled shell with configuration [Xe] $4f^7 5d^1 6s 6p$. The $4f^7$ electronic configuration of Gd is shown in Table 12.3 where its Hund's rule ground state ${}^8S_{7/2}$ is compared with those of the adjacent $4f^6$ and $4f^8$ configurations, for later reference.

The europium chalcogenides EuO, EuS, EuSe, and EuTe constitute an important exception to the typical 3+ valency of the rare ions. Eu^{2+} in the europium-chalcogenides exhibits the pure spin 4*f*-configuration of Gd. Of the chalcogenides, EuO, EuS, and EuSe are both semiconducting and ferromagnetic. Yet $T_{\rm C}$ is very low, namely 67 K, 16 K, and 4 K, respectively. The highest occupied electron states are the 4*f*-states inducing a number of unique properties like a large red shift of the optical absorption edge [552] and highly polarized photoelectrons at threshold [553]. The low ordering temperatures are due to the absence of conduction electrons mediating the exchange coupling between the 4*f*-states. This has been the main obstacle to their applications.

At room temperature and above all rare earth metals are paramagnetic. We see from Table 12.3 that the 4f shell contains the largest number of unpaired electrons and the magnetic moment of the rare earths is therefore dominated by the 4f electrons. Because of their strong localization as discussed in Sect. 7.2 the 4f shell does not participate significantly in bonding and its ligand field splitting is small, of order 10 meV, about an order of magnitude smaller than the spin–orbit coupling within the 4f shell (~200 meV, see Fig. 6.12) and considerably smaller than the exchange and Coulomb energy within the 4f shell which is about 10 eV, as discussed later. The local mo-

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ments can be very large, with Ho having the largest moment of $10.34 \,\mu_{\rm B}$ per atom.

Because the ligand field does not destroy the orbital moment in the 4fshell the total moment has both spin and orbital contributions, except for the case of Gd metal where the orbital 4f moment is zero due to the half filled shell. The fact that the magnetic ordering temperatures are below room temperature indicates a rather weak exchange coupling between the atoms. This coupling has two contributions. The first one arises from the indirect exchange coupling or RKKY interaction between the 4f atomic moments and involves predominantly the "itinerant" outer s-p electrons as discussed in Sect. 7.8. This interaction is long-range and oscillatory and for the rare earths is mostly antiferromagnetic. In addition, there is direct overlap of the 4f and 5d electrons on a given atom. This is directly seen in Fig. 12.5 where the radial charge densities, calculated by Harmon and Freeman [554], are shown for Gd metal. The overlap shown by the shaded region yields a strong direct exchange and polarizes the 5d electrons which assume a magnetic splitting and a magnetic moment. For example, the total moment for Gd metal consists of a 7.0 μ_B 4f and 0.6 μ_B 5d contribution. As in the 3d transition metals the 5d electrons can now give rise to a direct exchange contribution which may be ferromagnetic or antiferromagnetic.

The rare earths La through Eu with a less than half filled 4f shell remain paramagnetic to 91 K or less and then five of the seven become antiferromag-

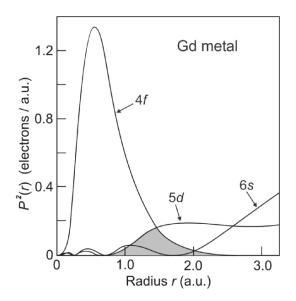


Fig. 12.5. Radial charge density within the muffin tin sphere for Gd metal $(4f^7 5d^1 6s^2)$ calculated by Harmon and Freeman [554] for the 4f state and a typical 5d band state near the Fermi level and a 6s band state. Only the 5d state has an appreciable overlap, shown shaded, with the 4f state

netic. Of the seven heavy rare earths Gd through Lu, six become ferromagnetic at sufficiently low temperatures and five (Tb through Tm) pass through an intermediate antiferromagnetic phase. Gd has the highest ferromagnetic transition temperature $T_{\rm C} = 289 \,\mathrm{K}$ and a simple arrangement of parallel spins. Other rare earths have complicated helical spin structure. For example, Ho is antiferromagnetic between 19 and 133 K and has a helical spin structure where the spins, which are perpendicular to the hexagonal c axis, progressively rotate about c from one layer to the next. Below 19 K the spiral structure is retained but a small ferromagnetic component is added along c, resulting in a conical spin arrangement.

In the following we shall take a closer look at the ferromagnetic phase of Gd metal. A key challenge in the description of the magnetic structure of the rare earths by first principles theory results from the similar energetic binding energies of the localized 4f and the "itinerant" s-p-d electrons. If a band calculation is performed by treating all electrons as "band-like" or itinerant one obtains two more-or-less localized flat bands corresponding to the filled majority and empty minority 4f states and the usual dispersive bands for the s-p-d electrons, which resemble those of the 3d transition metals shown in Fig. 7.8 for Cu and in Fig. 12.10 later for Ni [249,250]. The problem is that the energy positions of the spin polarized 4f bands does not agree with the locations determined by photoemission and inverse photoemission as shown in Fig. 7.18. While inverse photoemission finds the narrow minority 4f band located about $4.5 \,\mathrm{eV}$ above the Fermi level and photoemission finds the narrow majority band around $-8 \,\mathrm{eV}$ below the Fermi level [271,549,550], band theory places the empty minority band just above the Fermi level (at less than $\approx 0.5 \text{ eV}$) and the filled majority band at -4.5 eV, respectively. Most problematic is that the ground state is predicted to be antiferromagnetic. Clearly, a pure band-like LSDA calculation gives an incorrect result.

Another approach that treats the 4f shell artificially as a core shell and ignores hybridization of the 4f electrons with the s-p-d electrons gives the correct ferromagnetic ground state as discussed by Kurz, Bihlmayer, and Blügel [548] but this approach is fundamentally unsatisfactory since we know from Fig. 12.5 that there is overlap of the 4f and 5d shells.

Gd metal is well treated by the LDA+U method discussed in Sect. 7.6.3. Results for the density of states obtained from such a calculation are shown in Fig. 12.6 [548].

The calculation nicely shows the energetic dispersion of the 5d states and the localized flat bands originating from the 4f states. The empty $4f^*$ band is broadened by the 4f - 5d interaction. The LDA+U calculation also results in the proper ferromagnetic ground state and the 4f splitting is increased from 5 eV for the LDU calculation to 11.0 eV for LDA+U, close to the experimental splitting of 12.5 eV, observed by photoemission and inverse photoemission [549,550]. The experimental results are illustrated on the right side of Fig. 12.6, using the correspondence with (7.35). The $4f^7$ ground state configuration cannot be measured experimentally but instead the f^8 configuration

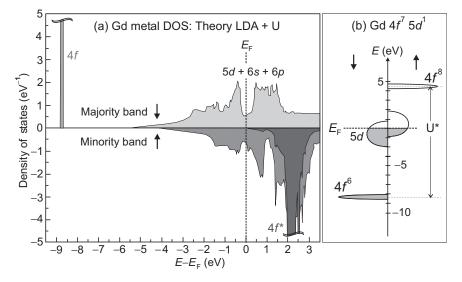


Fig. 12.6. (a) Spin resolved density of states for hcp Gd metal, calculated by Kurz et al. [548] within the LDA+U approximation discussed in Sect. 7.6.3. Note that for the minority band the empty $4f^*$ states, shown in darker shading are hybridized with the *s*-*p*-*d* states and their position is lower as that observed by inverse photoemission (see (b)). (b) Schematic of photoemission and inverse photoemission results after Himpsel and Altmann [249]. The difference of the peak positions measured with the two techniques is $U^* = 12.5 \text{ eV}$ and corresponds to $U^* = U + 6J = 11 \text{ eV}$ in the LDA+U calculation [280]

is measured in inverse photoemission and the $4f^6$ configuration is measured in photoemission [249].

12.4 Spectroscopic Tests of the Band Model of Ferromagnetism

Two experiments have been used to test critical features of the band model of ferromagnetism: photoemission of electrons (PE), in which the energy, momentum and spin of the photoemitted electrons are measured, and inverse photoemission (IPE), in which spin polarized electrons with a well defined momentum are injected into the ferromagnet and the intensity of light emitted at a preselected energy, mostly $\sim 9.5 \, \text{eV}$, is recorded. For recent reviews on photoemission see Kevan [555] and for inverse photoemission see Donath [250,275]. The historical context of these powerful techniques has been described in Sect. 1.3.1. Here we shall briefly review the techniques and summarize the results obtained for the spin dependent band model of ferromagnets.

It is important to state at the outset that the above electron spectroscopy techniques have a very small probing depth of a few atomic layers, which depends on the material, the electron kinetic energy, and the electron spin. The surface sensitivity arises from the extremely strong and spin dependent scattering of excited electrons in the ferromagnetic metals so that only electrons from the surface region can penetrate from or escape into vacuum as discussed in Sect. 12.6.

12.4.1 Spin Resolved Inverse Photoemission

The principle of IPE is explained in Fig. 12.7. A beam of low-energy, spin polarized and monochromatic photoelectrons from a GaAs-type photocathode

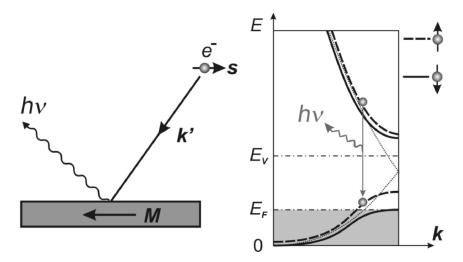


Fig. 12.7. Principle of inverse photoemission (IPE). Left: A well collimated, monochromatic low-energy spin polarized electron beam is incident on a single crystal sample. The experimental geometry is determined by the orientation of the electron spin s relative to the magnetization direction M and by the electron momentum in vacuum k' in the coordinate system of the single crystal. *Right*: In the magnetic solid the spin polarized electrons occupy well defined excited band states, determined by matching the electron momentum k' in vacuum to the momentum k inside the crystal. Radiative decay into lower lying band states under conservation of spin s and electron momentum k, produces low energy photons. The intensity of the photons of fixed energy, typically 9.4 eV, is measured as a function of incident electron energy and incidence direction \mathbf{k}' . IPE detects the unoccupied states $E(\mathbf{k})$ in the crystal as they depend on the direction of the spin relative to the magnetization. $E_{\rm F}$ and $E_{\rm V}$ are the Fermi energy and the vacuum-potential, respectively, with $\Phi = E_{\rm V} - E_{\rm F}$ being the work function. The thin dotted line represents a free electron like band dispersion according to (12.2), folded back into the first Brillouin zone at the zone boundary. At high energies the free electron bands are seen to approximate the actual band structure very well

is incident on a single crystal sample which is remanently magnetized in-plane. Outside the sample, in vacuum, the electron beam has a well defined direction, characterized by the momentum \mathbf{k}' , relative to the crystalline directions of the sample. Stray magnetic fields outside the sample need to be minimized in order not to affect the direction of the incident electrons. Upon entering the crystal the electron momenta in vacuum \mathbf{k}' and inside the crystal \mathbf{k} need to be matched. This is done as follows.

First, one considers energy conservation of the electron energy across the surface barrier using a free-electron band model. Inside the crystal the energy and momentum are related according to free electron dispersion relation

$$E_{\rm kin}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_{\rm e}} .$$
 (12.2)

In this model the zero of energy lies at the bottom of the parabolic free electron band where $\mathbf{k} = 0$, indicated by the thin dotted line in Fig. 12.7. The electron kinetic energy in vacuum is also given by (12.2). However, experimentally one measures the kinetic energy of the incident electrons $E_{\rm kin}(\mathbf{k}')$ relative to the energy of the vacuum level, $E_{\rm V}$. The energy $E_{\rm V} > 0$ is the separation of the vacuum level from the bottom of the free-electron like band, often referred to as the surface barrier or inner potential. This gives the energy conservation condition

$$\frac{\hbar^2 (k')^2}{2m_{\rm e}} + E_{\rm V} = \frac{\hbar^2 k^2}{2m_{\rm e}} \ . \tag{12.3}$$

If we decompose the electron momenta \mathbf{k} and \mathbf{k}' into orthogonal components parallel and perpendicular to the surface, e.g., $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_{\perp}$, the momentum component parallel to the surface is conserved, $\mathbf{k}'_{\parallel} = \mathbf{k}_{\parallel}$ and the perpendicular component inside the crystal, \mathbf{k}_{\perp} , is determined by energy conservation. The boundary conditions are:

$$k_{\parallel} = k'_{\parallel}, \quad k_{\perp} = \sqrt{(k'_{\perp})^2 + \frac{2 m_{\rm e} E_{\rm V}}{\hbar^2}}.$$
 (12.4)

For simplicity we have described all processes in the first Brillouin zone, as shown in Fig. 12.7 by folding the extended zones back into the first one by subtraction of a suitable reciprocal lattice vector \boldsymbol{G} . Once the spin polarized electrons have entered the magnetic solid they occupy well defined initial band states with energies $E_i^s(\boldsymbol{k})$, determined by the spin direction \boldsymbol{s} parallel or antiparallel to the magnetization direction \boldsymbol{M} , and the matching conditions (12.4).¹

Since the incident electrons occupy excited states well above the vacuum level, the electrons may undergo radiative transitions to lower-lying unoccupied final states $E_f^{\uparrow}(\mathbf{k})$ or $E_f^{\downarrow}(\mathbf{k})$, as shown on the right side of Fig. 12.7. In

¹Equation (12.4) implies that upon entering the solid the electron is refracted toward the surface normal. The refraction effect has in fact been measured by Williams et al. [556] in the opposite angle resolved photoemission process.

such transitions a photon $h\nu$ is emitted. The radiative de-excitation process is guided by the dipole operator which does not act on momentum or spin. In practice, the photon energy is of the order of 10 eV so that the photon momentum is very small compared to the electron momentum and can be neglected. One therefore has vertical transitions in the electronic band structure according to $h\nu = E_i^{\downarrow}(\mathbf{k}) - E_f^{\downarrow}(\mathbf{k})$ or $h\nu = E_i^{\uparrow}(\mathbf{k}) - E_f^{\uparrow}(\mathbf{k})$ as shown in Fig. 12.7, with conservation of both \mathbf{k} and \mathbf{s} . The photon intensity emitted at a fixed energy is measured as a function of the energy of the incident electrons and the incidence direction \mathbf{k} in the coordinate system of the crystal. In practice the photon detector is a Geiger counter behind a SrF_2 window which transmits photons of energy 9.4 \pm 0.1 eV. With careful consideration of the background and the energy resolution one obtains from IPE spectra the spin polarized unoccupied band structure $E(k)_{\downarrow}$ and $E(k)_{\uparrow}$ of the crystal.

As an example, we show in Fig. 12.8 the spin resolved IPE spectra obtained by Donath [275] for a Ni(110) surface and a reciprocal space direction of the crystal along $\Gamma - X$. The experiment tests one of the main predictions of the band model of ferromagnetism, namely the temperature dependence of the exchange splitting. In the band model, the exchange splitting of the 3*d*-states must collapse at the Curie-point $T_{\rm C}$. At low temperature, for $T^* = T/T_{\rm C} \to 0$,

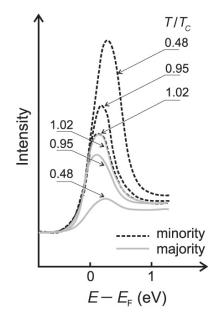


Fig. 12.8. Spin resolved IPE spectra for transitions into the top of 3*d*-derived bands along the $\Gamma - X$ direction of the Brillouin zone for three values of the relative temperature $T/T_{\rm C}$. It is evident that at room temperature, corresponding to $T/T_{\rm C} = 0.48$, the majority spin transitions are much weaker while at the Curie point $T/T_{\rm C} = 1$ majority and minority transitions are of equal strength

the majority part of the 3*d*-band is fully occupied, since Ni is a "strong" ferromagnet. We see that at room temperature, corresponding to $T^* = 0.48$ the transitions to majority spin states close to $E_{\rm F}$ are indeed quite weak, while close to $T_{\rm C}$, corresponding to $T^* = 1.02$ the majority and minority transitions exhibit equal strength. Since the remaining majority spin transitions at $T^* = 0.48$ are explained by the finite resolution of the experiment, this is a beautiful confirmation of the band model. The exchange splitting obtained from this measurement is $\Delta = 280 \pm 50$ meV at low temperature. If one plots Δ as a function of temperature one finds that it follows the temperature dependence of the bulk magnetization as expected on the basis of the band model.

IPE has delivered detailed information on the energy and exchange splitting of the unoccupied electronic bands, and on a large variety of surface and bulk induced magnetic surface states as well as resonance-like features. Careful tests have been performed at the close packed surfaces of Ni, Co, and Fe to distinguish bulk states from surface states and resonances [65]. The surface states may be classified into image potential induced surface states, adsorbate induced surface states, and crystal induced surface states [275] all of which show exchange splittings in the case of a magnetic surface. The study of magnetic surface states and resonances is an interesting topic by itself. It teaches us that magnetic surfaces and interfaces may be quite complex and hard to predict theoretically. This is an important point to remember in the interpretation of all experiments that depend on spin transfer across interfaces. The exchange splittings in the surface states lead to alterations of the magnetic moment in the surface, but so far it has not been possible to spectroscopically determine absolute values of surface magnetic moments. As shown in Sect. 13.2.3, a magnetic surface state of Gd is useful in tunneling microscopy.

Donath has carried out the most detailed analysis of the spin dependent band structure of Fe, Co, and Ni using IPE [557]. Contrary to the special case along the $\Gamma - X$ direction shown in Fig. 12.8, it is found that strict classification into 3d and s-p states is artificial since significant d contributions are found above $E_{\rm F}$ as well. This is in good accord with the hybridization between s, p, and d states predicted by modern band theory of Sect. 12.2.1. It should be noted that for a proper analysis of IPE data the longer mean free path of injected majority electrons compared to minority electrons must be taken into account [558]. This difference in the mean free path is due to spin selective inelastic electron scattering on the holes in the 3d shell, see Sect. 12.6.

The temperature dependence of the exchange splitting has been discussed in the literature for over 30 years. The spin asymmetry of photon production in IPE present at low T disappears at $T = T_C$ as expected. But the exchange splitting of the bands observed in IPE does not collapse in all parts of the Brillouin zone. If one assumes short range magnetic order to persist above T_C , then the spatially averaged spin polarization disappears while spin moments in a certain location may still be present albeit with no specific direction in space, hence zero space averaged polarization. Some bands show such a spin mixing scenario while the exchange splitting in other bands simply collapses in agreement with the SWS-band-model. According to careful and detailed experimental studies [557], all three magnetic transition metals exhibit both local moment behavior and collapsing exchange splitting simultaneously in different band states. Thus the IPE-experiments reveal an immensely complex electronic structure at magnetic surfaces which evades description in a simple picture².

12.4.2 Spin Resolved Photoemission

Photoemission (PE) consists of the excitation of a bound electron to an escape state by the absorption of a photon. In our case we are particularly interested in photoexcitation of valence electrons. In this case PE reveals the occupied part of the valence bands. Under time reversal, the IPE process becomes the photoemission (PE) process, but the two techniques measure the valence states on opposite sides of the Fermi level, making the combination of the techniques a powerful method to obtain complete information on filled and empty valence states.

The principle of PE is explained in Fig. 12.9. For the studies of magnetic materials, PE requires a magnetically saturated sample with minimal magnetic stray fields outside the sample if energy and momentum analysis of the photoemitted electrons is to be performed. In this process, spin s and linearmomentum \mathbf{k} of the photoelectron are conserved, since the electric dipole operator responsible for the transition does not act on either s or k. Just like in IPE one therefore has vertical transitions in the electronic band structure. By measuring the kinetic energy, the emission direction, and the spin with a detector in vacuum, outside the sample, one can determine where the electronic transition has taken place in the Brillouin zone and can therefore map the spin-resolved band structure along directions in the Brillouin zone. The schematic spectra in Fig. 12.9 show the energy distributions expected for spin polarized electrons and their sum, corresponding to a conventional photoemission experiment without spin analysis. We also show the cut-off at the energy $h\nu + E_{\rm F}$, which in high resolution spectra has the shape of the temperature dependent Fermi function given by (12.7).³

As in IPE spectroscopy, the measured properties outside the sample are mapped to those inside the sample by application of the boundary conditions (12.4). The boundary conditions are a good approximation because the final state of the excited electron lies well above the Fermi level where the bands

²Whether the spin mixing scenario is also present in the spin polarized PEexperiments is still a matter of debate. Some authors report a collapse of the spin splitting in all parts of the occupied band structure, while others believe that the exchange splitting of the occupied bands can persist to $T > T_{\rm C}$.

³For transitions within the small section of the Brillouin zone shown on the right side of Fig. 12.9 there would be no transitions allowed from states near $E_{\rm F}$, so we have implicitly assumed that such transitions originate from other sections of the Brillouin zone.

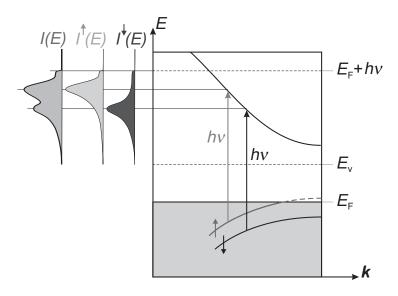


Fig. 12.9. Principle of photoemission (PE) of electrons. A photon of energy $h\nu$ is absorbed and leads to a vertical optical transition of an electron from an occupied state to a free electron like final state above the vacuum level from where it may be emitted into vacuum. The measurement of the kinetic energy, the emission direction and the spin of the emitted electron gives the spin resolved distribution curves $I^{\uparrow}(E)$ and $I^{\downarrow}(E)$ which when added give the spin integrated distribution curves I(E), as shown. The exchange splitting in the final state has been neglected which is appropriate for sufficiently high energies. The PE intensity drops to zero at $E \geq E_{\rm F} + h\nu$, with a temperature dependent shape of the Fermi distribution function. In contrast to IPE, PE thus measures the occupied density of electron states.

strongly resemble a free electron state with a parabolic dispersion relation, as shown in Fig. 12.7.

Figure 12.9 also shows schematically the shape of actual spin resolved photoemission curves $I^{s}(E)$ and the spin integrated curve, which is simply the sum. After each peak, marking a "direct transition", a tail of "secondary" electrons appears at lower kinetic energy due to those electrons that have lost energy in the process of transport to the surface, or due to a cascade of low energy electrons excited from $E_{\rm F}$ by the primary photoelectrons. Of course, photoemission transitions also have a finite width due to lifetime broadening and other physical phenomena discussed below.

In the interpretation of the spectra, it is often assumed that the photoemission structure can be directly linked to the band structure. This assumption is based on the validity of the independent electron approximation ignoring various kinds of electron–electron correlation effects. These include electron– hole and hole–hole interaction effects which are both important. The independent electron approximation works reasonably well only in simple cases like Cu metal, as shown in Fig. 7.8. In the simple one-particle interpretation of photoemission spectra, it is assumed that the hole left behind by the photoexcitation of one electron does not interact or relax toward $E_{\rm F}$ while the electron excited to an escape state is still present. Thus one assumes that the solid is left behind in one specific excited state. However, this assumption is not valid with magnetic materials where the electrons in the magnetic d- or f-states are interacting strongly thus affecting the kinetic energy of the escaping electron. Let us denote as $\varepsilon_0(N)$ the ground state energy of the N electron solid. After photoemission there are N - 1 electrons left behind and there may be more than one, say n, excited states. We can then denote the possible final state energies $\varepsilon_n(N - 1)$. Energy conservation yields the kinetic energy $E_{\rm kin}$ of the photoemitted electron, measured relative to the vacuum level energy $E_{\rm V}$, as

$$E_{\rm kin} = h\nu - \Phi - \left[\varepsilon_n(N-1) - \varepsilon_0(N)\right], \qquad (12.5)$$

where $\Phi = E_{\rm V} - E_{\rm F}$ is the work function.

The excitation spectrum $[\varepsilon_n(N-1) - \varepsilon_0(N)]$ of the hole state left behind leads to multiplet structure in I(E). The clearest examples are the 4f-photoemission spectra, as shown in Fig. 7.18. With the well screened 4f-electrons, N is only the number of 4f electrons per atom. The multiplets observed with the 4f-metals are given by Hund's rules and consequently very similar to the atomic multiplets because the centrifugal barrier and the closed outer shells isolate the 4f electrons from the metallic electrons [238], preventing screening and other relaxation effects. This is much less the case with the 3d-metals, but multiplet structure has also been found in this case, as demonstrated by Fig.12.11.

In the one-particle approximation, it is assumed that $\varepsilon_n(N-1) - \varepsilon_0(N)$ is equal to the binding energy $E_{\rm B}$ of the photoemitted electron. $E_{\rm B}$ is the energy that can be gained by a transition of an electron at $E_{\rm F}$ into the hole left behind after photoemission. Such a transition delineates the maximum energy available for the relaxation of the hole state. But the single particle approximation assumes that the hole state does not relax at all toward $E_{\rm F}$ while the photoexcited electron is still present. It is only with this dramatic assumption that $E_{\rm B}$ can be determined in photoemission from (12.5) by measuring $E_{\rm kin}$ and the photothreshold $E_{\rm V} - E_{\rm F}$, as illustrated in Fig. 12.9.

Correlation effects are generally strong and at the very heart of the important interactions in magnetic materials [249–251]. Typical band structure calculations are essentially independent particle calculations and describe the electronic ground state while the photoemission process, and therefore the measured spectra, correspond to an electron excitation from the ground to an excited band state with a hole left-behind in the valence shell. This so called *quasiparticle* state, which includes excitation and screening contributions from the surrounding electrons, can hardly be satisfactorily treated for the *d* electron systems of importance in magnetism. The discrepancy of the calculated band dispersion and that determined experimentally by photoemission is illustrated by a direct comparison in Fig. 12.10.

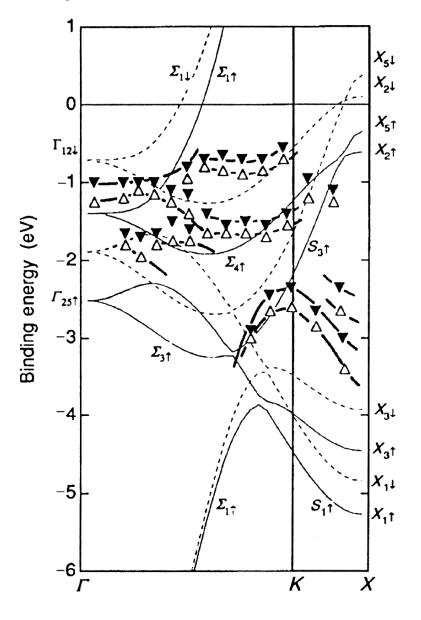


Fig. 12.10. Experimental dispersion of energy bands for Ni(110) with electron momentum over selected parts of the Brillouin zone, measured by spin and angle resolved photoemission by Kakizaki [251]. Also shown as thin lines are the results obtained from a one-electron band calculation in the local density approximation, for majority (*solid*) and minority (*dashed*) spins [559]

Figure 12.10 reveals that relative to band theory the measured experimental band width is reduced and the exchange splitting also has to be reduced by up to a factor of 2. In order to overcome this fundamental problem one often uses a parameterized tight binding band structure, originally due to Koster and Slater [245], and adjusts certain parameters to obtain a "good fit" of measured IPE and PE data [250] but this is unsatisfactory. From the comparison of experiment and theory presented by Kakizaki [251] one may summarize the main discrepancies between experiment and theory as follows:

- The *exchange splitting* observed in photoemission is reduced compared to its calculated value in the electronic ground state. The observed splitting changes throughout the Brillouin zone and differs from the rigid splitting predicted by band structure calculations.
- The *exchange splitting* of the bands in some cases exists to temperatures above the Curie point while is collapses in other cases.
- The observed *bandwidth* of the 3*d* states is narrower than predicted by band structure calculations.
- Experimental spectra contain multielectron satellites of the 3d valence band that appear out to $30 \,\mathrm{eV}$ from E_{F} . Such satellites are unaccounted for in conventional band theory.
- The *photon energy dependence* of majority spin spectra is different from that of minority spin spectra.

The last two points above, which contain information on the dynamics, are especially important since they appear to hold the key to understanding the first two observations. The last observation shows that the correlation effects and scattering channels are spin dependent so that the screening of a majority spin hole and its evolution in time is different from that of a minority spin hole. This dynamical effect explains a number of the deviations from the single particle approximation, in particular the reduction of the observed exchange splittings. It points to the importance of future ultrafast studies of the dynamics of spin polarized electrons in a ferromagnetic metal.

In conjunction with satellites, the satellite appearing at a binding energy of 6 eV below $E_{\rm F}$ in Ni shown in the PE spectra in Fig. 12.11 has attracted considerable interest. The original interest was stimulated by the observation in 1977 that the satellite is resonantly enhanced at photon energy $h\nu = 67 \, {\rm eV}$ [560]. In later studies its spin polarization was also measured [561, 562].

The prominent 6 eV satellite Fig. 12.11 arises from the simultaneous presence of two holes in the 3d orbitals of one and the same Ni atom. Ni fluctuates between an atomic $3d^9$ and $3d^{10}$ configuration. This is in good accord with its average magnetic moment of $0.5\mu_{\rm B}$ per atom, which in a simple model would be $1\mu_{\rm B}$ for $3d^9$ and 0 for $3d^{10}$. If the atom happens to be in the $3d^9$ initial state during the photon absorption process, the final state is $3d^8$ with two holes on the same atom. We have already discussed the multiplet structure of a $3d^8$ configuration in conjunction with Fig. 6.14 and the associated singlet and

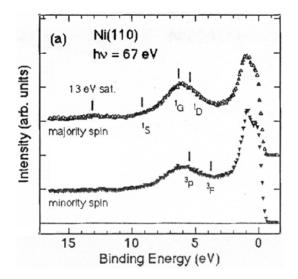


Fig. 12.11. Spin-resolved photoemission spectra of Ni(110) at a photon energy of 67 eV, corresponding to a resonantly enhanced satellite structure at 6 eV binding energy [251]. The vertical bars labelled by singlet and triplet multiplet states correspond to the energies of final states for a d^8 configuration, as discussed in conjunction with Fig. 6.14

triplet multiplets correspond to the 6 eV satellite, as indicated in Fig. 12.11. The energy shift from the main peak signifies that the $3d^8$ configuration must have a higher binding energy compared to a main peak, corresponding to only one hole, i.e., a d^9 final state. This clearly is not expected in a pure band-model and cannot be explained in a single electron picture. The interpretation is proven by the resonant enhancement of the satellite in Fig. 12.11. At a photon energy of $h\nu = 67 \,\text{eV}$ an electron is resonantly excited into $3d^9$ from the 3p core shell. The resulting configuration $3p^53d^{10}$ decays into $3p^63d^8 \ \equiv 3d^8$ since the p shell is now full) by emitting an Auger-electron. The additional Auger electrons enhance the measured intensity proving that the 6 eV satellite indeed corresponds to a $3p^63d^8$ final state. Other weaker satellites such as the one appearing at 13 eV below $E_{\rm F}$ are not so easy to understand.

Naturally, as evident from (12.5), the complexities arising from electron correlation are absent or quite weak in photoemission from initial states near $E_{\rm F}$. In that case, the hole left behind is already at $E_{\rm F}$ and the energy to be gained by relaxation is close to zero. In high resolution PE, one can study specifically the electron states at $E_{\rm F}$ and measure the associated momentum $k_{\rm F}$. Osterwalder [563] has reviewed the ability of angle resolved photoemission to determine the so called *Fermi surface* which is defined as the surface spanned by the endpoints of the $k_{\rm F}$ -vectors. Classical Fermi surface probes such as the de-Haas-van-Alphen effect, positron annihilation, and Compton scattering are essentially bulk probes and cannot be used to determine Fermi

surfaces in thin films and other magnetic materials of high current interest. Results for Fermi surfaces are needed to understand tunneling and other spin dependent phenomena at interfaces such as refraction and reflection of electrons discussed in Chap. 13, and are also essential for the understanding of the electrical resistivity (Sect. 12.5.2).

Fermi surface mapping requires the measurement of the number of states as a function of the electron momentum $k_{\rm F}$. We have already seen that only k_{\parallel} is conserved when the electron propagates through the surface potential barrier while k_{\perp} is reduced leading to a diffraction at the interface. For states at $E_{\rm F}$, one writes (12.5) as $h\nu = E_{\rm kin} + \Phi$, with $E_{\rm kin}$ measured relative to the vacuum level. The component k_{\parallel} is given by,

$$k_{\parallel} = \frac{1}{\hbar} \sqrt{2m_{\rm e} E_{\rm kin}} \sin \theta_m , \qquad (12.6)$$

where θ_m is the polar angle at which the photoelectron emerges, measured from the surface normal. As an example, Figure 12.12 shows a 2D-map of the states at the Fermi surface of Ni, for k_{\parallel} located in the Ni(111) surface plane [564]. Keeping the photon energy constant, and detecting electrons of kinetic energy $E_{\rm kin} = h\nu - \Phi$, only electrons from the Fermi surface are observed. In practice, the measurement of the wavevector dependent Fermi-surface then consists of mapping the emitted intensity as a function of electron emission angle. Points with a high density of states at the Fermi surface exhibit increased emission intensity. In practice, one scans the acceptance direction of the angle-resolved photoelectron spectrometer as a function of the polar angle θ_m from the surface normal and the azimuthal angle φ in the plane of the surface. From the measured angles θ_m and φ one calculates k_{\parallel} . Results for the Ni (111) surface are shown in Fig. 12.12a, obtained without spin analysis.

The corresponding part of the Fermi surface can also be calculated with a band structure code and is shown in Fig. 12.12b. There is a remarkable agreement between experiment and theory. One sees that most of the intensity emitted from states at $E_{\rm F}$ stems from minority spin bands which show a complex Fermi surface due to their 3*d*-character. The majority spin states contribute much less intensity and their Fermi surface approaches a spherical shape in agreement with their dominant *s*-*p*-character. The assignment of the spin character of calculated and observed Fermi-surfaces was verified on selected sections of the Fermi surface by measurement of the spin polarization of the emitted electrons [564]. On the whole, the band picture discussed in Sect. 12.2.2 is verified. Ni is indeed a "strong" ferromagnet.

The larger minority spin contribution at $E_{\rm F}$ manifests itself also in a quite different and much simpler experiment in which the spin polarization of electrons emitted at photoelectric threshold is measured. There the negative spin polarization of the electrons at $E_{\rm F}$ is directly observed with Ni [303, 565] as shown in Figs. 13.2 and 15.5. This occurs despite the stronger absorption of minority spins in ferromagnetic metals, the so-called spin filter effect, discussed in Sect. 12.6.1 later. The negative polarization is not observed with polycrys-

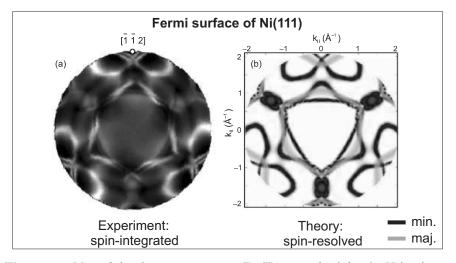


Fig. 12.12. Map of the electronic states at $E_{\rm F}$ (Fermi-surface) for the Ni(111) surface, determined by angle resolved photoemission. (a) Map of the measured spinaveraged photoemission intensities as a function of k_{\parallel} in the Ni(111) plane, obtained with a He-lamp ($h\nu = 21.21 \, {\rm eV}$) photon source. The intensities are given on a linear gray-scale, with white the highest and black the lowest intensity. (b) The corresponding calculated spin-polarized Fermi surface. Minority spin bands are shown in black, majority spin bands in gray. Courtesy of Jürg Osterwalder [564]

talline Ni-samples since inhomogeneities in the photoelectric work function, present in a polycrystalline sample, broaden the wave vector, and energy of the emitted electrons [62].

The reduced complexities associated with electron emission from states near the Fermi level led Greber and collaborators [566] to study photoemission from thermally excited states just above the Fermi level in Ni. The states were chosen at a part of the Fermi-surface where a minority d-band crosses $E_{\rm F}$. This is at $\theta_m \sim 40^\circ$ and for $\varphi = 23^\circ$ off $[\overline{1} \ \overline{1} \ 2]$ in Fig. 12.12. The states just above $E_{\rm F}$ are only weakly occupied by thermally excited electrons, yet by setting the energy analyzer to emission from these states and by employing highly monochromatic radiation, the photoelectric emission from thermally populated states can be separated from the much stronger emission out of the occupied part of the bands below $E_{\rm F}$ [567]. The observed intensity distributions must be normalized with the Fermi-function (12.7) to account for the energy dependent thermal population of the states. In the room temperature data two inverted parabolic bands are resolved in this location of the Fermi-surface. The exchange splitting found at the top of these d-bands is $280 \text{ meV} \pm 20 \text{ meV}$ and collapses at the Curie-temperature in perfect agreement with IPE results shown in Fig. 12.8.

Contemporary band-structure calculations typically yield a value for Δ that is twice as high. Manghi and collaborators [568] argue that the apparent reduction of Δ in PE-spectroscopy is due to spin dependencies in the hole

state correlation effects. In a more recent publication by the same group [569] it is argued that these spin dependencies are even stronger in the case of Co, leading to quenching of the majority channel quasiparticle excitations. Experimentally no sharp quasiparticle states are detectable in Co for binding energies larger than $2 \,\text{eV}$. Thus it is proposed that local correlations between holes in the *d*-bands can modify the energy position and dispersion of low energy excitations with respect to single particle band structure calculations.

Other metals, e.g., ferromagnetic Gd, have been studied by high resolution PE including spin polarization measurements as well. The linewidth of photoinduced transitions changes with temperature in this case, indicating that the lifetime of a majority spin hole in Gd is limited by electron phonon scattering, while that of a minority spin hole is limited by electron magnon scattering [570].

The value of Δ in Ni obtained from high resolution PE must be compared to results of other experiments. Threshold PE at $h\nu \approx 5 \,\mathrm{eV}$ in connection with unsophisticated single particle band structure calculations yield $\Delta = 330$ meV [565], that is within error margin the same result as high resolution PE with $h\nu = 21.21 \,\text{eV}$. According to the later Sects. 12.6 and 13.2.1 it is well established today that at low electron energy, the most important spindependent interaction of the photoelectron is with all the unoccupied d-states rather than with only its own photohole. If PE at an energy of 21 eV above $E_{\rm F}$ yields a similar value for Δ compared to PE with an electron of 5 eV above $E_{\rm F}$, one is led to the conclusion that many body corrections do not appear to be very large for Ni. Similarly, in the mindset of strong many-body corrections, it comes as a surprise that Δ is found to be identical in PE and IPE, as the final states are fundamentally different in both cases. Finally, we shall see later that spin polarized electron energy loss spectroscopy or SPEELS also yields a similar value $\Delta \sim 280$ meV (see Fig. 12.25). As illustrated in Fig. 12.24, SPEELS measures the energy of the spin exchange transition of an electron from a majority spin into a minority spin state, hence involves very different many body states.

Taken together, the various electron spectroscopy measurements of Δ suggest that $\Delta \sim 300$ meV. Indeed, it is interesting to note that over the years this value has changed little. As early as 1965, that is before any spectroscopic techniques had been developed to measure Δ , Wohlfarth predicted $\Delta = (350 \pm 50)$ meV for Ni [571]. Later, it turned out that this theoretical estimate is in line with the early spin polarized threshold PE experiments [572]. Various theoretical predictions for the width and exchange splitting of the 3*d*-bands in Ni prior to 1970 have been reviewed by Pierce and Spicer [573]⁴.

⁴In the early days, the 3*d*-bandwidth in Ni measured in photoemission seemed to be as large as 5 eV. This larger bandwidth required a larger exchange splitting to account for the Bohr magneton number. But in 1969, Eastman [574] showed that the measured width was due to improper surface preparation techniques, and that the *d*-bandwidth for a clean Ni surface is only 2.8 eV.

It must be remembered that Δ is not an adjustable parameter in the band theory of magnetism. Its value is fixed to yield the observed magnitude of the magnetic moment/atom from the density of states as discussed in Sect. 7.4.

In a certain regions in k-space, the s-p band is found to be very close in energy to the minority d band, forming 4s-4p-3d hybridized states. In these regions thermal fluctuations are sufficient to induce scattering between $(s-p)^{\uparrow}$ and d^{\downarrow} electrons [567]. Such scattering involves a spin flip and might be of interest for understanding the magnetic phase transition and electron dynamics. Furthermore, it is found that the s-p bands are also exchange split and exhibit a smaller, but definitely positive polarization at $E_{\rm F}$ in contrast to the 3d electrons which show negative polarization at $E_{\rm F}$.

It is well appreciated today that conventional band structure calculations do not account for dynamical multielectron effects and also fail in the proper treatment of intra-atomic correlation in the form of multiplet coupling, as evidenced by Fig. 12.11. Yet, considering the experimental evidence, it is evident that the various possible many-body corrections are perhaps not as important in spectroscopies that test the states near $E_{\rm F}$.

12.5 Resistivity of Transition Metals

In magnetic devices the electrical resistivity of the transition metals plays a key role. Particularly important is the spin-dependent resistivity of ferromagnets since it determines the read-out signal of many important devices. Another topic of great current interest is the injection of a spin polarized current from a magnetic material into another material, so-called *spin injection*. Again, the key to the understanding of this process lies in the understanding of spin dependent transport in metals. While most materials of interest today are in the form of thin films, as discussed in detail in Chap. 13 below, the understanding of the transport in bulk metals forms the basis for all such developments. It is for this reason that we need to discuss the transport properties in metals with a special emphasis on spin-dependent transport.

Before we discuss the spin-dependent resistivity of transition metals we will take a brief look at the basic principles that determine the resistivity of nonmagnetic metals. To describe the electrical conduction we shall use an extended Drude–Sommerfeld model, based on the relaxation time approximation, which has proven remarkable successful [219]. This will facilitate a later discussion of spin-dependent effects and their theoretical description.

12.5.1 Conduction in Nonmagnetic Metals

The metallic resistivity is determined by scattering processes of the valence electrons with energies close to the Fermi level. The scattering processes, to be specified later, occur with a certain probability per unit time, and the resistivity is directly proportional to this probability. In the description of the conduction electron scattering one typically makes the so called *relaxation* time approximation. It consists of describing the scattering probability per unit time by $1/\tau$, where τ is the time between scattering events, called the relaxation time. A further assumption in this approximation is that scattering events drive the electronic system toward local thermodynamic equilibrium, given by the Fermi function

$$f(E) = \frac{1}{\mathrm{e}^{(E-\mu)/k_{\mathrm{B}}T} + 1},$$
(12.7)

where μ is the chemical potential. The chemical potential⁵ plays an important role in the quantitative description of spin transport phenomena, such as spin currents across interfaces, discussed in Chap. 14. At T = 0 the chemical potential exactly equals the Fermi energy, and for most metals this relationship is still a very good approximation at room temperature (see footnote 5). In electronic systems, the chemical potential μ is equivalent to the negative of the potential energy $q\Phi$ of a test charge q in the electrostatic field $\mathbf{E} = -\nabla \Phi$, i.e., for an electron with q = -e we have

$$\mu = e \Phi. \tag{12.9}$$

For an electric field along the x direction, $E = -\partial \Phi / \partial x$, one can therefore write Ohm's law in terms of the chemical potential as

$$\frac{\partial \mu}{\partial x} = -\frac{e}{\sigma} j. \tag{12.10}$$

Figure 12.13 illustrates that in the absence of an electric field the chemical potential is constant as a function of distance along a nonmagnetic conductor, and at each point there will be local thermodynamic charge equilibrium expressed by the Fermi function (12.7). In the presence of a field there will be a gradient in the chemical potential along the conductor, yet at every position along the wire, the relaxation time approximation assumes that there is again thermodynamic equilibrium, given by (12.7). When extended to interfaces between metals this model has interesting consequences discussed in Sect. 14.1.1.

$$\mu = E_{\rm F} \left[1 - \frac{\pi^2}{12} \left(\frac{k_{\rm B}T}{E_{\rm F}} \right)^2 \right]. \tag{12.8}$$

⁵The chemical potential of a thermodynamic system is the change in the energy of the system when an additional constituent particle is introduced, with the entropy and volume held fixed. In Fermi gases and Fermi liquids, the chemical potential μ is temperature dependent and to lowest order in T is given by

At T = 0 the chemical potential is exactly equal to the Fermi energy and because $E_{\rm F} \gg k_{\rm B}T$ even at room temperature, we have $\mu = E_{\rm F}$ to a very good approximation. For systems containing particles which can be spontaneously created or destroyed, such as photons and phonons, the chemical potential is identically zero.

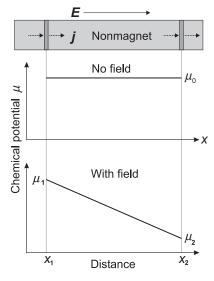


Fig. 12.13. Illustration of the role of the chemical potential in describing electron transport in a nonmagnetic conductor. In the absence of a field there is no current flow and the chemical potential is constant along the conductor. When an electric potential is applied along the conductor a current (positive charges) flows in the direction of E and the electric and chemical potential vary along the direction of current flow. At each local point, however, the relaxation approximation assumes that the scattering events of the conduction electrons maintain a local equilibrium, defined by the Fermi function (12.7), where μ is the local chemical potential

In the following we shall look at electron transport in nonmagnetic metals in more detail. In such systems there are three basic types of scattering processes. It turns out that the first two can be handled within an important approximation, the so called independent electron approximation, which neglects electron–electron scattering. Since within the independent electron approximation collisions can arise only from deviations from perfect periodicity, one scattering mechanism is due to impurities and crystal defects. This scattering mechanism is usually the dominant one at low temperatures. At elevated temperatures significant deviations from perfect periodicity also arise from *thermal vibrations of the atoms*, and this temperature-dependent scattering channel is usually the dominant scattering mechanism at room temperature.

The third scattering channel is due to *electron–electron scattering*. Its formal description requires a complicated multielectron theory.⁶ When electronelectron scattering is examined in *simple metals* such as Al, where no d states are present, one can make some simple arguments why such processes are ineffective for electrons with energies close to the Fermi level. Since electron–

⁶Some developments in this field are based on Landau's Fermi liquid theory.

electron scattering involves excitations in a very small phase space volume near the Fermi surface, the cross-section for this process is small because of the exclusion principle. The dependence of the scattering probability on the energy $E > E_{\rm F}$ of the excited electron and the temperature T is given by

$$\frac{1}{\tau} = A(E - E_{\rm F})^2 + B (k_{\rm B}T)^2, \qquad (12.11)$$

where A and B do not depend on E and T. At room temperature this scattering channel in simple metals is unimportant and therefore the properties of such metals can be described by assuming the independent electron approximation. The situation is very different in transition metals. As we shall see in Sect. 12.5.2, in transition metals the current is still carried by the s electrons as in the simple metals but the scattering of the s electrons into empty d states is the dominant scattering mechanism. It forms the basis for the understanding of the conductivity of the transition metals and their spin dependent transport properties.

In the relaxation time approximation we describe the scattering probability per unit time by $1/\tau$. This means that the electrons, on average, will travel for a time τ between scattering events, and τ is called the mean free time or *relaxation time*. Writing Ohm's law in the form

$$\boldsymbol{j} = \sigma \boldsymbol{E} \tag{12.12}$$

the conductivity σ , defined as the inverse of the resistivity R, may be expressed as a function of the number of free electrons per unit volume n and the relaxation time τ in terms of the *Drude relation*.

In the relaxation time approximation the conductivity σ and the resistivity $R \ [\Omega m]$ are determined by the number of free electrons per unit volume n and the relaxation time τ according to the Drude relation

$$\sigma = \frac{1}{R} = \frac{n e^2 \tau}{m_{\rm e}} = n e b, \qquad (12.13)$$

where $b = e\tau/m_{\rm e}$ is the mobility.

The final important point for the description of transport in nonmagnetic systems is an assertion called *Matthiessen's rule*. It states that the resistivity for a given transport channel in the presence of several distinct scattering mechanisms is simply the sum of the individual resistivities. Written in Drude's form, the resistivity associated with two scattering mechanisms denoted by subscripts a and b reads,

$$R = \frac{m_{\rm e}}{n \, e^2 \, \tau} = \frac{m_{\rm e}}{n \, e^2 \, \tau_a} + \frac{m_{\rm e}}{n \, e^2 \, \tau_b} = R_a + R_b \, . \tag{12.14}$$

The simple kinetic model can be extended to band theory. For free electron bands we have the relation

$$E_{\rm kin}(\mathbf{k}) = \frac{1}{2}m_{\rm e}v^2 = \frac{\hbar^2 k^2}{2m_{\rm e}}$$
(12.15)

and the *electron group velocity* is given by

$$v_{\rm G}(\boldsymbol{k}) = \frac{\hbar k}{m_{\rm e}} = \frac{1}{\hbar} \frac{\partial E_{\rm kin}}{\partial \boldsymbol{k}}.$$
 (12.16)

Since only electrons with energies close to the Fermi energy are mobile we can express the relaxation time τ in terms of the Fermi velocity $v_{\rm F}$ and an electron mean free path $\lambda_{\rm e}$

$$\lambda_{\rm e} = \tau \, v_{\rm F} = \tau \, \frac{\hbar \, k_{\rm F}}{m_{\rm e}} = \tau \, \sqrt{\frac{2E_{\rm F}}{m_{\rm e}}},\tag{12.17}$$

where $k_{\rm F}$ is the Fermi wave vector. Results obtained from this model for Fe and Cu are listed in Table 12.4 [219].

For bands with a more complicated structure, like the d bands shown in Fig. 7.8, we can extend the model by defining a band-index i and wave-vector dependent mean velocity. We write in analogy to (12.16)

$$v_i(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E_i(\mathbf{k})}{\partial \mathbf{k}} . \qquad (12.18)$$

Instead of using the bands from a band structure calculation to determine $v_i(\mathbf{k})$, one often approximates its k-dependence by using a free-electron band

Table 12.4. Some parameters for the metals Fe and Cu. Here *n* is number of free electrons per unit volume, *R* the resistivity, τ the relaxation time, $E_{\rm F}$ the Fermi energy, $k_{\rm F}$ the Fermi wavevector, $v_{\rm F}$ the Fermi velocity, and $\lambda_{\rm e}$ the electron mean free path

		R^{b}					
	$[10^{28} \mathrm{m}^{-3}]$	$[10^{-8}\Omega\mathrm{m}]$	$[10^{-15} \mathrm{s}]$	[eV]	$[10^{10} \mathrm{m}^{-1}]$	$[10^6 \mathrm{m/s}]$	[nm]
Fe	17.0	9.7	2.2	8.2	1.5	1.7	3.7
$\mathbf{C}\mathbf{u}$	8.5	1.7	24.6	8.7	1.6	1.8	44

^{*a*} From Ashcroft and Mermin [219].

^b Values at room temperature.

^c Calculated from n and R by means of (12.13).

^d Separation of $E_{\rm F}$ from bottom of the *s* band in photoemission [249, 250].

^e Calculated from $E_{\rm F}$ by means of (12.17).

^{*f*} Calculated from τ and $v_{\rm F}$ by means of (12.17).

of the form (12.15) with the electron mass replaced by an effective mass $(m_{\rm e})^* > m_{\rm e}$. When plotted as a function of \boldsymbol{k} the band appears flatter and therefore has a more localized character, since a completely localized band would be completely flat without any \boldsymbol{k} dependence. This is nicely seen in Fig. 7.8. In this formalism one then writes the conductivity of d electrons, for example, by the equation

$$\sigma = \frac{n_d \, e^2 \, \tau_d}{(m_e^d)^*},\tag{12.19}$$

where the *d* electron effective mass is much greater than that of *s* electrons, $(m_{\rm e}^d)^* \gg (m_{\rm e}^s)^* = m_{\rm e}^s$. In comparing the conductivity in the *s* and *d* electron channels one needs to recognize that Matthiessen's rule, given by (12.14) and corresponding to resistors *in series*, applies for each separate conduction channel. If however, conduction occurs in two separate channels, like via the *s* electron channel and the *d* electron channel, the resistances will add *in parallel* and the conductivities in series. We then have for the total *s* plus *d* channels conductivity

$$\sigma = \frac{n_s \, e^2 \, \tau_s}{m_{\rm e}} + \frac{n_d \, e^2 \, \tau_d}{m_{\rm e}^*} \tag{12.20}$$

and it is dominated by the larger s electron conductivity. Therefore, as first pointed out by Mott in 1936 [575–577], models for the conductivity of transition metals need to be based on the transport and scattering mechanism associated with s electrons.

12.5.2 The Two Current Model

The number of electrons per atom that can contribute to electrical conduction, $n(E_{\rm F})$, is proportional to the density of states at $E_{\rm F}$. Therefore one might expect from Fig. 12.1 that Cu is a bad conductor and that Fe, Co, and Ni with a large values of $n(E_{\rm F})$ are good conductors. Yet the opposite is the case. As listed in Table 12.5 the conductivity $\sigma = 1/R$ of Cu is about four times larger than that of Co and Ni, and Fe has the lowest conductivity of the three magnetic metals.

The answer to the puzzle was suggested in 1936 by Neville Mott [575, 576, 578]. Based on (12.20) Mott assumed that the *s* electrons carry the electric current and that the electrical resistance is due to a scattering processes in which the electrons jump from the *s* to the *d* band. The more *d* states are available, the stronger is this scattering. The scattering was proposed to be *spin selective* so that electrons can only jump into *d*-states of the same spin. Spin flips are forbidden. Spin selective scattering therefore results in the preferential loss of one spin component.

Table 12.5. Bulk Properties of 3*d* metals Fe, Co, Ni, Cu, and the 4*f* magnet Gd. Listed are the calculated number of *d* holes per atom, $N_{\rm h}^d$, the experimental magnetic moment per atom, $|\boldsymbol{m}|$, the room temperature resistivity, *R*, and the Curie temperature, $T_{\rm C}$.

element	$N_{\rm h}^{d~a}$	$ m{m} ~[\mu_{ m B}]$	$R^{\ b} \ [\Omega{\rm m}]$	$T_{\rm C}$ [K]
Fe (bcc)	3.90	2.216	9.71×10^{-8}	1043
Co (hcp)	2.80	1.715	6.25×10^{-8}	1388
Ni (fcc)	1.75	0.616	6.84×10^{-8}	631
Cu (fcc)	0.50	_	1.68×10^{-8}	_
Gd (hcp)	9.0	7.63	131×10^{-8}	289

^{*a*} From Table 12.1.

^b At 20°C, except for Gd at 25° C.

In the two current model spin-flips are assumed to be negligible, so that only spin-conserving excitations are allowed.

The high resistivity of the transition metals with a partially filled *d*-shell is thus produced by the dominant effect of *s* electron scattering on the *d* hole states. The model is illustrated in Fig. 12.14. In our modern thinking based on band theory, *s* and *d* electrons are strongly hybridized and excitations from *s* to *d* states therefore arise naturally. In some band calculations such excitations can actually be turned on and off through "hopping integrals" between and s-p and *d* orbitals [579].

Mott's model also explains the temperature dependence of the conductivity in the magnetic metals. As early as 1932 Walter Gerlach and coworkers had observed that the conductivity of Ni increases on cooling below $T_{\rm C}$. If the conductivity of a magnetic metal such as Ni is due to transitions in which the electron jumps from the s to the d band, it is clear that below $T_{\rm C}$ only half the electrons can make the scattering transition. Since below $T_{\rm C}$ all the states in the majority band are occupied as evident from Fig. 12.1, only the minority spins can scatter and this leads to a higher conductivity. In a noble metal such as Cu the scattering on d states is excluded because in a simple model the 3d band is full and there are no empty d states. Thus Cu is an excellent conductor. We have seen in Sect. 12.2.2 that this picture is oversimplified since band calculation suggest that even in Cu there are some d states above the Fermi level through hybridization with the s-p band.

The spin selective scattering on the holes of the d band is, in fact, the basis of the important two current model in which the two spin states carry the electric current in parallel without much mutual interaction. The name "two current model" was explicitly introduced in 1968 by Fert and Campbell [580] who conducted a careful study of the low-temperature resistivity of Ni metal

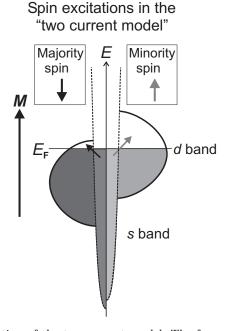


Fig. 12.14. Illustration of the two current model. The ferromagnet is assumed to be aligned by a field in the "up" direction, so that its magnetization M is also in the "up" direction. We have indicated the DOSs of the d electrons by a simple semicircle, as in Fig. 7.6, and have used a simple parabolic DOSs for the s electrons, as expected for a free-electron band, given by (7.44). In the two current model spin-flips are assumed to be negligible so that only spin-conserving excitations are allowed. The scattering process consists of spin-conserving transitions from filled s to empty d states near the Fermi level, as shown by arrows. Because the density of empty states near $E_{\rm F}$ is larger for the spin-up (minority) than for the spin-down (majority) channel, the scattering probability and hence resistivity for spin-up electrons is larger

doped with different transition metal impurities and showed the model to explain their data. It is the cornerstone of recent developments in magnetism discussed in Chap. 14.

At the heart of the two current model is Fermi's "Golden Rule" (see Sect. 9.5.2) which states that the scattering probability of the conduction electrons, which leads to a reduction in conductivity, is proportional to the density of final states, i.e., the density of empty d states above the Fermi level. We can formulate the two current model by denoting the spin relaxation time for the separate up and down channels by τ_{\uparrow} and τ_{\downarrow} . Since conduction may occur in two separate channels the resistances of the two channels add in parallel

and the conductivities add in series so that we have the relation

$$\sigma = \frac{n e^2 \tau_{\uparrow}}{m_{\rm e}} + \frac{n e^2 \tau_{\downarrow}}{m_{\rm e}}.$$
 (12.21)

The resistivities of the individual spin channels follow Matthiessen's rule

$$R_{\rm tot}^{\boldsymbol{S}} = R_0^{\boldsymbol{S}} + R^{\boldsymbol{S}},\tag{12.22}$$

where R_0^S is the scattering contribution due to impurities and R^S describes the spin-dependent $s \to d$ scattering for the separate channels $S = \uparrow$ or \downarrow . The latter channel is proportional to the number of empty d states

$$R^{\boldsymbol{S}} = \text{const. } N_d^{\boldsymbol{S}} . \tag{12.23}$$

Electrical conduction depends on electrons with energies near the Fermi level. In this case the electrons zigzag along their conduction path, and this is referred to as diffusive transport. One may also "shoot" electrons with energies well above the Fermi level through a thin foil. In this case one speaks of *ballistic* transport because of the a well defined k-vector of the electrons. The two current model remains valid even in the ballistic regime, as found from measurements of the transmission of low-energy spin-polarized electron beams through magnetic thin films. These experiments are discussed in Sect. 12.6 below.

We can summarize this section as follows.

The two current model, the cornerstone of recent developments in magnetism, assumes that the electric current flows in two independent spin channels, and that the total conductivity is given by the sum of the two channels.

The *resistivity* is increased when electrons in either spin channel can undergo *spin-conserving* scattering processes to empty d states.

12.5.3 Anisotropic Magnetoresistance of Metals

The change of the resistance of a material under the influence of an applied magnetic field H is known as *magnetoresistance*. It was discovered by William Thomson (1824–1907) (later Lord Kelvin) in 1856, who found that the resistance of an iron conductor was increased by 0.2% when a magnetic field was applied along the conductor and the resistance decreased by 0.4% when the field was applied perpendicular to the current flow.

The effect discovered by Lord Kelvin is today known as anisotropic magnetoresistance (AMR). It is of the order of a few percent, depending on the material, and is illustrated in Fig. 12.15. By defining the resistances R^{\parallel} for current flow parallel to the magnetization, $\boldsymbol{j} \parallel \boldsymbol{M}$, and R^{\perp} for $\boldsymbol{j} \perp \boldsymbol{M}$, the AMR effect is defined as Anisotropic magnetoresistance

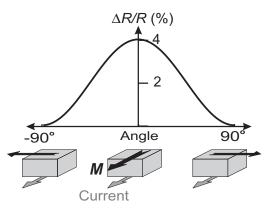


Fig. 12.15. Illustration of the effect of anisotropic magnetoresistance exhibited by a ferromagnetic material. The resistance is highest when the magnetization M is parallel to the direction of the current (R^{\parallel}) and lowest when it is perpendicular (R^{\perp}) . For many years, sensors of magnetic fields were based on this mechanism, before they were replaced by giant magnetoresistance sensors (see Fig. 14.3)

$$\frac{\Delta R}{R_{\rm avg}} = \frac{R^{\parallel} - R^{\perp}}{(R^{\parallel} + 2R^{\perp})/3} \ . \tag{12.24}$$

It is used in many magnetic sensors and was the preferred method of reading the bits on a magnetic recording disk used in data storage until the simple permalloy based thin-film AMR read heads were replaced by ones utilizing the larger giant magnetoresistance effect discussed in Chap. 13.

The microscopic origin of the AMR effect lies in the spin-orbit coupling, as first suggested by Smit [581]. With our knowledge from Sect. 12.5.2 this may be understood as follows. For simplicity we shall assume that we have a strong ferromagnet so that the majority (spin down) states are filled and the conduction is in the spin-up states, only. According to (12.22) and (12.23), the two current model then links the resistivity to the number of empty minority (spin-up) d states, $N_{\rm h}^{\uparrow}$, which for a strong ferromagnet directly determines the magnetic moment $|\mathbf{m}|$. We can write

$$R = R_0 + R^{\uparrow} = R_0 + \text{const.} N_{\rm h}^{\uparrow} = R_0 + \text{const.} |\boldsymbol{m}|.$$
(12.25)

The term R_0 is isotropic, to a good assumption. We know that the magnetic moment $|\mathbf{m}|$ created by the exchange interaction is also intrinsically isotropic. However, in the presence of the spin–orbit interaction we have seen in conjunction with (7.66) that there are second order correction terms to the spin moment that scale with the square of the ratios of the spin–orbit and the ligand field interactions, $(\zeta/\Delta_{\rm CF})^2$, and the spin–orbit and the exchange interactions, $(\zeta/\Delta_{\rm ex})^2$, respectively. The term $(\zeta/\Delta_{\rm CF})^2$ arises from mixing of

the same spin states while the term $(\zeta/\Delta_{ex})^2$ is due to spin-flip terms. There has been much debate in the literature which of the two terms is more important [582, 583]. Of importance to us here is only that the anisotropy arises in second order in the spin-orbit coupling.⁷ When the magnetization is rotated by an external magnetic field relative to the current direction an asymmetry in scattering arises because the magnetic moments and the number of empty minority spins will change. This is the origin of the AMR effect. We can write

$$\Delta R = R^{\parallel} - R^{\perp} = \text{const.}(|\boldsymbol{m}^{\parallel}| - |\boldsymbol{m}^{\perp}|) , \qquad (12.26)$$

where the labels \parallel and \perp refer to the orientation of \boldsymbol{m} relative to the current direction. As seen in Fig. 12.15 the AMR effect has a $\cos^2 \theta$ dependence on the angle θ between the moment and current direction. This fact was derived as early as 1938 by Döring [584].

Today, many kinds of magnetoresistance effects are known and distinguished. Among them are giant magnetoresistance [79, 80], tunnel magnetoresistance [585], colossal magnetoresistance [586], ballistic magnetoresistance [587], and extraordinary magnetoresistance [588], to name a few.

12.6 Spin Conserving Electron Transitions in Metals

In the following two sections we consider the spin dependent transitions of electrons as they traverse a metal. Of primary importance to us are two types of processes already discussed in Sect. 8.6.2. The first one involves transitions between opposite spin states, the other transitions within the same spin states. Both of these processes fall under the name *spin selective* transitions, but one process involves "spin flips" while the other preserves the spin in the scattering event. We shall discuss spin conserving transitions first.

12.6.1 Spin Conserving Transitions and the Photoemission Mean Free Path

The two current model of electrical conduction implies that the electrical resistivity is given by *spin conserving* scattering. The two spin bands have different scattering rates, and thus the scattering is spin selective. Transitions from the spin up to the spin down band and vice versa are sufficiently rare so that such spin nonconserving transitions can be neglected in the electrical resistivity.

However, spin nonconserving transitions must occur nevertheless to allow the thermal equilibrium to be established and to return the magnetization to the equilibrium after external excitation. For example, if a ferromagnetic metal is heated to a higher temperature, the magnetization is reduced as we

⁷This is in contrast to the *magnetocrystalline anisotropy* which is first-order in the spin–orbit coupling.

know from experience. This will require a reduction of the spin polarization of the electrons generating the magnetization, and hence, no matter how complicated the intermediate processes may be, in the end there must have been electron transitions between the two different spin states. It is important to remember that three simultaneously valid conservation laws, namely conservation of angular momentum, linear momentum, and energy impose severe restrictions on transitions between the spin states.

Transitions between spins states have to satisfy the three basic conservation laws of energy, angular momentum, and linear momentum.

The conservation laws are ultimately the reason for the general validity of the two current model. As discussed later it turns out that a generalized two current model exists, that is valid not only for electrons with energy near $E_{\rm F}$, so called *diffusive electrons* that determine the conductivity, but also for electrons with kinetic energies far above $E_{\rm F}$, so called *ballistic electrons*. The latter are of interest in spin polarized photoemission and experiments with spin polarized beams and in the following we shall discuss the information obtained on the transport of such electrons through solids.

One of the most general results obtained with spin polarized electrons concerns the electron probing depth $\lambda_{\rm e}$. It is the distance from the surface, measured perpendicular to the surface, from which the electrons originate. Assuming that the contribution from layers below the surface decays exponentially toward the bulk, one defines $\lambda_{\rm e}$ as the length from which the fraction $1-(1/e) \approx 2/3$ of the total signal originates. The *spin-averaged* probing depth $\lambda_{\rm e}$ is related to the *spin-dependent* probing depths of the spin-up, $\lambda_{\rm e}^+$, and spindown, $\lambda_{\rm e}^-$, electrons according to $1/\lambda_{\rm e} = (1/\lambda_{\rm e}^+ + 1/\lambda_{\rm e}^-)/2$. The length $\lambda_{\rm e}$ can be translated via the group velocity v into the lifetime $\tau_{\rm e}$ of an electron in excited states within the solid according to $\tau_{\rm e} = \lambda_{\rm e}/v$. This lifetime is very short in the case of metals for energies of several eV above the Fermi energy $E_{\rm F}$, typically of order of 10^{-15} s, but becomes longer for $E \to E_{\rm F}$.

The reason for the short lifetime in the excited states is that the electrons interact via the Coulomb field with the metallic electrons, losing energy very rapidly by formation of a cascade of low energy electrons. It is thus clear that the measurement of $\lambda_{\rm e}$ yields information on the fast electron dynamics, and if the spin is included in the analysis, it provides information on the spin dependence of the electron interactions as well.

Let us first consider the determination of λ_e without spin analysis. A large amount of data has been accumulated from the *overlayer method* in which the attenuation of a prominent substrate photoemission peak is measured as a function of the overlayer thickness x and the intensity decrease is fitted with an exponential decay e^{-x/λ_e} . This methods is quite elegant and is based on the fact that photoemission peaks correspond to "elastic" electrons that have remained unscattered on the way to the detector. Scattered electrons have a lower energy and hence do not contribute to the measured peak in-

tensity. Also, different materials can be distinguished by their characteristic photoemission peaks. The data for many materials are often displayed in an oversimplified way as a "universal curve" which shows $\lambda_e(E)$ as a function of energy E, independent of material parameters [237]. While the overall energy dependence with a certain spread of values indeed follows a "U"-shaped curve, with a minimum around 50 eV and larger values at lower and higher energies, the detailed low energy behavior depends very much on the material, as we shall see later.

In the determination of the escape depth a problem is encountered for electrons that have a kinetic energy of nearly zero. Since the kinetic energy of the detected electrons is measured relative to the vacuum level, zero kinetic energy means that the electrons can barely escape from the solid. The photoemission spectrum at such low energies is entirely dominated by a huge background of scattered electrons, the so-called *inelastic peak*. The conventional method of measuring an elastic peak intensity does no longer work since the elastic peak intensity cannot be reliably determined because it is swamped by the inelastic tail. Therefore electrons from the underlayer and the overlayer cannot be distinguished.

However, the problem in determining the mean free path of electrons with very low kinetic energy can be overcome. This is quite fortunate because of the importance of very low energy electrons in the magnetic interactions. It is these electrons that have comparable energies to the 3d valence electrons and therefore can strongly interact via the exchange interaction. In fact, the very interaction mechanisms are the main topic of the present section.

The trick to obtain information on the mean free path of low energy electrons is the measurement of spin polarization [589]. In analogy to the overlayer method one deposits either a nonmagnetic layer on top of a magnetic substrate, or vice versa. The art of fabricating such ultrathin magnetic structures is by now well established [250]. Electrons are excited by an incident primary electron or photon. The provenance of the low energy electrons is tagged by their spin polarization which is zero for emission from a nonmagnetic film but different from zero for emission from a magnetic film. The increase or decrease of the spin polarization of the emerging secondary electrons is measured by a spin analyzer as a function of overlayer thickness x [590]. If a magnetic layer is the overlayer the spin polarization will increase with magnetic thickness, if a nonmagnetic layer is on top the spin polarization will decrease with its thickness. From analysis of such magnetization versus thickness curves one can therefore obtain accurate values for the spin-averaged probing depth $\lambda_{\rm e}$ of the low energy electrons.

The results for the spin-averaged electron absorption coefficient $\mu_e = 1/\lambda_e$ shown in Fig. 12.16 were obtained by such measurements of the attenuation of the spin polarization. They are valid for the 0–2 eV kinetic energy range that one can detect with ease in secondary emission. The striking result is that the transition metals with open d shells exhibit larger electron absorption coefficients, that is shorter probing depth λ_e , compared to the noble metals Cu, Ag, and Au. It is evident that μ_e increases with the number of d holes. In

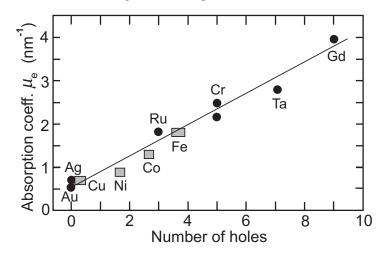


Fig. 12.16. The *spin-averaged* absorption coefficient or inverse mean free path, $\mu_{\rm e} = 1/\lambda_{\rm e}$, for low energy electrons of 0–2 eV kinetic energy versus the total number of unoccupied *d* states for various metals labeled in the figure. The attenuation coefficients were taken from [590]. We have used the values for the number of *d* holes in Fe, Co and Ni 3.4–3.93 for Fe, 2.5–2.80 for Co, and 1.5–1.78 for Ni, as discussed in Sect. 12.2.2. It is evident that the absorption depends on the number of unoccupied *d* states and is not a universal curve as assumed previously

particular, the series Ni, Co, Fe, and Cr shows this trend beautifully. This is analogous to Mott's model developed for very low energy electrons, discussed in Sect. 12.5, where the electrical resistivity is due to scattering on the *d*holes. Drouhin [591] has discussed various effects associated with scattering of electrons on *d*-holes, but he neglects the correction of the number of *d*-holes arising from hybridization with s-p states as discussed in Sect. 12.2.2.

Figure 12.16 is the key why all low-energy electron spectroscopies measure the electronic and magnetic properties of the layers very near the surface with metals having open d-shells. We already made use of this feature in the determination of the temperature dependence of the surface magnetization in Fig. 11.6. From the dependence of the electron absorption on the number of d-holes one concludes that *ferromagnetic* transition metals will be spin filters, absorbing preferentially minority spins because the existence of the magnetic moment requires that there are more minority spin holes in the d states compared to majority spin holes. These important results must be remembered.

The scattering length of low energy electrons decreases with increasing number of d holes.

Ferromagnetic transition metals are *spin filters* with preferential *absorption of minority spins*.

12.6.2 Determination of the Spin-Dependent Mean Free Path using the Magnetic Tunnel Transistor

With the spectroscopic techniques discussed so far, the smallest electron energy that can be studied is limited by the vacuum potential of the ferromagnetic layer. Consequently, the information on transport properties are limited to electron energies $E > 4-5 \,\mathrm{eV}$ above $E_{\rm F}$. These energies are larger than the upper edge of the minority *d*-bands in ferromagnetic transition metals and therefore far away from the energy range in which maximum spin selective scattering is expected. The electron interactions at low energies are most important for applications in new solid state devices based on the manipulation of spin polarized currents. Techniques that can explore the energy range close to $E_{\rm F}$ are needed for the development of spin based electronics or "spintronics" in which the spin rather than the charge of the electron is carrying the information.

Several techniques have emerged to study electron transport through ferromagnetic metals without forming an electron beam in vacuum. One of the new techniques applicable to electron energies of 1–2 eV from $E_{\rm F}$ is Ballistic Electron Magnetic Microscopy (BEMM) [592]. It uses the tip of a scanning electron microscope to inject a finely focused electron beam into a trilayer, e.g., Co/Cu/Co. The electric current transmitted to the semiconducting substrate of the trilayer film depends on the relative orientation of the magnetization of the Co layers. The first Co layer acts as a polarizer of the electron current and the second as an analyzer. If the magnetization in the two layers is parallel, the transmission is high, but if it is antiparallel, the transmission is low. BEMM makes it thus possible to study the efficiency of spin filtering as it depends on the voltage between the tip and the film determining the energy at which the electrons are ballistically injected.

Another important device, the spin valve transistor or magnetic tunnel transistor (MTT) was introduced in 1995 by Monsma and collaborators [594]. The MTT is a three terminal device in which the spin polarization of the injected electrons is determined by spin filtering in the base region of the device. By a suitable choice of materials, the spin polarization can be very large [136]. With a MTT, spin selective electron attenuation as well as the measurement of the spin polarization can be performed at electron energies of $1-2 \,\mathrm{eV}$ from $E_{\rm F}$ without ever taking the electrons out of the metal into vacuum.

Figure 12.17 shows one form of the MTT in which a spin valve structure is used as the base. Typically, the spin valve structure consists of 5 nm $\text{Co}_{70}\text{Fe}_{30}/4$ nm Cu and 4 nm Au/5 nm Ni₈₁Fe₁₉. The emitter layer is 30 nm Cu. The CoFe and NiFe layers have different coercivities. In large magnetic fields, the magnetic layers in the base are aligned parallel. When the field is reversed, the magnetization in the NiFe layer switches first while the magnetization of the CoFe layer remains in the previous orientation up to a field of 10^4 A/m . The switching of the layers from parallel (P) to antiparallel (AP)

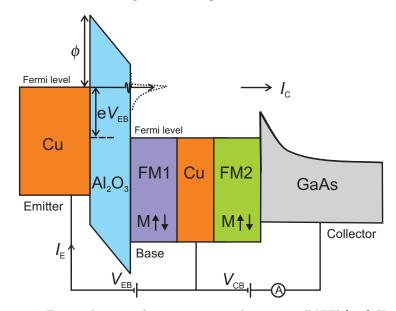


Fig. 12.17. Energy diagram of a magnetic tunnel transistor (MTT) [593]. Unpolarized electrons are emitted from Cu through the Al₂O₃ tunnel barrier and traverse the ferromagnet FM1 whereby they are spin filtered and emerge with a polarization P into the Cu base. To reach the GaAs-collector, the electrons have to traverse a second ferromagnet FM2 which can be magnetized parallel or antiparallel to FM1. There is a very large asymmetry A in the current I_c measured in the collector depending on the relative magnetization direction in FM1 and FM2

gives rise to a huge asymmetry of the transmitted current. This asymmetry is explained by the spin dependent attenuation. The attenuation length $\lambda_{\rm e}$ is calculated from the current measured in the collector by assuming an exponential attenuation of the injected current I_0 with film thickness *s* according to $I_0 \exp(-s/\lambda_{\rm e}^{\pm})$ where $\lambda_{\rm e}^{\pm}$ stands for the attenuation length of majority (+) and minority (-) spin electrons. $\lambda_{\rm e}^{\pm}$ is the inverse of the inelastic attenuation coefficient $\mu_{\rm e}^{\pm}$. The energy of the electrons injected from the Cu emitter is determined by the voltage $V_{\rm EB}$ applied between base and emitter. The energy window accepted by the GaAs collector is determined by the voltage $V_{\rm CB}$ applied between base and collector. The MTT is a powerful tool to study spin dependent transport of hot electrons. In fact, it shows that one can come close to realizing the conditions pictured in Fig. 12.20.

Figure 12.18 shows results for the electron attenuation length $\lambda_{\rm e}$ obtained by Parkin and collaborators [595] for Ni₈₁Fe₁₉. We see that the spin dependence of the attenuation is indeed much larger at the low electron energies. According to Fig. 12.18 we find $\lambda_{\rm e}^+/\lambda_{\rm e}^- = 6.3$ at $E = 1 \,\mathrm{eV}$. The majority spin absorption length $\lambda_{\rm e}^+$ is found to decrease more rapidly with increasing electron energy than the minority spin absorption length increases. At higher

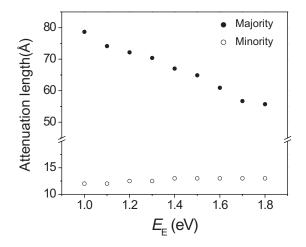


Fig. 12.18. The attenuation length of majority and minority spin electrons in Ni₈₁Fe₁₉ versus the electron energy $E_{\rm E} = eV_{\rm EB}$, as determined with the MTT [595]

energy one therefore finds a reduced value of $\lambda_{\rm e}^+/\lambda_{\rm e}^-$. This is confirmed by measurements at $E = 12.6 \,\mathrm{eV}$ above $E_{\rm F}$ in Fe, where Donath finds a ratio of $\lambda_{\rm e}^+/\lambda_{\rm e}^- = 1.7 \pm 0.3$ [558].

This behavior can be qualitatively understood by plotting the ratio of the hole states of majority to minority spins shown in Fig. 12.3 versus energy. It is in agreement with the model for the spin dependent attenuation set forth in Sect. 12.6.1. However, Jansen and collaborators [596] found that the magneto-current defined by $I_{\rm MC} = (I^{\rm P} - I^{\rm AP})/I^{\rm AP}$ is reduced when the MTT, made from Ni₂₀Fe₈₀ permalloy, is heated to room temperature from 70 K. This is interpreted as evidence for transitions of minority spins to majority spin states concomitant with the generation of low energy spin waves. Now we have to realize that it takes a ballistic electron with velocity $v = 3 \times 10^6$ m/s the time $t = s/v = 3 \times 10^{-15}$ s to traverse a distance of s = 10 nm. This time is not long enough to generate spin waves in appreciable quantities. Electron scattering on spin waves on this fast time scale is therefore questionable, and the experimental evidence presented in [596] needs clarification.

According to Parkin and collaborators [597], the electron spin polarization injected into the collector can be measured by the degree of circular polarization of the light emitted from a GaAs/In_{0.2}Ga_{0.8} multiple quantum well light emitting diode. The emission of circularly polarized light is in reversal of the process of emission of polarized electrons from GaAs in Section 8.2. In this way, it should be possible in the future to perform experiments similar to the ones with free electron beams in devices. This is expected to greatly facilitate the magnetic engineering of "spintronic" sensors and memories [598].

12.6.3 Probability of Spin-Conserving relative to Spin-Non-Conserving Transitions

In evaluating how important transitions between the two spin states are in comparison to spin-conserving transitions one looks at the interaction of a monochromatic spin-polarized electron beam with a magnetic sample. In practice, such beams are obtained from a GaAs photocathode and by changing the accelerating voltage one can create monochromatic (typically $\Delta E \sim 0.1 \text{ eV}$) electron beams of energy E_0 that are either unpolarized or polarized with a freely chosen direction of the spin polarization vector \boldsymbol{P} in space. A typical experimental geometry for a transmission experiment is shown in Fig. 12.19. Experiments can also be performed in a reflection geometry, as indicated [599]. The *elastic scattering* experiment illustrated in Fig. 12.19 only looks at the intensity and polarization of the electrons scattered without energy loss.

Since the interpretation of the results is simpler for a transmission experiment because of the absence of spin–orbit contributions to the measured spin-polarized intensity, we shall discuss transmission results here. They are found to be in complete agreement with reflection results if the latter are corrected for spin–orbit effects [599].

In order to assess the importance of spin-flips in the elastic transport of low-energy (of order $10 \,\mathrm{eV}$) electrons through a magnetic material one

Quasi-elastic transmission or reflection

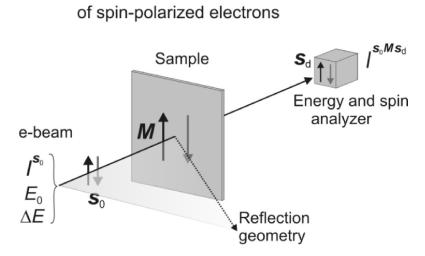
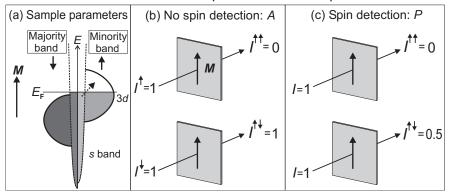


Fig. 12.19. Schematic of two different transmission experiments on spin-polarized electron transmission through magnetic thin films, as discussed in the text. A reflection geometry is also shown as a dotted line. The intensities are labelled with subscripts that follow the order in the figure: spin of incident beam s_0 , sample magnetization M, detected spin s_d



Two current model - spin selective absorption

Fig. 12.20. Schematic of two experiments, with and without spin detection, to determine the importance of spin-flip scattering as discussed in the text. (a) Defines the relative spin and magnetization orientations in the sample. We assume an idealized situation where a strong ferromagnet with filled majority states and suitable thickness completely absorbs incident minority (spin-up) spins but transmits all majority (spin-down) spins. Spin-flip scattering by the sample is assumed to be zero. This gives the transmitted intensities for the cases shown in (b) and (c). The experimental results for experiment (b), i.e., polarized incident beam and no spin detection, are used to determine the asymmetry A in (12.27). Those for experiment (c), i.e., unpolarized incident beam and spin detection, are used to determine the degree of spin polarization P in (12.28)

performs two different experiments and compares their results. In order to demonstrate the method we shall, for simplicity, assume that the incident beam is 100% spin polarized and that the sample is magnetically saturated in the "up" or "down" direction, as illustrated in Fig. 12.20. The spin of the incident beam, s_0 , is chosen to be parallel or antiparallel to the magnetization M of the sample.

In the first experiment, we use a *spin polarized incident beam* with spin direction s_0 and simply measure the intensity of the transmitted beam, without spin analysis, for s_0 parallel and antiparallel to M. In this experiments the measurement provides two numbers, the intensities for the two relative orientations of s_0 and M. In the second experiment we use an *unpolarized incident beam* and measure the intensity of the transmitted beam with a spin resolving detector aligned in the direction s_d , for s_d parallel and antiparallel to M. Hence we again measure two intensities, corresponding to the relative orientations of M and s_d .

From an experimental standpoint one views the process by the spin polarization of the beam and the magnetization, as shown in Fig. 12.19. By reference to this figure we can now discuss the two experiments. In the first experiment (Fig. 12.20b) we distinguish the case where s_0 and M are antiparallel, characterized by a transmitted intensity $I^{\uparrow\downarrow}$, and the case where the two are parallel with $I^{\uparrow\uparrow}$. The measured *spin asymmetry A* is defined by (8.32) as

$$A = \frac{I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}{I^{\uparrow\downarrow} + I^{\uparrow\uparrow}} . \tag{12.27}$$

In the second experiment (Fig. 12.20c) we use an unpolarized incident beam and measure the spin polarization P that has developed in the transmission process for $s_{\rm d}$ parallel and antiparallel to M. The measured polarization Pis defined according to (8.17),

$$P = \frac{I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}{I^{\uparrow\downarrow} + I^{\uparrow\uparrow}} . \tag{12.28}$$

It can be shown [344] that the condition for no spin-flip scattering is,

$$\boxed{A=P}.$$
 (12.29)

The relation (12.29) therefore states the condition for the validity of the two current model in electron transmission through a magnetic sample. If shown to hold, it would extend the two current model for conduction electrons with energies close to the Fermi energy, discussed in Sect. 12.5.2, to higher electron energies.

In order to make (12.29) plausible let us perform a Gedanken-experiment as outlined in Fig. 12.20. We assume an idealized spin filter similar to what actually exists in optics for polarized light. This spin-filter consists of a "strong" ferromagnet of suitable thickness which completely absorbs incident minority (spin-up) spins but transmits all majority spins, as illustrated in Fig. 12.20a. That is, we assume that the sample thickness is much larger than the minority spin absorption length λ^{\uparrow} and that $\lambda^{\downarrow} = \infty$ so that the majority electrons are not absorbed. In Fig. 12.20b, c we show the results for the two Gedankenexperiments that determine A and P according to (12.27) and (12.28), respectively.

From Fig. 12.20b we see that for the conditions outlined in (a), the measured intensity is binary if no spin-flips occur. Incident spin-up electrons are absorbed while incident spin-down electrons are transmitted. We would get A = +1 for the experiment in Fig. 12.20b. Similarly, for the case shown in Fig. 12.20c we would get P = +1, since again one of the intensities would be zero and for the other case only 50% of the incident electrons, those with spin down, would be detected.

If we now assume that there are spin flips induced by the sample we would convert spin-up into spin-down electrons and vice versa. If we do *not* detect the spin of the transmitted beam as in (b) we would measure an intensity $I^{\uparrow\uparrow} > 0$ and $I^{\uparrow\downarrow} < 1$ and therefore |A| < 1. If we detect the spin as in (c), however, we would still have $I^{\uparrow\uparrow} = 0$. Since the intensity $I^{\uparrow\downarrow}$ would certainly

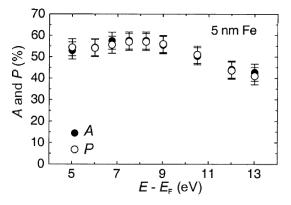


Fig. 12.21. Experimental results by Weber et al. [600] for the spin asymmetry, A, and spin polarization, P, determined for the elastic transmission of low energy electrons. The experiments were performed as illustrated in Fig. 12.20 using a 5 nm thick Fe film

be finite, we would have P = 1, as before. In the presence of spin flips we would therefore measure $A \neq P$!

Experimentally one finds A = P within experimental error for low energy electrons as shown in Fig. 12.21 [600]. The attenuation of the elastic electrons is strong in both spin channels. Minority spins are removed with higher probability from the "quasielastic" channel but do not reappear as majority spins. The qualification "quasielastic" is necessary because the energy resolution in any experiment is of course finite, meaning that electrons that have lost some small amount of energy, in the experiment [601] up to $\approx 0.5 \,\mathrm{eV}$, are included in the measurement of the elastic channel. Such small energy losses will accompany a transition from the minority spin state to the majority spin state by the excitation of a spin wave. At ambient temperature, spin waves have an energy of typically <100 meV. Minority electrons having generated a spin wave and thus made a transition to the majority spin state would therefore remain in the quasielastic channel. Because of P = A the experiment proves that such spin transitions are rare enough so that they cannot be detected on the background of spin conserving transitions. Hence the ferromagnet acts very much like a polarization filter in optics that absorbs one type of polarized light but does not "flip" the polarization. The conclusion is that spin wave excitations are rare on the scale of the total electron-electron scattering cross-section and that spin filtering is simply due to spin conserving $s \to d$ transitions as discussed for the conductivity in Sect.12.5. We can summarize as follows:

The *electron mean free path* is dominated by *spin-conserving scattering* events. The two current model remains valid at larger electron energies.

Despite their low probability relative to the total scattering probability, spin-flips can nevertheless be observed by careful measurements that investigate the energy region just outside the elastically scattered intensity. Such high-resolution spin-polarized electron-energy-loss spectroscopy or SPEELS measurements will be discussed in Sect. 12.7.2 later.

12.6.4 The Complete Spin-Polarized Transmission Experiment

Instead of having the electron spin polarization P_0 at incidence either parallel or antiparallel to the magnetization M as in Sect. 12.6.3, we now consider what happens when P_0 is perpendicular to M. This initial configuration is unstable and tends to relax into the stable configuration where P is antiparallel to M. One can now observe the effect of the exchange interaction on the injected spins leading to precession of P about M. The precession of P establishes unique information on the energy dependence of the elusive exchange field.

Furthermore, one observes a rotation of \boldsymbol{P} into the direction of the majority spins. This relaxation or damping motion, discussed in Sect. 3.6.2, is perpendicular to the precession and is induced by preferential scattering of the minority spins. The integral pathway of \boldsymbol{P} on the sphere of Poincaré is formally derived in Chap. 8. As an additional bonus, the motion of \boldsymbol{P} reveals the torques acting on the injected spins. This arises because the time derivative of the angular momentum \boldsymbol{S} connected to the spins is $\partial \boldsymbol{S}/\partial t = \boldsymbol{T}_s$ according to (3.30) where \boldsymbol{T}_s is the torque acting on the injected spins. Assuming conservation of angular momentum, it follows that an equal but opposite torque \boldsymbol{T}_s must be acting on the vector \boldsymbol{S} of the spins in the material into which the electrons are injected. The observation of the motion of \boldsymbol{P} can thus form the basis for evaluating experimentally the torque acting on the magnetization by the injected spins which is of high current interest as discussed in Sect. 14.2.1. For the experiment, both, a spin polarized incident beam and a spin analyzer for detecting the motion of the spin polarization \boldsymbol{P} are needed.

The spin polarization vector \boldsymbol{P} of the transmitted electrons is calculated from the expectation values of the Pauli matrices as shown in Sect. 8.4. If we chose our experimental geometry in accordance with the notation of Fig. 8.8, as shown in Fig. 12.22a, with \boldsymbol{P}_0 parallel to the *x*-axis, the electron beam direction along y, and \boldsymbol{M} antiparallel to z, the precession is described by an azimuthal angle φ in the x - y plane and the damping or relaxation by a polar angle θ measured from the *z*-axis as described by (8.35) and (8.36). Figure 12.22a shows that for \boldsymbol{M} along -z the transmitted beam will have a preferential up-spin polarization. This comes about as follows. The incident beam can be described as a superposition of up spins (along z) and down spins (along -z). If the magnetization vector \boldsymbol{M} is along -z, the *minority* spins in the sample are also along -z (see Fig. 7.6), and hence incident down spins are preferentially absorbed by spin-conserving excitations within the minority band.

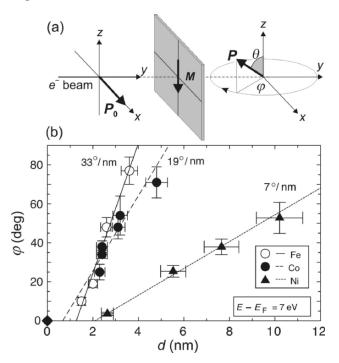


Fig. 12.22. (a) Experimental geometry for transmission of a spin-polarized beam, propagating along y and polarized along x, through a thin-film sample with in-plane magnetization M along -z. (b) Measured azimuthal spin precession angle φ versus magnetic film thickness d for Fe, Co, and Ni sandwiched between polycrystalline Au, measured with elastic electrons of 7 eV above $E_{\rm F}$. The data point at d = 0 is obtained with a pure Au-film of thickness d = 20 nm which apparently generates no precession. Note that there are dead magnetic layers of $d \approx 1$ nm for Fe and Co and $d \approx 2$ nm for Ni. From [600, 602]

The motion of the spin polarization vector \boldsymbol{P} has been observed by letting a beam of spin-polarized electrons traverse a ferromagnet and measuring the direction and magnitude of the spin polarization vector \boldsymbol{P} of the elastic electrons [600, 601]. One result of the transmission experiment has already been shown in Fig. 12.21, but in the earlier version of the experiment, \boldsymbol{P}_0 was either parallel or antiparallel to \boldsymbol{M} , which yields the spin dependent absorption \boldsymbol{A} . Now we want to observe the precession of \boldsymbol{P} which requires that \boldsymbol{P} of the incident beam is chosen perpendicular to \boldsymbol{M} .

In practice, a spin polarized low energy electron beam is passed through a ferromagnetic film of thickness $d \sim 1-10$ nm. Of course, such a ferromagnetic film is too thin to be free standing and it has to be supported mechanically and protected chemically against corrosion. In the experiment [600, 603] the support is provided by a substrate consisting of 20 nm of polycrystalline gold, and another 2 nm of gold is added on top for chemical protection. It is im-

portant to avoid pinholes in such Au/FM/Au trilayer structures. Even the smallest pinholes will let electrons pass without traversing the ferromagnet thereby masking the effects of the spin dependent interactions.⁸ The spin polarization \boldsymbol{P} of the emerging electrons is measured on the very small fraction of electrons that have traversed the trilayer without losing energy (we are again speaking of "quasi"-elastic electrons as the resolution of the energy analyzer is finite, in the example ~0.5 eV). The electrons require less than a femtosecond (10^{-15} s) to traverse 1 nm. Hence the precession and rotation of \boldsymbol{P} occurs at the femtosecond time scale due to the high value of the exchange field and the short time scale of electron-electron scattering.

Figure 12.22b displays the observed precession angle φ as it depends on the film thickness d for Fe, Co, and Ni. It is valid for electrons at an energy of 7 eV above $E_{\rm F}$. A linear fit describes the observations with all three ferromagnetic metals signaling that the precession is a bulk property of the ferromagnets. The slope is the *specific precession angle*, i.e., the angle per unit film thickness, which for Fe, Co, and Ni is found to be $\overline{\varphi} = 33^{\circ}/\text{nm}$, $19^{\circ}/\text{nm}$, respectively. The fact that the linear fits intersect the abscissa at finite film thickness is attributed to dead layers at both Au/FM interfaces.

The time t spent by the electrons within the ferromagnet of thickness d determines both the group velocity $v_{\rm G} = d/t$ (see (12.16) of the electrons in the ferromagnet and the precession angle $\varphi = t\Delta/\hbar$ (see (3.59)), where Δ is the exchange splitting. We therefore obtain for the specific precession angle,

$$\bar{\varphi} = \frac{\Delta}{\hbar v_{\rm G}}.\tag{12.30}$$

The observed specific precession can thus be compared to the exchange splitting Δ and group velocity $v_{\rm G} = ({\rm d}E/{\rm d}k)/\hbar$, obtained in band structure calculations. The data shown in Fig. 12.22 as well as the energy dependence of $\overline{\varphi}$ reported in [600] agree with the expectations. The smaller specific precession in Ni for instance is consistent with the small magnetization and the lower $T_{\rm C}$ of this metal. The large value of the specific precession points to sizeable exchange splittings persistent to electron energies of $\approx 10 \,\mathrm{eV}$ above $E_{\rm F}$. This is consistent with the results of band structure calculations, predicting $\Delta \approx 1 \,\mathrm{eV}$ even at electron energies as high as $15 \,\mathrm{eV}$ above $E_{\rm F}$.

Experimental data for the damping angle θ enclosed by P with the z-axis are shown in Fig. 12.23. The angle θ decreases with increasing thickness d of the Fe, Co, and Ni polycrystalline films sandwiched between Au, as expected. The relaxation of P into the direction of the majority spins antiparallel to M occurs within a few nanometers from the point of injection corresponding to a few femtoseconds. It is due to the spin conserving inelastic scattering of minority spins. This scattering is much larger in Fe and Co compared to Ni, reflecting the smaller density of unoccupied minority states in Ni. The motion

⁸This is probably the reason for the smaller spin dependent absorption reported earlier in [604].

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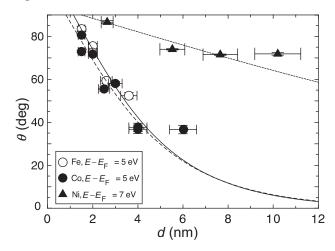


Fig. 12.23. The evolution of the polar angle θ of P with the thickness d of Fe, Co, or Ni. Initially, at incidence of the electrons, $\theta = 90^{\circ}$, but in these polycrystalline samples, there were dead layers at the interfaces to Au in which no rotation occurred. The measurement was done on the quasielastic electrons of energy 5 and 7 eV above $E_{\rm F}$. The curves through the data points are from absorption experiments [603], corrected for incomplete polarization of the incident electron beam (Fe: continuous line, Co: dashed line, Ni dotted line). From [600, 602]

of P into the direction of the z-axis corresponds to a damping of the spin precession as discussed in Sect. 3.6.2.

Assuming again conservation of angular momentum, it must generate what is called a "damping torque" acting on M that can be used for magnetization switching. It is seen that this torque may be generated solely by spin conserving scattering processes, i.e., the preferential absorption of minority spins, and does not require transitions between the two spin states. Therefore, the "damping torque" can develop on the time scale of femtoseconds which is essential for the applications discussed in Sect. 14.2.1.

The angular momentum change that occurs in both systems when a spin polarized electron beam of polarization P_0 interacts with a thin ferromagnetic film of magnetization M, orientated at a finite angle with P_0 , is due to the preferential spin-conserving absorption of minority spins, and not to transitions between opposite spin states.

The rotation of P into the z-axis can also be derived from the quite different absorption experiments illustrated in Fig. 12.20. If the injected spins s_0 are parallel to the *majority* spins in the ferromagnet, the transmitted intensity is $I = I_0 \exp(-\mu_e^+ d)$, and for s_0 along the minority spin direction we have $I = I_0 \exp(-\mu_e^- d)$, where μ_e^+ and μ_e^- are the absorption coefficients for majority and minority spins, respectively. The spin asymmetry of electron absorption given by (8.32), as a function of film thickness d, has been measured, as well [603]. The angle of rotation calculated from these measurements with (8.36) is indicated for Fe, Co, and Ni in Fig. 12.23. It agrees within experimental uncertainty with the rotation angle θ obtained by the direct measurement of \boldsymbol{P} . We can summarize as follows.

Precession and relaxation of ballistically injected spins proceed over a very short distance of nanometers, corresponding to a time scale of 10^{-15} s. The relaxation of the injected spins into the direction of the majority spins does not require transitions between opposite spin states.

12.7 Transitions Between Opposite Spin States in Metals

In this section we shall explore various types of excitations between opposite spin states and discuss experiments aimed at their detection and understanding.

12.7.1 Classification of Transitions Between Opposite Spin States

We have learned that the rarity of transitions between opposite spin states is the essence of the two current model. But such transitions must nevertheless occur to establish the equilibrium after an excitation of the magnetization. The interesting question is how fast the equilibrium can be established, or in other words, how important are transition involving a change in spin in comparison to spin conserving transitions. To discuss this question, let us first consider the basic processes that can induce a change of the spin state of an electron.

"Spin flips" may be induced by application of a magnetic field oscillating perpendicular to an applied steady magnetic field. The spin flip transition occurs when the frequency ω of the oscillating magnetic field is equal to the spin precession frequency in the steady field. It involves the absorption of a magnetic field quantum $\hbar\omega$. This process has been discussed in Sect. 3.6.3 and forms the basis of NMR and ESR. It occurs on a time scale which is determined by the energy separation ΔE of the spin up and spin down states according to $\tau = 1/\omega = \hbar/\Delta E$. Unfortunately, the term "spin flip" is often used incorrectly, including situations when the spin is conserved during the process. For example, it is important to distinguish "spin flips", involving transitions between opposite spin states from the spatial separation of the two spin states, as in the Stern Gerlach experiment, or more generally from the case where spin conserving transitions lead to preferential absorption of one spin component, as in a spin filter.

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"Precessional spin switching" may be accomplished by letting the spin precess about a perpendicular magnetic field pulse of suitable length [605]. This method, also called "ballistic switching", is important in magnetization reversal, and its time scale is given by the precession frequency ω of the magnetic moment in the magnetic field as discussed in Sect. 3.6, with a typical value of 10 ps for a 90° precession in a 1 T field. Precessional switching with a magnetic field pulse is discussed later in Sect. 15.6.

"Scattering on spin waves" may occur if a minority spin electron excites a number of atomic spins to quantized oscillations about their equilibrium position, called a spin wave, as discussed in Sect. 11.1.5. The excitation of one spin wave is possible by the transition of one electron from a *minority* spin state $s_z = \hbar/2$ to a majority spin state $s_z = -\hbar/2$ with a change $\Delta s_z = -\hbar$ in angular momentum. To conserve angular momentum, a spin wave must then have an integer spin of $-\hbar$ and is therefore a Boson (see Sect. 11.1.5). Vice versa, a *majority* spin electron can absorb a spin wave and thereby undergo a transition to the minority state. This latter process happens only when spin waves are present, that is at elevated temperature. The time scale of the transition of an electron from one spin state to the other is given by the energy $E_{\rm sw}$ of the spin wave. According to (11.25) $E_{\rm sw} \propto q^2$, where $q = 2\pi/\lambda$ is the wave vector of the spin wave. The wavelength λ of spin waves cannot be smaller than the lattice constant. In this limiting case, a spin wave involves the excitation of just one electron. This excitation has the highest energy and is often called a "Stoner excitation" for historical reasons. Generally, the excitation and hence the spin transition of the exciting electron occurs on a time scale $\hbar/E_{\rm sw}$ corresponding to $\sim 3 \times 10^{-13}$ s at ambient temperature.

"Spin exchange scattering" occurs in electron-electron scattering due to the quantum mechanical exchange interaction. If the incoming electron is in a spin-down state, and the target electron in a spin-up state, the indistinguishability of the electrons can lead to spin exchange so that the outgoing electron is now in a spin-up state and the target electron in a spin-down state. Such excitations are treated in many textbooks under the heading *Stoner excitations* [281](see Sect. 11.1.5). With the alkali-atoms, the outer valence electron can be prepared in a specific spin state. If an electron is elastically scattered on such an atom, the spin exchange rate can be very high at low scattering energies [606]. However, in the presence of the exchange interaction in magnetic solids, there is a change of energy involved as soon as an electron changes its spin state. Hence purely elastic spin exchange scattering as with atoms is not possible in solids but has to occur together with a change in momentum and energy. In particular, the large energy associated with the exchange splitting, makes spin exchange scattering very rare for magnetic materials.

The time scale of spin exchange scattering is the time scale of the electronelectron interaction, typically of the order of 10^{-15} s. It governs ultra-fast magnetization dynamics. At present we only understand some basic elements of electron–electron scattering in magnetic materials. Scattering of two electrons takes place with a complex amplitude f_1 in the singlet state $|S = 0, S_z = 0\rangle$ or with a complex amplitude f_3 in one of the triplet states $|S = 1, S_z = 0\rangle$ or $|S = 1, S_z = \pm 1\rangle$. A primary electron with spin $s_z = +1/2$ can collide with a target electron of either spin. If it collides with a majority electron $s_z = -1/2$, the initial state is a superposition of singlet and triplet states $(|1,0\rangle + |0,0\rangle)/\sqrt{2}$ and leads to a *direct scattering* amplitude $f_d = (f_3 + f_1)/2$ and an *exchange scattering* amplitude $f_e = (f_3 - f_1)/2$ on account of the indistinguishability of the electrons [134]. The relative amplitude and phase of f_1 and f_3 depend critically on the interaction potential which we do not know with sufficient confidence. It is therefore difficult at present to predict how electron–electron scattering proceeds in magnetic materials [607].

Besides being the active mechanism in ultra-fast electron dynamics, electron-electron collisions are important in many technical applications such as the photomultiplier and scanning electron microscopy (SEM) since they determine the formation of the low energy cascade of secondary electrons. Penn and collaborators [608] have shown that the spin polarization P(E) of the cascade electrons from the magnetic metals is governed by the ratio of the lifetimes of majority to minority spin electrons. In contradiction to other theoretical work, these authors reach the conclusion that the direct scattering of the spins into *empty states of the same spin* can explain the two to threefold enhancement of the spin polarization of the cascade electrons. Hence the exchange scattering does not play a significant role in the formation of the cascade. The enhancement of the polarization is due primarily to the spin-filter effect (see Sect. 12.6.1), or the larger density of states for minority spins compared to majority spins in ferromagnetic metals. This simple picture where the spin polarization of the secondaries does not depend on the spin polarization of the primary electrons does not apply to smaller energies of the primary electrons exciting the cascade electrons. While the total yield of secondary depends only very little on the spin polarization of the primary electrons [609]. the direction and magnitude of the spin polarization of the secondary electrons is influenced at lower energies of the primary electrons by two electron exchange scattering processes [610].

"Spin–lattice scattering" may occur when electrons scatter on phonons or when a spin wave is annihilated in scattering on the lattice. The condition for such events is that the crystal lattice accepts the change in angular momentum \hbar connected with the spin transition of an electron or with the annihilation of a spin wave. The spin angular momentum is coupled to the lattice by the spin–orbit interaction. Ultimately, these are the processes by which thermal equilibrium of the magnetization with the crystal lattice is established. The dynamics of the equilibrium between the electron gas, the phonon gas, and the spin system will be discussed in Chap. 15.

12.7.2 The Detection of Transitions between Opposite Spin States

Generally, when a magnetic sample is bombarded with monochromatic primary electrons, one observes secondary electrons in a continuous range of

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energy losses, carrying valuable information related to magnetism, already discussed in Chap. 8.

For the detection of low-energy transitions between opposite spin states one uses a technique called spin polarized electron energy loss spectroscopy (SPEELS), as reviewed for instance by Hopster [350]. A monoenergetic beam of spin polarized electrons is scattered off a surface and the spin polarization as well as the energy spectrum of the scattered electrons is recorded, as a function of the relative direction of the magnetization, the spin polarization of the incident electron beam and the momentum transfer between the incident and scattered beam.

In specular reflection or in a diffracted beam, the inelastic event is a two step process, consisting of a large angle elastic diffraction process that is preceded or followed by an energy loss event with a small momentum change. With ferromagnetic surfaces, one has to distinguish between excitations in which the electron spin is conserved and excitations in which the spin of the scattered electron is inverted. Electron-hole pair excitation can occur with or without a change in spin state of the exciting electron, while the excitation or absorption of spin waves always necessitates a spin flip transition of the exciting electron.

In Fig. 12.24 we consider the case where the incident beam is polarized in the direction of the *minority* spins. For simplicity we assume that the electron is already inside the sample since we have learned in Sect. 12.4.1 how to handle the beam transmission across the vacuum-sample interface. Inside the sample the incident electron occupies an excited free-electron-like minority state with energy $E_{\rm kin}^i$. Similar to the inverse photoemission process the electron may decay by a spin-conserving transition to a lower-energy unfilled minority band close to $E_{\rm F}$. However, in the present case the transition is radiation-less⁹ and the transition energy is transferred to an electron of opposite spin, in the filled majority band. This electron is excited to an energy $E_{\rm kin}^f$ and its energy is measured after escape from the sample. The energy difference $E_{\rm kin}^i$ – $E_{\rm kin}^f$ and the momentum transfer $\boldsymbol{q} = \boldsymbol{k}_i - \boldsymbol{k}_f$ are supplied by the incident electron. When observed in a diffraction spot, the momentum transfer q is small. Therefore, spin exchange collisions in weak ferromagnets such as Ni and Co where the majority spin band is full, are characterized by an energy loss of the order of $E_{\rm kin}^{i} - E_{\rm kin}^{f} \sim \Delta$ by the incident electron and a change in its spin state from minority to majority spin. This is balanced by an opposite spin transition in the sample consisting of the excitation of a single electron from the majority to the minority band.¹⁰

The change in spin state of the incident electron makes it possible to detect the weak spin exchange scattering processes on the background of the

⁹Radiation-less transitions are driven by the Coulomb operator, while radiative transitions are due to the dipole operator.

¹⁰In Fe, and in Ni and Co at higher temperatures, spin exchange collisions are also possible with a majority spin electron.

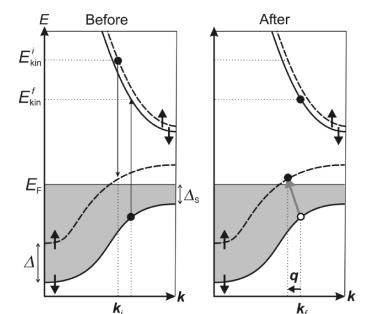
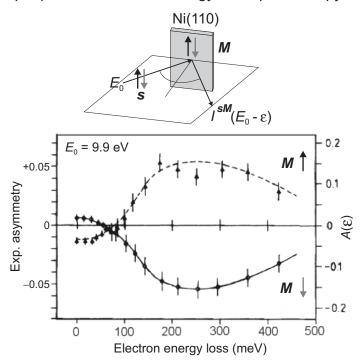


Fig. 12.24. Spin exchange scattering induced by an incident minority spin electron. On the left is shown the situation before the scattering event. The incident electron occupies an excited spin-up state with energy $E_{\rm kin}^i$. In the scattering event consisting of transitions indicated by arrows, the excited electron undergoes a radiation-less transition to an empty $3d^{\uparrow}$ state and excites a $3d^{\downarrow}$ state. On the right we show the situation after the scattering event. The energy loss $E_{\rm kin}^i - E_{\rm kin}^f \approx \Delta$ is observed through the energy analysis of the majority spin electron after escape into vacuum. In the scattering process an electron has made a transition from $3d^{\uparrow} \rightarrow 3d^{\downarrow}$ with a change in linear momentum $\mathbf{k}_i - \mathbf{k}_f = \mathbf{q}$. The momentum transfer can also be determined, in principle, from the directions of the incident and scattered beams

dominant spin-conserving inelastic scattering processes [611, 612]. The latter processes involve radiationless transitions between the same spin states, leading to the excitation of an electron hole pair in the minority spin band. Hence both, a polarized incident beam and polarization analysis of the scattered beam are necessary to distinguish the spin-conserving from the exchange scattering processes. The experimental geometry and results of the initial experiment of Kirschner et al. [611] with a Ni(110) single crystal are shown in Fig. 12.25. In this case the specular beam, corresponding to zero momentum transfer (q = 0) was measured and the data directly reveal the exchange splitting Δ .

The energy loss spectrum shown in Fig. 12.25 exhibits a peak around 300 meV in the asymmetry parameter. The measured peak corresponds to a spin exchange transition with q = 0 and the measured value reflects the exchange splitting Δ , in accordance with the results from direct and inverse photoe-

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Spin-polarized electron-energy-loss spectroscopy

Fig. 12.25. Geometry of a spin-polarized inelastic electron-energy-loss measurement in a reflection geometry by Kirschner et al. [611]. The incident spin polarized electron beam has an energy of $E_0 = 9.9 \,\mathrm{eV}$ and an energy width of 35 meV. It is incident on a magnetized single crystal of Ni(110) at an angle of 75° from the surface normal which gives rise to a strong specular reflection. The energy loss ϵ of the specularly reflected beam is measured in meV as it depends on the relative orientation of incident spin and sample magnetization direction, giving the spin asymmetry A defined in (12.27). At zero energy loss, A changes sign due to spin dependence in the elastic scattering discussed in Sect. 13.3. In the data shown underneath the experimentally observed asymmetry $A_{\rm exp}$ (left ordinate) is reduced relative to the true asymmetry $A(\epsilon)$ because the incident beam was only 35% polarized. The asymmetric peak centered around $\epsilon \approx 250$ meV constitutes the q = 0 spin exchange excitation in Ni often referred to as Stoner excitation

mission [275, 567]. Δ determined in this way with SPEELS does not seem to depend on temperature, at least in the case of Ni [613]. In total, two spin transitions have occurred, that of the "beam electron" and that of the "sample electron" thus conserving angular momentum in the total scattering process. In our case the incident electron has provided the angular momentum, the energy and linear momentum.

In practice, the small probability of the spin exchange transition makes it very difficult to perform a q-dependent experiment since due to diffraction on the crystal lattice, most of the scattered intensity occurs at q = 0. A qdependent experiment involves a monochromatic, collimated, and polarized incident beam and measurement of the polarization, the energy, and angle of the scattered beam. Nevertheless, it has been carried out in a reflection geometry on Ni by Abraham and Hopster [614] and on Fe by Venus and Kirschner [615].

An even more difficult SPEELS experiment consists of the observation of the spin and momentum of both the "beam electron" and the "sample electron". The exchange scattering in a SPEELS experiment depicted in Fig. 12.24 involves two simultaneous electronic transitions. In our discussion above we have concentrated on the detection of the higher energy majority spin electron shown in the right panel in Fig. 12.24 in a state well above the vacuum level. Owing to its higher energy it can be observed by an outside detector, and representative results are shown in Fig. 12.25. However, we ignored the second electron involved in the scattering process. In doing so one loses valuable information about the exchange scattering event. In principle, this can be overcome by also measuring the lower energy electron shown above the Fermi level in the right panel in Fig. 12.24. It occupies an empty state in the minority band but its low energy poses a problem. If its energy is below the vacuum level one cannot observe it, and even if its energy is above the vacuum level, after leaving the sample it will be buried under the huge intensity of the broad inelastic tail of scattered electrons. This can be overcome by use of coincidence techniques taking advantage of the fact that the two electrons of interest are emitted simultaneously. This very difficult low-count-rate experiment has nevertheless been performed [616]. Improved future studies are expected to clarify in more detail the fundamental electron-electron interactions in ferromagnets. Unfortunately, such spectroscopic measurements do not cover the energy range close to $E_{\rm F}$ which is important in solid state devices.

SPEELS with incident minority spin electrons may also be used to detect the excitation of *spin waves*. Upon excitation of a spin wave, the incident minority spin electron makes a transition to a majority spin state just as in exchange scattering but the energy loss in the transition is given by the energy of the spin wave. Depending on the wave vector k of the spin wave, such excitations lie in the 10–100 meV range. Therefore, very high energy resolution is necessary combined with the measurement of the spin polarization to distinguish the spin wave excitation from the stronger electron phonon excitation involving no spin flip. Kirschner and collaborators [493] were first able to detect spin wave excitation by electrons.

Data obtained in a more recent version of the experiment [617], shown in Fig. 12.26, suggest that it might be possible to omit the measurement of the spin polarization of the scattered electrons. It is then sufficient to scatter a highly polarized and very monochromatic electron beam from the magnetic surface and measure the energy loss of the scattered beam again with

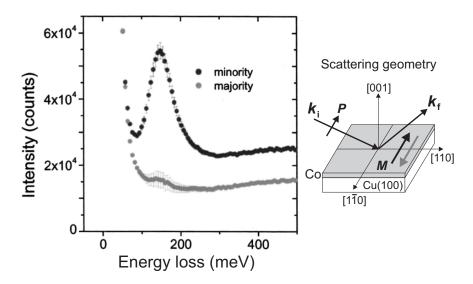


Fig. 12.26. Spin polarized energy loss spectra (SPEELS) performed in reflection from a sample of 8 monolayers Co on Cu(001), in a geometry shown on the right. The incident beam is spin polarized P = 81% and the spin polarization of the scattered beam is not measured. The incident electron beam has an energy $E_0 = 6.5 \text{ eV}$ and is incident with a wavevector \mathbf{k}_i at an angle of 67.5° from the surface normal with the electron spin either parallel or antiparallel to the magnetization M of the surface. By variation of the wavevector \mathbf{k}_f of the reflected beam the linear momentum transferred in the inelastic scattering event can be varied. The shown data are for a momentum transfer $k_{\parallel} = 0.087 \text{ nm}^{-1}$. The spectra are normalized to the spin averaged reflection intensity at zero energy loss. A loss feature at 170 meV appears in the scattering of incident minority spins (P parallel to M). The spurious loss feature for the incident majority spins (P antiparallel to M) is explained by the incomplete polarization. The energy independent inelastic loss difference between minority and majority spins is attributed to Stoner excitations, compare Fig. 12.25. Data courtesy of Kirschner

a resolution in the 10 meV range. Possible interference with spin dependent reflection at a magnetic surface discussed in Sect. 13.3 can be excluded when the electronic structure and the band gaps are well known.

If the spin of the incident electrons is parallel to the minority spin direction in the sample, spin waves can be excited. In contrast, spin wave *absorption* is necessary to change the spin state of an incident majority spin electron. Spin wave absorption would lead to an energy gain. Since it depends on the presence of spin waves it is very weak at lower temperatures. On the other hand, spin wave excitation is always possible independent of the temperature. Thus, given sufficient experience to exclude possible interference of spin dependent reflection on a band gap, see Sect. 13.3, combined with a spin independent energy loss, the spin dependence of the spin wave excitation process allows one to distinguish a spin wave loss feature from other loss features induced by phonon excitations. The phonon excitation features appear in both, the spin up and the spin down spectra.

The results shown in Fig. 12.26 for 8 monolayers Co epitaxially deposited on the Cu(001) surface convincingly demonstrate an energy loss of 170 meV which is exclusively present in the minority spin channel. The loss peak is significantly broadened, and we need to remember that such a spin wave energy is unusually high. Corrected for the finite energy resolution of the experiment, the width ranges from about 40 to 75 meV [617]. If this width is exclusively attributed to the lifetime of the spin wave, it would correspond to a lifetime of only ≈ 10 fs. In comparison, the spin wave life time observed with neutron scattering in fcc Co at smaller wave vectors is 300 fs [618]. Kirschner and collaborators [617] point out that the SPEELS peak might contain an unresolved optical mode of lower intensity, because it is slightly asymmetric. Yet another possible reason for the short lifetime detected in SPEELS particularly at high k_{\parallel} is the possibility that the high energy spin waves have an enhanced tendency to decay into Stoner-excitations, that is revert to single particle excitations.

Figure 12.27 shows the spin wave dispersion for a Co/Cu(001) surface derived from electron energy loss spectra similar to the one shown in Fig. 12.26 by varying the angle Θ_0 of observation. The results of neutron scattering obtained with crystals of fcc Co containing 8% Fe [618] are also shown. The SPEELS and neutron data are not for identical samples since fcc Co is not stable at room temperature in form of a large single crystal (needed for neutron scattering) unless it is alloyed with some Fe. One nevertheless would expect

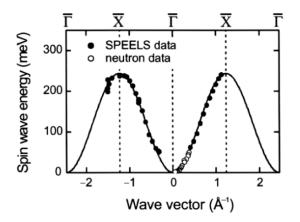


Fig. 12.27. Spin wave energy versus k_{\parallel} derived from SPEELS for 8 ML Co/Cu(001) [617]. The solid line is the calculated surface mode of semi-infinite fcc Co assuming the Heisenberg model with nearest neighbor interaction of $\langle s \rangle J_{01} = 15$ meV (see Section 11.1.2). Neutron scattering data for bulk fcc Co alloyed with 8% Fe are also shown [618]

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close similarity of the results. The agreement of the experimental data with a simple theory based on a Heisenberg model with nearest neighbor interactions is surprising. The solid line in Fig. 12.27 is the surface mode of semi-infinite fcc Co, calculated with the nearest neighbor Heisenberg model. For low k_{\parallel} , it coincides nicely with the bulk spin wave dispersion curve along the [110] direction using the identical values for the exchange and spin moment in the Heisenberg model as employed for the calculation of the surface mode. More sophisticated calculations of the dynamic spin susceptibility for fcc Co are not available at present. Future theoretical and experimental investigations will have to decide wether the surprisingly good agreement of the observed spin wave energies with expectations based on the nearest neighbor Heisenberg model is accidental or not.

The new simplified but by no means simple SPEELS experiment discussed above marks an important progress. It is expected to lead to a better understanding of the dynamic magnetic properties at surfaces and in thin films. To appreciate this, one has to remember that although spin waves at surfaces and in thin films have been investigated in the past by ferromagnetic resonance and by Brillouin light scattering, the traditional methods are limited to the study of *small wave vector* spin waves. The bulk-sensitive neutron scattering technique can measure all spin waves but it is not well suited for the study of samples with lower dimensionality which are at the forefront of magnetism research today. Hence the detection of spin waves with polarized electrons in SPEELS is effectively the only technique capable of measuring large wave vector spin waves in thin films and at surfaces.

12.8 Remaining Challenges

We finish this chapter with a brief summary of present limitations in our understanding which, of course, are the challenges of tomorrow. Generally, our mathematical understanding of ferromagnetism in Fe, Ni, and Co is still quite limited. According to Fröhlich and collaborators, there are no substantial mathematically rigorous results on realistic models of the ferromagnetic metals that provide understanding of ferromagnetic order at finite temperature [113].

The development of density functional band theory and its implementation in terms of ab initio computational schemes has led to some degree of understanding the electronic ground state at T = 0. The two main problems with the methods are that LDA is restricted to T = 0 and it underestimates electronic correlation effects such as operative in scattering and screening. A key quantity of ferromagnetism, the Curie temperature, is therefore hardly tractable as discussed in great detail in [247]. The other challenge lies in the description of excited states. Excited states come in many different forms.

The most important excited states in magnetism come from raising the temperature of the system, a situation experienced in all "real" systems. Most of the theoretical progress made in the description of finite temperature magnetism has been based on models in which the electronic structure is described in terms of empirical parameters. At present there is no practical scheme to extend density functional theory to elevated temperatures. The grand challenge is to develop first-principles parameter-free schemes that describe not only the T = 0 ground state but the magnetic excitations responsible for the decrease of the magnetization with temperature, and especially the phase transition at the Curie or Néel points.

From a spectroscopy point of view other "excited states" are of interest too. Because electronic excitations are involved, the system needs to be described not only in its ground state but the excited state, as well. In most cases, "excited states" consist of different electronic configurations with a certain lifetime. The lifetime and its relation to the measurement time have important implications for the proper evaluation of dynamical effects. In the interpretation of experimental IPE and PE spectra and also X-ray absorption spectra of metals (see Chap. 10) one still uses the independent particle band method discussed earlier. We have seen its limitations for the description of finite temperature correlation effects. In addition, the proper interpretation of spectroscopic data requires an understanding of the correlation effects in the final excited state. Such a theory does not exist.

Even for metals, excited multiplet configurations play a role, as evidenced for example by the 6 eV satellite in Ni metal or the difficulty to understand the spectroscopic exchange splitting Δ . At present a gap exists between the description of electronic states by a quasi-one-electron band theory and a full multielectron multiplet theory [266]. Multiplet theory treats the intraatomic interactions, like the coupling of spin and orbital degrees of freedom, in great detail. This atomic theory can include the effects of neighboring ligands through the parameterization of a symmetry based ligand field model. Multiplet theory has proven surprisingly successful for the interpretation of spectra of ionic crystals, such as the transition metal oxides and organometallic compounds [254]. It is also no surprise that it works very well for the description of the magnetic properties of the 4f states in the rare earths [238] because of the localization effects caused by the centrifugal barrier. Clearly, band theory and multiplet theory place different emphasis on itinerant versus localized effects. The problem is that Nature is not black or white. In particular, the 3d-states are not entirely itinerant but retain a considerable amount of atomic-like interactions. No comprehensive theory exists to this day that can treat both effects on an equal footing.

13.1 Overview

In this chapter we discuss studies of surfaces and interfaces of magnetic materials and we shall touch upon some key topics of interest in contemporary magnetism research. As discussed in Chap. 1, contemporary research on magnetic materials and phenomena is associated with structurally and magnetically engineered thin films. As the material thickness or lateral dimension is reduced, more and more atoms are located at interfaces or surfaces. This simple scaling argument alone argues for the increasing importance of interfacial effects. In addition, much evidence points to the key importance of interfaces in determining the properties of new devices. Key examples are the giant magnetoresistance effect and phenomena such as excitations of the magnetization associated with electron and spin transport across interfaces, as discussed in Chap. 14.

Unfortunately, even today, we have not mastered the study of "real" interfaces. By real we mean buried interfaces between materials, for example between sandwich-like structures. With the exception of cross-sectional transmission electron microscopy, which provides structural information, we are still mostly in the dark about the electronic and magnetic properties of such interfaces. Partly because of their inaccessibility, much work over the last thirty years has focused instead on a special kind of interface, the surface. Much of our detailed knowledge stems from studies of the *materials-vacuum* interface by means of science techniques, some of which offer even lateral resolution down to atomic dimensions.

It is therefore only natural that we start this chapter with some classic measurements on magnetic surfaces based on spin-polarized electrons. We then discuss static magnetic interactions across interfaces, which fall under the general category of *proximity effects*. In particular, we shall discuss three important effects: the existence of *induced magnetic moments* in "nonmagnetic" atoms, and the phenomena of *exchange coupling* and *exchange bias*.

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The latter two are distinguished by a preferential *uniaxial* versus *unidirectional* alignment of the ferromagnetic magnetization, respectively.

13.2 Spin-Polarized Electron Emission from Ferromagnetic Metals

While electron transport from one solid into another is of great practical importance in electronic or magnetic devices, as discussed in detail later in this chapter, the study of electron emission into *vacuum* has the advantage that energy, spin, and linear momentum can all be measured by a suitable detector, for example an electron energy analyzer that is equipped with a Mott detector for spin analysis. This is more difficult in the case of transfer of electrons into another solid. Therefore it is advantageous to first discuss emission of spin-polarized electrons into vacuum.

13.2.1 Electron Emission into Vacuum

Electrons may be extracted from solids into vacuum by supplying energy to overcome the surface barrier potential, called the *work-function* Φ . Depending on how the energy is supplied, one speaks of thermionic emission (heat), field emission (external electric field), photoemission (photon irradiation), or secondary electron emission (photon or particle irradiation). Electron emission from solids has been studied for more than 100 years. It contributed significantly to the development of quantum mechanics and surface science. In contrast, the emission of *spin-polarized* electrons from solids has only been successfully investigated for about 35 years, starting in 1969 [61]. Over the years, most of the classical models for emission of electrons, particularly in the low energy range, needed to be modified or refined in order to understand the observed spin polarization of the electrons.

The spin-polarized band model makes definite predictions about the sign of the spin polarization in the various electron states. For electrons emitted from states at the Fermi energy $E_{\rm F}$, i.e., at the energetic threshold of electron emission, one expects minority spins in the case of Ni and Co, but majority spins in the case of Fe according to the densities of states shown in Fig. 12.1. This simple picture, however, does not hold in practice because of two complicating effects. First, we have seen in conjunction with Fig. 12.4 that the magnetic properties can be modified near surfaces. Secondly, we have learned in Sect. 12.6.1 that spin-up and spin-down electrons scatter differently as they traverse a magnetic material and this changes the original polarization through the spin filter effect. Both effects will lead to modifications of the spin polarization of the low-energy electrons emitted into vacuum from that expected from the bulk band structure.

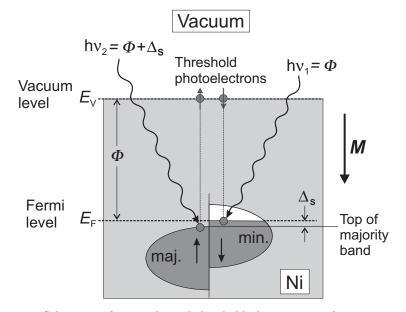


Fig. 13.1. Schematic of spin-polarized threshold photoemission from a strong ferromagnet into vacuum. We have assumed that the majority spins are fully occupied with the top of the majority spin band having a separation $\Delta_{\rm S}$, called the Stoner gap, from the Fermi level $E_{\rm F}$. The incident photon energy is chosen to be greater than the work function $\Phi = E_{\rm V} - E_{\rm F}$ of the material. The photoemission threshold corresponds to $h\nu = \Phi$ and at this energy only minority spins are emitted into vacuum. The polarization of the electrons emitted into vacuum is determined with a Mott-polarimeter. Above a threshold energy $h\nu = \Phi + \Delta_{\rm S}$ majority spins may also be excited into vacuum, lowering the spin polarization of the emitted electrons

Best established and confirmed by experiments in different laboratories are the spin polarization results obtained from near threshold photoemission. The principles of such measurements are illustrated in Fig. 13.1.

Figure 13.2 summarizes measured results for the photon energy dependence of the spin polarization from a Ni(111) photocathode, measured as the spin-polarized total photoelectric current, also called the spin-polarized *electron yield*. In order to conveniently use the more powerful visible light sources, the work function of this surface was lowered to $\Phi = 1.56 \text{ eV}$ by depositing a fraction of a monolayer of Cs onto the atomically clean surface. The experiments show that a small amount of Cs does not affect the spin polarization.

The degree of spin polarization P is defined in (8.17) as

$$P = \frac{n^{\text{maj}} - n^{\text{min}}}{n^{\text{maj}} + n^{\text{min}}} , \qquad (13.1)$$

so that P is positive for preferential majority spin emission and negative for preferential minority spin emission. Close to photoelectric threshold one observes negative P that is predominance of minority spins, but within

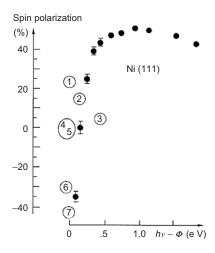


Fig. 13.2. Spin polarization of electrons extracted from states close to $E_{\rm F}$ in Ni. Filled points: Photoemission from Ni(111) + Cs with photons of energy $h\nu$ in units of eV, the work function is $\Phi = (1.56 \pm 0.05) \, \text{eV}$ [619]. Other experimental results are numbered (1) electron tunneling into superconducting Al [620], (2) polarization of low energy cascade electrons, (3) average polarization of all 3*d*-electrons, (4) polarization in thermionic emission [621], (5) polarization in field emission [622], (6) electron tunneling into GaAs [623], (7) electron capture by swift H-atoms [624]

~100 meV from threshold there is a steep turnover to quite high positive P. This agrees with the expectation based on the density of states for a strong ferromagnet, as illustrated in Fig. 13.1 (also see Fig. 12.1). At photoemission threshold $h\nu = \Phi$ only minority spins can be excited and the spin polarization is negative. As the photon energy is raised to $h\nu = \Phi + \Delta_{\rm S}$, where $\Delta_{\rm S}$ is the separation of the top of the majority band from the Fermi level or the *Stoner gap* (see Fig. 7.7), the threshold for majority spin excitation is reached and the contribution of these spins to the measured signal starts to change the sign of the measured polarization as the photon energy is increased.

In Fig. 13.1 we have tacitly assumed the so-called three-step model of photoemission. It divides the process of photoelectron emission into three successive steps (1) spin-conserving optical excitation of an electron to a higher energy band state in the crystal, (2) spin-conserving elastic transport of the excited electron to the surface, (3) spin-conserving escape over the surface barrier potential. Use of the three-step model for the quantitative interpretation of the measured energy dependence of the spin-polarized total yield gives the exchange splitting $\Delta = 0.3 \text{ eV}$ [565], in good agreement with the later performed energy and momentum resolved spin-polarized PE and IPE experiments discussed in Chap. 12, but in contradiction to the larger splitting $\Delta = 0.5 \text{ eV}$ obtained from band structure calculations [247]. Part of this discrepancy may be due to the fact that the three-step model ignores any changes in spin polarization during the transport step to the surface and it also neglects modifications of the magnetic properties at the surface. In particular, the inelastic spin filtering effect, consisting of preferential scattering of minority electrons during electron transport to the surface, will lead to a suppression of the minority spin intensity.

The case of Co provides a striking example of the importance of spin filtering in transport to the surface. As shown in Fig. 12.3, in Co one has about 2.5 holes per Co-atom in the minority band compared to only about 1.5 in Ni. Hence in Co one would expect the scattering (absorption) of minority spins to be much stronger compared to Ni, as illustrated in Fig. 12.16. Indeed, with thick Co-films no negative polarization is detected no matter how closely one approaches threshold [619, 625]. This is explained by the spin filtering effect which adds an approximately constant positive value to the polarization, so that the polarization in a plot like that in Fig. 13.2 is shifted upward and becomes positive. In Co, this happens to such a large extent that the negative excursion of the polarization is not observed at all. Only if one suppresses the spin filtering effect by use of films that are thin compared to the escape depth does one find a negative polarization [626].

The average polarization of all 3*d*-electrons is given by the difference in spin-up and spin-down electron occupation $N_{\rm B} = N_{\rm e}^{\rm maj} - N_{\rm e}^{\rm min}$ and the sum $N_{\rm e} = N_{\rm e}^{\rm maj} + N_{\rm e}^{\rm min}$ that is the number of all 3*d*-electrons, as discussed in Sect. 7.4.2. In Ni one has $N_{\rm B} \approx 0.6$ and $N_{\rm e} \approx 9$ and therefore $P = N_{\rm B}/N_{\rm e} \approx 0.07$. One therefore expects to measure this value for P if the sample is excited with high energy primary electrons so that there is sufficient energy to excite all occupied electrons with equal probability. But the measured polarization of the low energy secondary electrons, the so called cascade electrons, is larger, $P_{\rm casc} = 0.17$ [350]. The enhancement of $P_{\rm casc} > P$ proves that the simple density of states model cannot explain the observations in the case of Ni, as well, and that spin selective electron scattering has to be taken into account to explain the polarization of the measured electron cascade [590, 591].

By going to elevated temperatures, yet staying below $T_{\rm C}$ so that the electrons in the 3*d*-bands are still substantially polarized, it has been possible to also measure the spin polarization in thermionic emission. However, the spin polarization of thermionically emitted electrons turned out to be much smaller than in photoemission, in fact it was found to be zero within experimental uncertainty in both Fe and Ni [621]. Helman and Baltensperger [627] have explained the vanishing spin polarization in thermionic emission by considering the spin polarization of the electron cloud in thermal equilibrium with a ferromagnetic surface. They find that the spin polarization decays to zero within a few atomic distances from the surface.

A similarly disappointing result has been obtained when the electrons were extracted by a very high electric field to induce field emission. In this case P shows only a very small negative value with atomically clean surfaces and when the spin polarization is measured correctly [622]. The low Pobserved in field emission of electrons into vacuum has been attributed to

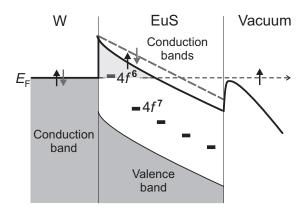


Fig. 13.3. Field emission from a thin film of EuS on a W-tip [628]. At the W/EuS interface, there is a charged nonmagnetic layer, resulting in a spin-dependent Schottky barrier. Spin-up electrons experience a thinner Schottky barrier, resulting in a enhanced spin-up current in vacuum

the predominance of *s*-electrons in the process of tunneling into vacuum. The *s*-electrons are believed to be unpolarized or perhaps positively polarized in the 3*d*-ferromagnets. This seems to be in conflict with another experiment in which electrons are extracted from the magnetic surface by the electric field of an ion. In this "ion neutralization spectroscopy," a beam of swift H-atoms passes by a magnetic surface at distances of few atomic diameters. The hydrogen atoms capture electrons thereby producing neutral hydrogen atoms. Rau [624] found astonishingly that it is exclusively minority spins that are captured at a Ni-surface.

However, the experiment reported by Müller [628] and coworkers shows that almost completely polarized electrons can be extracted by tunneling from a W-tip covered with few monolayers of the ferromagnetic insulator EuS. The magnetic moment in EuS is generated by ferromagnetic ordering at $T_{\rm C} = 16$ K of the half full 4*f*-shell in the ${}^{8}S_{7/2}$ ground state configuration carrying a pure spin moment of $7\mu_{\rm B}$ as discussed in Sect. 12.3. The empty 6s-5d conduction bands of EuS are exchange split. Due to this exchange splitting, the majority (spin-up) spins encounter a thinner (shaded) Schottky barrier at the W/EuS interface and thus tunnel with much higher probability into the conduction bands of EuS compared to the minority spins. The energy diagram for the EuS/W field emission tip is illustrated in Fig. 13.3. The electrical field applied to the W-tip accelerates the electrons once they are within the ferromagnetic insulator. This leads to field emitted electrons with a high degree of spin polarization P = 0.85 along the direction of the EuS magnetization. This result has been confirmed later by Kisker and collaborators [629].

The experiment is remarkable in that it demonstrates a tunneling barrier that transmits one spin state only. EuS thus acts as an almost ideal spin filter for the electrons field-emitted from the tungsten tip. Note that this spin filter

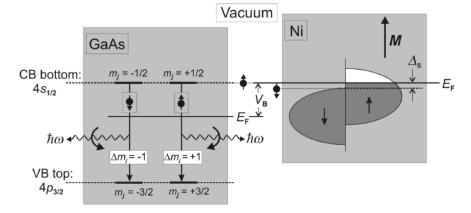


Fig. 13.4. Tunneling of spin-polarized electrons from Ni through vacuum into GaAs. The tunnel current and its spin polarization are dependent on the bias voltage $V_{\rm B}$ between Ni and GaAs. The Stoner gap in Ni is labeled $\Delta_{\rm S}$. The spin polarization of the electrons tunneling into the GaAs conduction band can be measured by observing the circular polarization of the luminescence radiation, emitted when a spin-polarized electron performs a radiative transition between the states $4s_{1/2}$ and $4p_{3/2}$. This detection scheme is an inversion of the optical pumping of spin-polarized electrons with circularly polarized light in the GaAs photocathode shown in Fig. 8.1

is not dependent on inelastic electron scattering as opposed to the magnetic tunneling transistor of Sect. 12.6.2. Except for the low $T_{\rm C}$ necessitating the operation at liquid He temperatures, the W/EuS-tip provides an ideal emitter that could be useful in spin-polarized tunneling spectroscopy discussed in Sect. 13.2.3.

13.2.2 Spin-Polarized Electron Tunneling between Solids

In the light of recent interest in the tunneling magnetoresistance phenomenon involving metal oxide structures and the direct spin injection from metals into semiconductors of interest in the field of spintronics [630, 631], it is of interest to review work exploring the tunneling of spin-polarized electrons from a ferromagnetic metal through vacuum or an insulator into solids in the form of a metal or semiconductor.

We start with experiments that explored the spin-polarized tunneling from a ferromagnet through vacuum into a semiconductor first carried out by Alvarado in 1995 [632]. In particular, he studied tunneling of electrons from a ferromagnetic Ni tip through vacuum into GaAs.

The principles of tunneling from a metal through vacuum into a semiconductor are shown in Fig. 13.4 for the example of Ni and GaAs. The choice of GaAs allows one to measure the magnitude and sign of the spin polarization of the tunnel current by observing the degree of circular polarization of the

photon luminescence. The process is simply the inversion of that used in the GaAs spin-polarized source shown in 8.1. In the present case, a spin-polarized electron that has tunneled into the conduction band of GaAs undergoes a radiative transition from the bottom of the $4s_{1/2}$ conduction band into the highest $4p_{3/2}$ valence band. Since a radiative transition needs to satisfy the dipole selection rule the spin is conserved during the transition. This imposes special angular momentum constraints on the matrix element of the transition because of the spin–orbit coupling in the $4p_{3/2}$ valence band, the "final state" of the transition. These angular momentum constraints lead to an angular momentum of the emitted luminescent photon which is therefore circularly polarized.

The experimental arrangement provides considerable flexibility. It is possible to vary the tunneling barrier by changing the distance between the ferromagnetic tip and the GaAs surface. Also, the energy of the electron states contributing to the tunneling current may be selected by applying a bias voltage $V_{\rm B}$ between the ferromagnetic tip and GaAs. As the GaAs Fermi level is successively lowered relative to that of Ni the GaAs conduction band edge will become aligned with the Ni Fermi level and, at threshold, the tunnel current will consist of minority spins. As the voltage is increased majority spins may also tunnel into GaAs. The sign of the observed spin polarization of the tunnel current is therefore expected to exhibit a voltage dependence that reflects the energy dependence in the photoemission yield. This general behavior is indeed observed. The crossover from negative to positive P occurs at $0.1 \,\mathrm{eV}$ from threshold in the case of the Ni(100)-surface [303] and at 0.2 eV with Ni(111) [565] while in tunneling, it occurs at $\sim 1-2 \,\mathrm{eV}$ from threshold. The reason for the different crossover energies are not completely understood.

LaBella and coworkers [633] claimed that almost completely polarized electrons had been injected into GaAs from a Ni tip. However, it has been pointed out [634] that the actual polarization was probably similar to the one observed by Alvarado [632]. While Alvarado's experiment shows that ballistic injection works, diffusive injection through an ohmic contact of the semiconductor to a metallic ferromagnet is not possible unless one assumes the ideal and fairly unrealistic case of a half metallic ferromagnet. This can be readily shown by analysis of the diffusive injection from a metal into a semiconductor in terms in of a simple resistor model [635]. Injection into GaAs-type structures leads to an effective optical detection of spin polarization [597] which is extremely useful for the development of spin based electronics.

Of particular technological importance are tunneling studies between two ferromagnets, separated by an oxide layer. This tunneling experiment has been pioneered by Jullière in 1975 [337] and its principle is shown in Fig. 13.5.

By applying a bias voltage $V_{\rm B}$ between F_1 and F_2 , the electrons at $E_{\rm F}$ in one metal will tunnel into unoccupied states of the second ferromagnet. The tunneling magnetoresistance (TMR) depends on the electronic structure of both ferromagnets, the bias voltage $V_{\rm B}$, and the relative magnetization

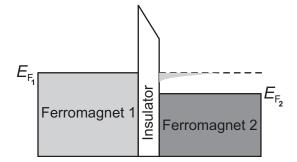


Fig. 13.5. Energy scheme for tunneling of electrons from a ferromagnet F_1 through an insulating layer into another ferromagnet F_2 . The tunnel magnetoresistance (TMR), defined as $(R_P - R_{AP})/R_{AP}$, depends on the bias voltage between F_1 and F_2 , the relative magnetization directions and spin-polarized band structures of F_1 and F_2 , and on the insulator

direction in F_1 and F_2 . In the limit of $V_B \rightarrow 0$, one expects that TMR is lowest if two identical ferromagnets are magnetized in parallel (P) and highest when they are magnetized antiparallel (AP). This is called "normal" zero-bias TMR. Yet, depending on the nature of the insulator and on the ferromagnetic metal, one has also observed "inverse" zero bias TMR [636]. This shows that analysis based on Jullière's original model is not possible. Two basic assumptions are made in this model, namely (1) that the spin is conserved in the process of tunneling, and (2) that the tunneling probability is proportional to the density of states in the metals. While (1) is valid, (2) is not. Critical theoretical analysis of TMR shows that one has to account in full detail for the properties of the insulating layer, as well, specifically for the decay of the evanescent waves within this layer [637–639]. The electrons most likely to tunnel into the insulator are those with linear momenta perpendicular to the interface. Furthermore, a wave-function whose projection into the plane of the insulating film is a circle like an *s*-state has a higher probability of transmission compared to a wave function whose projection has the clover leaf pattern of a d-state.

Based on such detailed analysis, theorists expect TMR defined as $(R_{\rm A} - R_{\rm AP})/R_{\rm AP}$ to exceed 1,000%. Unfortunately, pinholes in the oxide cannot be eliminated easily and thus add uncertainties to the interpretation. But amazingly enough, several laboratories have now demonstrated TMR-values at room temperature exceeding 200% [598, 640], employing simple magnetic elements and insulators such as sputter deposited FeCo-alloys and MgO. Magnetoresistive devices with such a high performance are advantageous for three spintronics applications. TMR based magnetoresistive sensors can read smaller data bits or scan the same sized bits more rapidly compared to the GMR-sensors. Magnetic random access memories yield better read-out signals

if based on TMR, and TMR-based devices can be used as reprogrammable logic processors [640].

Spin-polarized resonant tunneling or coherent electron tunneling between two ferromagnets has been observed by Yuasa and coworkers [641]. Insertion of a thin Cu layer between the tunnel barrier and the ferromagnetic tunnel junction produced oscillations in TMR that depended on the thickness of the nonmagnetic Cu layer. The amplitude of the oscillations was large enough to produce a sign change of TMR. The oscillation period depends on the applied bias voltage $V_{\rm B}$ and reflects the energy band structure of Cu. This is yet another example of standing spin-polarized electron waves discussed in Sect. 13.4.5 and demonstrates coherent electron tunneling.

Other important spin-polarized tunneling studies involve a superconductor (S). In one case, S is deposited directly onto a ferromagnet (F) in a small transparent contact with an area that is small compared to the mean scattering length of an electron. In another, S deposited on an insulator (I) in contact with F. The energy schemes of these two different tunneling devices, F/S and F/I/S, are illustrated in Fig. 13.6.

The Andreev reflection process [642] converts the quasiparticle current in a metal into the Cooper pair current in the superconductor. In the case of a F/S contact, Andreev reflection is suppressed due to the spin imbalance in F since not every electron can find a partner to form a superconducting pair. Therefore, by measuring the modification in the electrical conductance when S makes the transition from a normal metal to a superconducting metal, one can determine the spin polarization of the "conduction" electrons in F. The superconducting phase can be suppressed at constant temperature by applying a strong magnetic field. Andreev reflection has been evaluated by a number of authors [643–645] for its applicability to measure the degree of

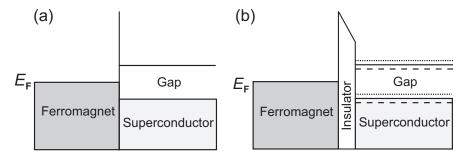


Fig. 13.6. Energy scheme for two different structures. (a) A superconductor deposited on a ferromagnet in a small transparent contact area that is small compared to the mean scattering length of an electron is used to study Andreev reflection. (b) Insertion of a tunnel barrier between a ferromagnet and a superconductor is used to study tunneling of electrons from the ferromagnet into the quasiparticle states of the superconductor. A magnetic field is applied, causing a spin splitting at the edge of the superconducting gap of magnitude $\pm \mu_{\rm B} H$

spin polarization of the conduction electrons. Naturally, the sign of the spin polarization remains hidden. The simple model mentioned earlier, based on the need for an electron to find a partner of the other spin state in order to penetrate into the superconductor, explains the basic features. But in order to describe the measurements, a more sophisticated theory is necessary that takes into account the band structures of F and S.

The other technique to determine the spin polarization of conduction electrons with a superconductor has been pioneered by Meservey and Tedrow [70]. Meservey–Tedrow tunneling relies on electron tunneling from F through an oxide, for example Al₂O₃, into a simple BCS-superconductor such as Al. The presence of the insulator makes it possible to shift the Fermi-level $E_{\rm F}$ of F with respect to the quasiparticle density of states in S. This quasiparticle density of states exhibits an energy gap of width given by the energy of a Cooper pair. In an applied magnetic field of strength H, the edges of the energy gap exhibit a Zeeman splitting by $\pm \mu_{\rm B} H$. Yet due to the presence of the energy gap, no electrons can tunnel from F into S. If a voltage $V_{\rm FS}$ is applied that brings $E_{\rm F}$ in F close to the upper edge of the gap in S, electrons can tunnel from F to S. The magnitude of this current is proportional to the tunneling current of majority spins with $\mu_{\rm B}$ parallel to **H** at the lower edge of the spin split gap and to the electrons with $\mu_{\rm B}$ antiparallel to **H** at the upper edge of the gap. In this way, one determines the spin polarization $P_{\rm t}$ of the electrons tunneling from F into S including its sign. By reversing $V_{\rm FS}$, one obtains $P_{\rm t}$ for electrons tunneling from S into F. Since the voltages are of the order of mV, one expects that both $P_{\rm t}$ are identical which is indeed observed.

With all three ferromagnetic metals Fe, Co, and Ni, one observes positive spin polarization [620], while negative polarization is expected at $E_{\rm F}$ from the band-structure in the case of Co and Ni. This rather high positive polarization has posed a serious problem in our understanding, as illustrated by Mott's letter in Fig. 1.10. Mazin [646] has proposed to discuss the polarization observed in tunneling in terms of the polarization of two currents I_{sp} and I_d produced by s-p and d electrons, respectively. The observed polarization is weighted by the respective Fermi velocity squared, but chemical bonding at the interface with the insulator can promote or suppress the relative s-p-contributions as well. The currents from states with different parentage thus have to be weighted with a transfer function. Generally, as observed already with field emission into vacuum [622] and with the electron injection into GaAs [623], s electrons with more extended wave function have a larger tunneling probability through a thick barrier compared to d electrons. And indeed, when the tunneling barrier is made thinner, the relative tunneling probability of the negatively polarized d electrons increases [647] leading to an overall decrease of the spin polarization of the tunneling current. The positive spin polarizations observed in the famous experiments by Meservey and Tedrow [620] may then be understood by predominance of s-electron tunneling and the specifics of the insulating layer between the two metals.

Buhrman and collaborators [643] have compared $P_{\rm t}$ from the Andreev reflection process with the one obtained in Meservey–Tedrow tunneling. For Co, $P_{\rm t} = +0.35$ in both cases, but with Ni, $P_{\rm t} = +0.32 \pm 0.02$ in Andreev reflection and $P_{\rm t} = +0.23 \pm 0.03$ with Meservey–Tedrow tunneling.

13.2.3 Spin-Polarized Electron Tunneling Microscopy

The dependence of the tunneling current on the electronic structure of a surface has been utilized with great success for nearly 20 years in scanning tunneling microscopy (STM). The idea that the tunneling current must also depend on the magnetic structure of the surface [648] has been explored since about 1990 by a number of researchers [458]. The basic experimental implementation of spin-polarized STM (SP-STM) utilizes a magnetic tip and tunneling through the vacuum barrier. Ferromagnetic or even an antiferromagnetic tips made from chromium have been used as illustrated in Fig. 13.7.

The tunneling current is measured as a function of the tip position on the surface and depends on the relative orientation of the magnetization of the atoms at the tunneling tip and at the magnetic surface, directly underneath the tip. The sensitivity to the magnetic structure arises because the ferromagnetic tip emits electrons in a specific spin state at a specific energy and momentum while the surface can only accept electrons if a suitable electronic state is available. When two magnetic materials have their magnetization aligned in parallel, these conditions are different as compared to the case when the magnetizations are aligned perpendicular or antiparallel. Today, SP-STM microscopy comes in several different variants and much progress has been made since the first attempts. The progress has been particularly great and impressive during the first years of the new millennium and today it is the magnetic microscopy method with the most impressive spatial resolution, down to atomic dimensions [456].

The highest spatial resolution has been reported by Bode and collaborators [458, 652]. They report atomic resolution images by use of a W-tip, coated with a layer of ferromagnetic Gd or even antiferromagnetic Cr. Clearly, it is advantageous to use an antiferromagnetic (AFM) tip (consisting of chromium) because it does not have any stray magnetic field that could easily disturb the magnetic object under investigation. While the net magnetization in an AFM

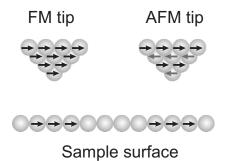


Fig. 13.7. Principle of spin-polarized tunneling. A ferromagnetic tip (FM tip) [649–651] or even an antiferromagnetic tip (AFM tip) [458,652,653] has been used to explore the spin structure of the surface with very high resolution

tip vanishes, the spin polarization of the outermost atom at the tip is proposed to be responsible for the tunneling process. Some tips are said to be sensitive to the in-plane, and others to the out-of-plane component of the magnetization depending on the thickness of the chromium layer. The fabrication and control of the magnetization at the tip surface and its understanding in terms of the load put on the last atom with the probing current still present challenges, but spectacular results such as the imaging of a magnetic vortex [652] have been presented.

An example of a high resolution SP-STM image is shown in Fig. 13.8. The image shows the magnetic contrast of single atomic height Fe islands deposited on a W(110)-surface covered by a full monolayer of Fe, investigated with a ferromagnetic Gd-tip at a temperature of 70 K. The first layer of Fe on W(110) is magnetized in plane, but the addition of a second layer of Fe islands tends to turn the magnetization of the islands into the perpendicular direction. The image shows the second layer islands with perpendicular magnetization, M either up or down, sitting on top of a closed monolayer of Fe. The change of the direction of M from in-plane in the closed monolayer to out-of-plane in the second layer islands requires the formation of a 90°-domain wall. The domain wall energy is proportional to the length of the circumference of an island while the energy gained by directing M into a perpendicular direction is proportional to the area of the island. This makes it energetically unfavorable

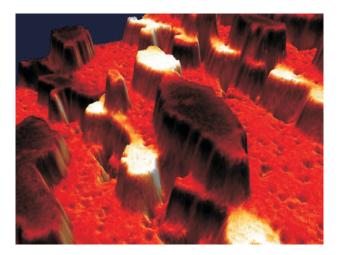


Fig. 13.8. Spin-polarized tunneling image of single step Fe islands (height exaggerated) sitting on a closed monolayer of Fe on W(110), measured as $\partial I/\partial U$, with a Gd tip [458]. At the positions of the islands, M tends to be \perp to the film plane either up (dark) or down (white). The big island in the center is 30 nm long with a domain wall in the constriction at the far end. The small island to the left of the constriction is neither black nor white indicating that its M is still in plane to avoid the formation of a domain wall

for the smallest islands to have a perpendicular magnetization. This is indeed seen as pointed out in the figure caption.

Clearly, to image the spin structure it is necessary to distinguish the spin signal induced by the different magnetization directions from the background signal coming from the topographical contrast. This is achieved in the case of Fig. 13.8 by taking the derivative dI/dV of the tunneling current I with respect to the tunneling voltage V. Due to an exchange-split surface state, the Gd-tip exhibits a sharp spin-dependent structure whose amplitude is characteristic for the spin polarization of the tunneling current along a quantization direction, given by the magnetization direction in the Gd-tip.

The antiferromagnetic ordering in body centered tetragonal (bct) Mn(001) films has been observed by Yamada and collaborators [651] by SP-STM with a lateral resolution of 1 nm. These authors used W-tips that were coated with 7–10 nm Fe, magnetized in-plane. The slope dI/dU of the tunneling characteristic I(U) was used as in the work by Bode [458] to eliminate topographical contrast. But in this case, a spin-dependent peak in the density of states on the bct-Mn(001) sample surface was found by band structure calculations to be responsible for the spin signal.

Another variant of SP-STM has been implemented by Ding and collaborators [650]. Their ferromagnetic tip was made from the amorphous magnetic material CoFeSiB and the magnetic structure of the Co(0001) surface, including a surface state, where probed. Amorphous materials, as used for the tip, have washed out energy bands and in this way the conditions for tunneling are somewhat relaxed. To eliminate signals of nonmagnetic origin the magnetization in the scanning tip is periodically switched from parallel to antiparallel relative to the tip axis and the resulting variation of the tunneling current is measured with a lock-in amplifier. The experiment yielded a lateral resolution of 10 nm [654].

In a later experiment [649], a soft magnetic CoFeSiB ring with a small coil around it is used to obtain spin sensitivity for the in-plane magnetization of the sample. The ring is oriented perpendicular to the surface so that one probes the in-plane surface magnetization of the sample, projected along the tangential ring magnetization direction at the tunneling point. By use a ring shaped magnetic probe, the stray magnetic field is significantly reduced similar to the case of an AFM-tip. While the tunneling current between the ring and the sample surface is measured, the magnetization of the ring is periodically switched, with an AC-current flowing through the coil. The tunneling current depends on the relative orientation of the ring and the sample spin, causing modulations of the tunneling current due to tunneling magnetoresistance. These modulations depend only on spin and contain no topographic information. Simultaneously, the topographic image is derived from the average tunneling current. With this technique, the step-induced frustration in the antiferromagnetic ordering of manganese overlayers on Fe was investigated. The magnetic frustration is of interest for the understanding of the exchange bias phenomenon discussed in Sect. 13.4.3.

13.3 Reflection of Electrons from a Ferromagnetic Surface

While photoemission of electrons prompted the discovery of the particlenature of the electromagnetic waves through the famous work of Einstein in 1905, studies of the reflection of low energy electrons from surfaces by Davisson and Germer [655] led to the discovery of the wave-like nature of the electrons 22 years later. These scientists observed diffraction spots in elastic scattering of electrons of $\sim 100 \,\text{eV}$ energy from a nickel crystal. For $100 \,\text{eV}$ electrons the DeBroglie-wavelength is $0.123 \,\text{nm}$, of similar magnitude as the lattice constant, so that crystals act as diffraction gratings for low-energy electrons. Today, *low energy electron diffraction* or LEED is the major tool for the determination of surface structures. The surface sensitivity of LEED is due to the short mean free path of low-energy electrons.

Spin-dependent scattering from surfaces can occur via two mechanisms. For nonmagnetic surfaces spin-orbit coupling can lead to spin dependencies and for magnetic surfaces both spin-orbit and exchange scattering may be present. The occurrence of spin polarization in LEED had not been found in the original experiment by Davisson and Germer [656] due to erroneous evaluation of the experimental data [657]. Early theoretical work [658] assumed a sinusoidal variation of the periodic crystal potential and owing to this oversimplified assumption also did not predict the existence of spin-dependent scattering effects. It was not until 1966 that Maison [659], a graduate student at that time, recognized that spin-orbit coupling which, according to the work of Mott and Massev [134] produces sensitivity to the electron spin in elastic scattering, requires a better description of the crystal potential that includes the steep gradient of the potential near the atomic cores. Maison then predicted that sizeable spin dependencies can occur in low energy electron scattering from solid surfaces and this was soon thereafter confirmed by experiments on disordered Hg surfaces [660]. In 1975 O'Neill and collaborators [661] reported the observation of spin polarization in LEED from a single crystal tungsten surface. The first comprehensive relativistic calculations were done by Feder [662], laying the foundation for spin-polarized low energy electron diffraction (SPLEED) which can be very helpful in determining surface structures [343].

Besides the spin polarization effects due to spin-orbit coupling, one expects additional spin dependencies in scattering from a magnetic surface arising from the exchange interaction $J\langle s_i\rangle\langle s_j\rangle$ between the incident electrons of average spin $\langle s_i\rangle$ and the spins in the ferromagnetic sample with the spin expectation value $\langle s_j\rangle$. The exchange integral J is difficult to predict since it varies strongly with electron energy and momentum. According to Sect. 8.4 the spin polarization of the incident electrons is given by the spin polarization vector \mathbf{P}_0 , and the spin polarization of the electrons in the magnetic surface is proportional to the magnetic order parameter $M^* = M(T)/M(0)$

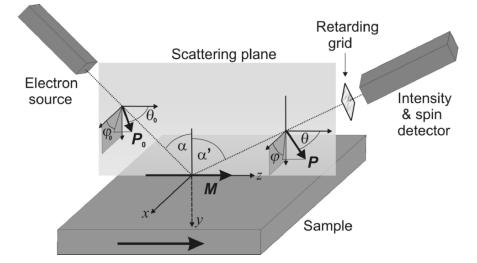


Fig. 13.9. Principle of a spin-dependent reflectivity measurement from magnetic surfaces. The electron source delivers a polarized electron beam with the vector of polarization \mathbf{P}_0 pointing into a freely chosen direction in space. The direction is labelled by a polar angle θ_0 and azimuthal angle φ_0 in the x, y, z coordinate system of the sample, chosen so that z is along the sample magnetization \mathbf{M} and x lies in the plane of the surface. The scattering plane is defined by the surface normal and \mathbf{M} . The beam is incident at an angle α from the surface normal. The intensity I and, in the complete experiment, the spin polarization vector \mathbf{P} of the electrons scattered into an angle α' from the surface normal is measured. A retarding grid before the detector eliminates inelastically scattered electrons.

(see Sect. 11.1.1). It follows that the magnitude of the magnetic reflectivity is proportional to the scalar product $M^* \cdot P_0$.

Using the GaAs source of polarized electrons, the exchange part of the spin-dependent reflectivity, or "magnetic reflectivity," was first detected by Celotta and coworkers [663]. The basic layout of a reflectivity experiment that measures the elastic scattering of electrons from a magnetic surface is sketched in Fig. 13.9. The source of the spin-polarized electron beam is usually a GaAs-type photocathode. The polarized beam with polarization vector P_0 impinges at an angle α from the surface normal onto a ferromagnetic surface with magnetization M. The reflection plane is chosen to contain the surface normal and M. The elastically reflected electrons are measured at an angle α from the surface normal. A retardation grid before the detector is used to eliminate inelastically scattered electrons. In the complete experiment, the spin polarization vector P of the scattered electrons is also measured by use of a "polarimeter" typically based on Mott-scattering (Fig. 3.11).

The magnetic reflectivity can be distinguished from the one caused by LScoupling because it changes sign when the magnetization is switched to the opposite direction while the LS-coupling contribution remains the same. By modulating the spin polarization of the incident electron beam, it is possible to detect the exchange scattering on the background of the spin averaged Coulomb scattering. Since spin-polarized electrons reveal magnetic effects at the surface in contrast to the weaker interacting neutrons which are preferentially sensitive to the bulk, one may think of polarized electrons as "surface neutrons."

The *magnetic reflectivity* of spin-polarized electrons from surfaces arises from exchange scattering. It gives information on the magnetic order parameter of the surface.

Much basic information has been obtained with this technique on the magnetic properties of surfaces including changes due to chemisorption and surface reactivity and on the temperature dependence of the magnetization at surfaces and in thin films [341,342]. The most spectacular recent work is based on the development of the spin-polarized low energy microscope (SPLEEM) by Bauer and co-workers [74,664]. SPLEEM relies on the spin dependence of low energy electron reflection from a magnetic surface. It is most powerful for ordered magnetic surfaces where the discrete diffraction features of SPLEED can be utilized.

13.3.1 Simple Reflection Experiments

A simple but important experiment consists of measuring the reflected intensities I^{P_0M} without spin analysis for P_0 parallel $(I^{\uparrow\uparrow})$ and antiparallel $(I^{\downarrow\uparrow})$ to M. This corresponds to the cases $\theta_0 = 0$ or $\theta_0 = \pi$ in Fig. 13.9, respectively, and gives the *spin asymmetry* A of the elastic scattered intensity, defined by (8.32) as

$$A = \frac{I^{\uparrow\downarrow} - I^{\uparrow\uparrow}}{I^{\uparrow\downarrow} + I^{\uparrow\uparrow}} = \frac{I^{\text{maj}} - I^{\text{min}}}{I^{\text{maj}} + I^{\text{min}}} .$$
(13.2)

where $I^{\uparrow\uparrow}$ and $I^{\downarrow\uparrow}$ are the intensities of the electrons reflected or transmitted with spin parallel or antiparallel to M, respectively. The asymmetry A depends on the energy of the electrons and the scattering angles α and α' . It is of the order of 0.1 at intermediate electron energies but decreases to ~0.01 at energies $\geq 100 \text{ eV}$. A is defined for the ideal case that the incident electrons are completely polarized $P_0 = 1$. In practice, $P_0 < 1$ and A is then obtained from $A = A'/P_0$ where A' is the asymmetry observed with the incompletely polarized electrons.

The relative changes of the magnetization with temperature, chemically induced changes of the surface magnetization, and hysteresis loops of magnetically soft materials can be readily determined by measuring A. For instance, the critical exponent with which the surface magnetization disappears at $T_{\rm C}$ has been determined in a number of materials [665]. However more often than

not, magnetic materials change primary magnetic properties such as saturation magnetization, anisotropy, and type of magnetic order together with their lattice parameter in the layers near the surface. The modified surface magnetic structure shown in Fig. 13.17 is one simple example of such changes. One has to interpret A including the possibility that such changes in the primary magnetic properties occur simultaneously with changes of the crystal lattice. This poses considerable problems due to the superposition of diffraction and exchange scattering [665]. In contrast to neutrons, where the magnetic interaction is the well-known dipole interaction, for electrons one has to deal with the elusive exchange interaction and its dependence on energy and momentum. We have seen in Sect. 12.4.2 that our treatment of the exchange interaction in solids is still not firmly in hand.

A special case where electron diffraction effects are simplified are liquid metals or metallic glasses. The elastic scattering cross-section on the atomic cores is then dominant in determining the elastic reflection of the electrons. Furthermore, multiple scattering can be neglected in measurements of the normal-incidence reflectivity from the surface of metals. Although several successive atomic scattering events by small angles taken by themselves would yield a stronger intensity in the backscattering direction, these multiple scattering processes require a longer path of the hot electrons in the solid and are therefore more attenuated compared to single large-angle atomic scattering events. Therefore, the large-angle *elastic scattering* cross-sections $\sigma_{\rm e}^+$ and $\sigma_{\rm e}^$ for majority and minority spins, as well as the corresponding spin-dependent attenuation lengths $\lambda_{\rm e}^+$ and $\lambda_{\rm e}^-$, are expected to be relevant in determining the spin asymmetry A in near-surface-normal elastic electron reflection from amorphous ferromagnets [666]. In this simple picture, the backscattered intensity I is given by $I = \lambda_e \sigma_e$, yielding an estimate for the expected spin asymmetry A:

$$A = \frac{\lambda_{\rm e}^+ \sigma_{\rm e}^+ - \lambda_{\rm e}^- \sigma_{\rm e}^-}{\lambda_{\rm e}^+ \sigma_{\rm e}^+ + \lambda_{\rm e}^- \sigma_{\rm e}^-} \approx \frac{1}{2} \left[1 - \left(\frac{\sigma_{\rm e}^-}{\sigma_{\rm e}^+}\right) \left(\frac{\lambda_{\rm e}^-}{\lambda_{\rm e}^+}\right) \right].$$
(13.3)

This equation shows that both elastic $\sigma_{\rm e}^-/\sigma_{\rm e}^+$ and inelastic $\lambda_{\rm e}^-/\lambda_{\rm e}^+$ spin dependencies determine the value of A which renders the interpretation of magnetic reflection experiments difficult even in the simple case of the magnetic glasses.

Figure 13.10 shows the results of the experiment with the metallic glasses $Fe_{40}Ni_{40}B_{20}$ and $Fe_{81.5}B_{14.5}Si_4$ in comparison to those for single crystal Fe(001). In all cases, specular reflection at near-normal incidence to the surface was studied, that is $\alpha = \alpha' \approx 0^\circ$ in Fig. 13.9. The effects of diffraction present in Fe(001) produce considerable oscillations in A, while for the metallic glasses, where diffraction is absent, A is a smooth function varying in the range 0.01–0.03. The most interesting feature in Fig. 13.10 is that A changes sign at electron energies above about 50 eV, where the very intense super Koster–Kronig transition $3p \rightarrow 3d$ can be excited in the Fe-atom [351]. The glass containing Ni atoms exhibits a slightly enhanced A at electron energies above about 60 eV where the super Koster–Kronig transition can be excited

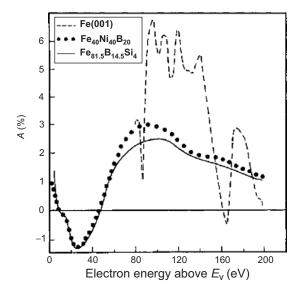


Fig. 13.10. Energy dependence of spin reflection asymmetries A in percent for two metallic glasses and an Fe(001) crystal, recorded in near-surface-normal reflection of polarized electrons [666]. The incident spin polarization P_0 as well as the magnetization M lie in the scattering plane (see Fig. 13.9) so that LS-scattering can be neglected

in the Ni atom. This different behavior of Ni and Fe is explained by the work of Landolt and coworkers [351] who studied the super Coster–Kronig spin-polarized Auger transition $3p \rightarrow 3d$ and found considerable differences between Fe and Ni due to different screening mechanisms of the 3p-hole.

It is known that $\lambda_{\rm e}^-/\lambda_{\rm e}^+ \leq 1$ at all electron energies because of the inelastic spin filter effect discussed in Sect. 12.6.1. The sign change in A from negative to positive as the energy varies through the super Koster–Kronig transition threshold therefore means according to (13.3) that the elastic scattering cross-section changes from $\sigma_{\rm e}^-/\sigma_{\rm e}^+ > \lambda_{\rm e}^+/\lambda_{\rm e}^-$ below the core transition threshold to $\sigma_{\rm e}^-/\sigma_{\rm e}^+ < \lambda_{\rm e}^+/\lambda_{\rm e}^-$ above it. The intermediate excitation of the intraatomic resonances and its influence on the spin-dependent scattering has been discussed by Nesbet [667]. Further interesting observations on the secondary electron production in metallic glasses have been reported by Hopster and coworkers [668].

At a specific energy of the incident electrons, typically around $100 \,\text{eV}$, the electron current absorbed by the metal and the current produced by diffuse inelastic secondary electrons leaving the sample, are exactly of the same magnitude. At that energy, an Ampere meter connected to the sample measuring the absorbed current reads zero while the primary beam of electrons is incident. This arises because the yield of secondary electrons in reflection of

primary electrons increases with electron energy. At energies smaller than the point of compensation, the current absorbed by the sample is larger than the current reflected from the sample, but above the compensation point, the reflected current wins over the absorbed current because the yield of secondary electrons becomes >1. At electron energies slightly above and below the compensation point, the spin asymmetry $A_{\rm abs}$ of the current absorbed by the sample is complete, that is $A_{\rm abs} = \pm 1$ [609], providing a very simple yet still largely unexplored detection scheme for spin polarization. The phenomenon arises from the fact that the energy where the compensation of reflected and absorbed current occurs, depends on the spin polarization of the incident electrons relative to the magnetization. At the point where the current induced by one spin state is completely compensated, only the current excited by the other spin state is observed.

One can avoid electron diffraction even with crystalline surfaces by going to low electron energies where the De Broglie wavelength becomes larger than the lattice constant. In that case, the first diffraction spot would appear at an angle $\alpha' > \pi/2$, hence there is only the specularly reflected beam, usually referred to as the [00]-beam. Besides removing the difficulty of sorting out the effects of lattice diffraction, this leads to a large reflected intensity. In this case, the spin-dependent reflection comes about because the exchange interaction in the ferromagnet causes a splitting of the bands into majority spin and minority spin subbands as discussed in Chap. 12. This splitting exists for the bands below and above the Fermi energy. The unoccupied bands above the vacuum level are the relevant bands for the incident electrons. The strongest effect on the reflectivity can be expected when, at one specific energy, states are available for one spin but not for the other.

An example of such a low-energy measurement by use of the [00]-beam is shown in Fig. 13.11 for an epitaxial film of α -Fe(001) grown on an Ag(001) substrate [669].

The electrons were incident almost normal to the surface, and the intensity of the reflected [00]-beam was measured for P_0 parallel and antiparallel to M. Figure 13.11 shows the measured asymmetry A of the total reflected intensity. The measurement was performed without applying a voltage to the retardation grid in Fig. 13.9. Figure 13.11b shows the dependence of the normalized (to the incident current) reflected currents on the relative orientation of the incident spins and the magnetization of the sample. The largest negative peak in the asymmetry A occurs at an electron energy of ~10 eV where, according to the calculated bands shown in the inset (c), the majority spins have states available in the crystal, hence are less reflected compared to the minority spins. All of the observed structure in A is clearly related to the spin-gaps in the band-structure.

The large spin asymmetry A = -0.21 combined with a high reflectivity of ≈ 0.1 makes reflection from Fe(001) a good detector for electron spin polarization. The sensitivity of Fe to oxidation requires operation of such detectors in UHV, but Bertacco and Ciccacci [670] reported that the Fe surface can be

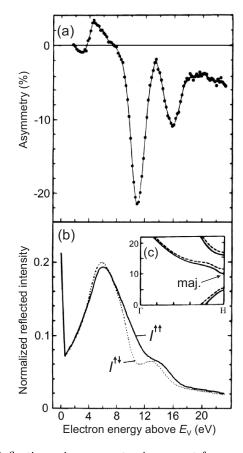


Fig. 13.11. (a) Reflection spin asymmetry in percent from an Fe(100) crystalline surface versus electron energy [669]. (b) The reflected intensities $I^{\uparrow\uparrow}$ and $I^{\uparrow\downarrow}$ normalized to the incident current. (c) The inset shows the spin-split bands of the crystal along the normal incidence direction of the electrons. The electron energy is low enough so that the incident beam is reflected specularly without higher-order diffraction. No retardation voltage was applied

stabilized by oxidation, enhancing the figure of merit and prolonging its useful lifetime as a polarimeter. The quality of a polarimeter is determined by the time it takes to measure the degree of the spin polarization within a given statistical accuracy. This so defined figure of merit is given by A^2I , which is 3.5×10^{-3} in the present case. This is larger by a factor of 20 than that of traditional Mott polarimeters [671] and therefore speeds up the measurement by a of factor 20!

Ten-times larger figures of merit were reported by Zdyb and Bauer [352], and they were exceeded later by yet another factor of 10 [672]. Altogether

one can then expect to save a factor of 100 in the time needed to measure the spin polarization. These improvements in the spin sensitivity occur when the density of states for one specific spin is amplified at certain thicknesses of the ferromagnetic film by standing electron waves. Such quantum well (QW) states play the decisive role in the periodic exchange coupling between two ferromagnetic films across a nonmagnetic spacer layer discussed in Sect. 13.4.5. The spin-polarized low energy electron microscope (SPLEEM) relies on spindependent reflectivity. Due to its high lateral resolution it is very suitable to find locations at the surface of a thin film where the conditions for QW states are optimally fulfilled.

These examples show that there is great potential for improving the measurement of the spin polarization over the currently used method based on LS-scattering, usually referred to as Mott-scattering (Sect. 3.5.2), which has poor efficiency. The use of magnetic exchange based spin dependencies will make spin resolved electron spectroscopy almost as easy as conventional spectroscopy.

13.3.2 The Complete Reflection Experiment

While numerous studies have been done on scattering of polarized electrons from ferromagnets, only one study, carried by Weber et al. [601], is available so far in which the information to be gained from electron reflection is complete. Such a complete experiment is distinguished by the fact that the polarization \boldsymbol{P}_0 of the incident electrons is chosen to be *perpendicular* to the magnetization rather than parallel or antiparallel to it, as shown in Fig. 13.12. It is only with this non-collinear unstable initial configuration that one can observe how the reflected vector of polarization P is different from the incident vector P_0 . Analogous to the motion of P_0 in the transmission experiment discussed in Sect. 12.6.4, a motion of P_0 occurs in reflection, as well. The motion arises because the exchange field exerts a torque on \boldsymbol{P}_0 and the elastic reflection of electrons depends on spin. The former leads to a precession of P_0 about M while the latter induces a rotation of P into the direction of M or -M. Again, as in transmission, one can separately measure the angle of precession φ and the change in the angle θ induced by the rotation (see Fig. 13.12). But in contrast to transmission, both the sense of precession and the sense of rotation can change sign, depending on the energy of the electrons.

The samples investigated by Weber et al. [601] were Co films grown on two types of substrates, namely a (111)-textured polycrystalline Au film on glass and a Cu(001) single crystal. The first type of substrate generates a polycrystalline Co film while the second type of film is single crystalline fcc Co. Of importance in the experiment is the observation that both films exhibit full magnetic remanence, i.e., they can be investigated while in a single domain state without applying an external magnetic field. The presence of an external magnetic field is unwanted because it could disturb the electron trajectories due to the Lorentz force and cause additional spin precession.

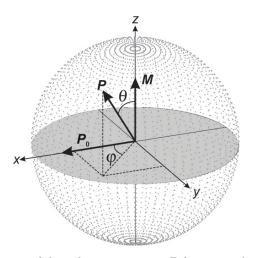


Fig. 13.12. Movement of the polarization vector P for a special reflection geometry of Fig. 13.9, characterized by the incident spin polarization P_0 along x. Shown is the orientation of the reflected electron spin polarization P relative to that of the incident spins P_0 and the magnetization direction M

The direction of the incident electron polarization vector \mathbf{P}_0 is chosen to be along the *x* axis, perpendicular to $\mathbf{M} \parallel z$, in both Figs. 13.9 and 13.12. The position of \mathbf{P}_0 at incidence is thus characterized by $\varphi_0 = 0^\circ$ and $\theta_0 = 90^\circ$.

To distinguish the precession from the rotation, the direction of P_0 in space as well as the relative alignment of P_0 and M must be interchanged. On reversing P_0 , only φ changes sign, while on reversing M, the sense of both precession and rotation changes. In this way it is possible to obtain the contribution of each motion separately. The technique of changing both the absolute direction of P_0 and M as well as their relative orientation also eliminates the effects of the LS-interaction.

Figure 13.13 shows the results of the experiment [601] for specular elastic electron reflection from fcc Co for $\alpha = \alpha' = 45^{\circ}$ (defined in Fig. 13.9) and for electron energies 5–90 eV above $E_{\rm F}$. With polycrystalline Co, φ is always positive and θ is always reduced from its initial value of $\theta_0 = 90^{\circ}$. The sense of the precession and the sense of rotation are identical to what is observed in electron transmission. This is expected since in every reflection, the electron wave penetrates up to a characteristic depth of the order of one wavelength into the medium. During this penetration, the spins are exposed to the exchange field and experience spin selective scattering just as in transmission leading to the motion of P_0 as described in Sect. 12.6.4. However, Fig. 13.13 also shows that in the case of single crystalline Co, both the precession and the rotation show strong variations and may exhibit the other sign at some specific electron energies.

To understand this phenomenon occurring with single crystalline surfaces, we first take a look at what determines the direction of the precession. In

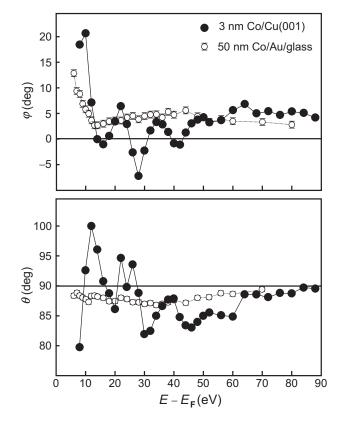


Fig. 13.13. Measured angle φ of precession and the angle θ of rotation of P with single crystalline (•••) and polycrystalline (•••) Co versus the energy of the reflected electrons above $E_{\rm F}$ [601]

addition to the precession of the spin caused by the different phase velocities of the two partial waves in the exchange field, there is also a jump in the phase of the waves upon reflection at the spin-dependent potential of the ferromagnetic surface. This jump in phase evolves from 0 to π as the electron energy E is changed from the bottom to the top of a band of the electron states in the solid. A commonly used expression for the energy dependence of the phase shift is given by (13.13) in Sect. 13.4.5.

Since majority and minority spin bands lie at different energies, the phase shift in reflection is spin-dependent. The difference in the phase shift for the two spin states leads to a change in φ that is superimposed on the spin precession. The spin asymmetry in the phase jump in reflection can be larger than the precession angle in the exchange field. The contribution to φ from the phase jump in reflection is dominant near band edges. As the electron energy reaches the onset of a new band, the majority spins will experience less phase shift upon reflection compared to the minority spins. Hence, near the onset of

a new energy band, the phase shift is determined by the minority spins and makes the precession appear reversed.

Let us now discuss the causes of the reversed sense of rotation of P. The reversed rotation occurs at selected electron energies which, according to Fig. 13.13, are close to those energies in which the reversed precession is observed. We have already seen in Fig. 13.11 that the spin-dependent absorption can change sign at the bottom of a new, exchange-split energy band. If majority spins have states available, they can penetrate into the ferromagnet. This leads to the observed preferential reflection of minority spins, reversing the sign of the spin asymmetry A in reflection. Equation (8.36) shows that the angle θ changes sign when A changes sign.

Altogether, one then expects the reversed sense of precession and rotation to occur near gaps in the exchange-split energy bands. One also understands that these reversals do not occur with polycrystalline metals where one does not encounter well-defined band gaps. Figure 13.13 confirms this expectation. Reversals of both the precession φ and the rotation θ are observed at electron energies around 16 and 24 eV. Tight binding band structure calculations show that at these energies, there are indeed relative band gaps along the **k**-lines determined by the angle of incidence $\alpha = 45^{\circ}$, corresponding to the experimental condition. Because of the non-normal incidence of the electrons, the band structure along high symmetry k-directions of the Brillouin zone is not sufficient. Instead, for each energy, an independent calculation has to be performed. The result of such calculations [601] is shown in the inset of Fig. 13.14. The agreement between the energies of the structures observed in φ and θ and the location of the band gaps is not perfect but satisfactory, keeping in mind that the calculations cannot account for many-body effects like energy shifts and life-time broadening, as discussed in Sect. 12.4.2.

Figure 13.14 shows an important additional result of the complete reflection experiment. The derivative $-\partial \varphi / \partial E$ traces closely the energy dependence of θ . Elementary optical dispersion theory connects the reflection, absorption and the index of refraction n. The quantity 1/n is proportional to the phase velocity in the medium, which changes abruptly on going through a peak of the reflection where the medium resonates with the waves. The rate of change of electron spin precession $\partial \varphi / \partial E$ corresponds to the rate of change of the rotation of the plane of polarization in the reflection of EM-waves [673]. Figure 13.14 thus suggests that there is an analogy between magneto-optics and polarized electron reflection. In fact, the reflection of polarized electrons from a magnetic surface is formally identical to the longitudinal magnetooptic Kerr effect. In both magneto-optics and polarized electron scattering, the matrix I that, according to (8.31), connects the incident wave ψ_0 with the reflected wave ψ , contains the material constants A and φ , while the off-diagonal elements that mix the two polarization or spin channels, remain zero. The analogy to optics is caused by the fact that the contribution of elastic spin exchange collisions is negligible according to Sect. 12.6.3. If spin exchange collisions involving a spin flip were important in elastic reflection

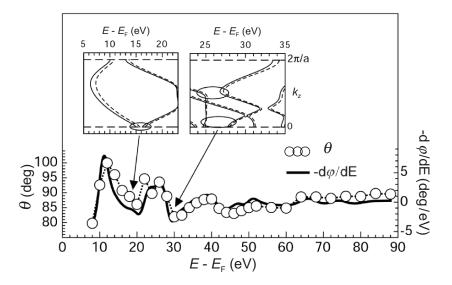


Fig. 13.14. Plot of the derivative $-\partial \varphi/\partial E$ of the precession angle versus electron energy for single crystalline fcc Co (solid line). The plot for $\theta(E)$ (open circles) is taken from Fig. 13.11. The inset shows the result of self-consistent band structure calculations along the **k**-lines relevant in the experiment. The solid lines are majority spin bands, the dashed lines minority spin bands. The **k**-line is along $0 \le k_z \le 2\pi/a$ in both cases. In the left inset, $k_x = k_y = 0.425(2\pi/a)$, and in the right inset, $k_x = k_y = 0.2(2\pi/a)$ [601]

from magnetic surfaces, "magneto-optics" with electrons would be entirely different from magneto-optics with EM-waves.

Lastly, Figure 13.15 shows the variation of the precession angle with the thickness of a single crystalline fcc Co film on the Cu(001) substrate. As Cu will not produce any precession of the spin, one expects that φ grows from zero to its final value when the thickness of Co is comparable to the penetration depth of the electrons in reflection and/or when the spin-polarized ferromagnetic band structure of Co has reached its final configuration. At the electron energy 9 eV, φ indeed saturates, corresponding to an inelastic mean free path $\lambda_{\rm e} \approx 1 \,\mathrm{nm}$. This value for $\lambda_{\rm e}$ is consistent with other work [674]. In contrast, at an energy of $28 \,\mathrm{eV}$, a linear decrease of φ occurs up to a thickness of 20 nm, followed by a slower increase at still larger thickness. This ongoing variation of φ indicates that the band structure is still not established even at these sizeable thicknesses. In fact, it is known that the strain induced by the misfit between the Co overlayer and the Cu substrate relaxes from $2 \,\mathrm{nm}$ thickness onwards, but even at $7 \,\mathrm{nm}$ thickness, the lattice parameter of the Co film is still changing both in the interior and at the surface [675]. An extraordinary sensitivity of the hybridization gap at 28 eV to the crystal structure must be postulated to understand this behavior. The fact that the

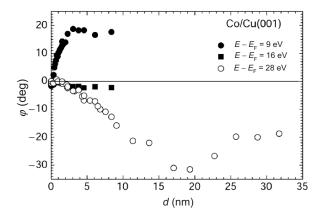


Fig. 13.15. Plot of the precession angle φ versus thickness of a single-crystalline fcc Co(001) layer grown on Cu(001) for three selected electron energies [601]

transformation of fcc Co into hcp Co occurs from 20 nm thickness onwards [676] correlates with the turning point of φ at this thickness. "Ellipsometry" with polarized electrons is thus a very promising technique to study finer details of magnetic surfaces, and its full potential has not been utilized.

The occurrence of large positive precession angles in the reflection of lowenergy electrons points to yet another important phenomenon discussed in detail in Sect. 14.2. The precession of the spin in reflection reveals that a torque is exerted on the spins by the magnetic exchange interaction. This torque must be balanced by an opposite torque exercised by the reflected electrons on the magnetization by virtue of Newton's law of equal and opposite reaction. The torque per volume is equivalent to a pressure acting on M, tending to turn the magnetization antiparallel to the direction of P. This pressure can also be thought of as an effective magnetic field $H_{\rm eff}$ generated in the NEXIinteraction defined in Sect. 14.2.1. From the precession angle $\varphi = 20^{\circ}$ that the electrons acquired over the distance of penetration $\approx 1 \,\mathrm{nm}$ in the experiment in Fig. 13.13, one can calculate $H_{\rm eff}$ from (14.37). With the highest current densities achievable in nanocontacts, the torque resulting from reflection of polarized electrons acting in a surface layer of $\sim 1 \text{ nm}$ would be equivalent to $H_{\rm eff} \sim 10^5 \ {\rm A m^{-1}}$. It is likely that at lower energies close to $E_{\rm F}$ such torques will be even larger than at 5 eV above $E_{\rm F}$. At any rate, the torques generated in reflection of spin-polarized electrons have been neglected so far. They are an interesting supplement to the spin injection torques.

13.4 Static Magnetic Coupling at Interfaces

The interaction of magnetic materials through physical contact has been of interest since the very early days of magnetism. A first technical application

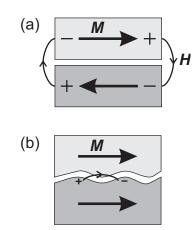


Fig. 13.16. Magnetostatic coupling of two ferromagnetic specimens. (a) depicts coupling of two homogeneously magnetized thin film samples through the stray field from the end poles, leading to antiparallel alignment. This is important in single-domain nanoscopic elements used, e.g., in magnetic random access memories (MRAMs). (b) shows how thin films with surface roughness may favor parallel alignment of the magnetization. The surface roughness induced coupling is often referred to as Néel coupling or orange peel coupling

is the fabrication of compass "needles" by rubbing regular sewing needles on lodestone. In 1902, C. Maurain reported that an electrodeposited Fe-film separated by thin Cu spacer layers from an Fe cathode had a tendency to align its magnetization parallel to that of the cathode [677]. Generally, the magnetic interaction can be described as the transfer of an effective magnetic field between the contacted magnetic materials. The effective field can be a regular magnetic field or an effective magnetic field produced by the quantum mechanical exchange interaction.

13.4.1 Magnetostatic Coupling

The simplest interaction that may exist between two magnetic specimens is the magnetostatic interaction where the transferred field is a stray magnetic field. Prior to the era of surface science, atomically clean interfaces could not be prepared, and only magnetostatic coupling could be studied in detail [678]. Magnetostatic coupling can lead to parallel or antiparallel alignment of the magnetization in two adjacent ferromagnetic thin films. These two important cases are illustrated in Fig. 13.16.

Parallel coupling may be induced by surface roughness and is sometimes referred to as Néel or *orange peel coupling*. Antiparallel alignment is caused by the stray field of the magnetic poles at the end of the sample. It is particularly important with nanoscopic specimens that are in a single domain state. In thin film structures, magnetostatic coupling is sometimes difficult to separate from another type of coupling, namely the quantum mechanical exchange coupling which, through pinholes in the interface layer, may lead to direct contact between the magnetic materials.

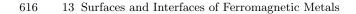
The exchange coupling between an antiferromagnet and a ferromagnet was discovered in 1956, before the advent of surface characterization on an atomic scale [679]. Convincing proof that exchange coupling exists even through a metallic spacer that is not magnetic, such as Cu, was provided by the discovery that the coupling between two ferromagnetic thin films changes sign periodically with the thickness of the spacer layer [82]. In the following we will concentrate on phenomena induced by the exchange coupling, referring the reader to the book of Hubert and Schaefer [54] for a more detailed discussion of magnetostatic coupling.

When it became possible to produce atomically clean crystalline surfaces of a metal and add atomically engineered additional layers of a different metal, a very rich field of new magnetic phenomena opened up. Many of the phenomena observed for many-layer systems or multilayers are also present for the simplest systems containing only two ferromagnetic layers, and we shall therefore confine our discussion to such systems. If the two magnetic layers are in direct atomic contact, it is clear that exchange coupling should be present between the adjacent atomic layers. However, two ferromagnetic layers may also be coupled via an intermediate layer that is not magnetic by itself. We will discuss these two cases separately.

13.4.2 Direct Coupling between Magnetic Layers

The simplest case of a magnetic double layer is the surface layer of a bulk ferromagnet. The first layer of a magnetic specimen usually has a magnetization $M_{\rm S}$ and crystalline anisotropy $K_{\rm S}$ that are different from those of the bulk. $M_{\rm S}$ also has a different temperature dependence as discussed in Sect. 11.1.5. The change of the magnetic interaction and anisotropy at the surface can lead to rather dramatic phenomena. For instance, the surface may have an ordering temperature $T_{\rm CS}$ different from the bulk, or antiferromagnetic ordering may occur on the surface of ferromagnets. Possible magnetization profiles near a vacuum surface have been described by Binder [680].

The exchange coupling is expected to be weakened on a path perpendicular to the surface, because there are fewer nearest neighbors in the surface layer and the lattice parameter is known to expand in the direction perpendicular to the surface [490]. This has been investigated systematically with surface sensitive spin-polarized electron spectroscopies [681]. Another large body of investigations is concerned with the phase transition at naturally occurring surfaces and in surface layers that are artificially decoupled from the bulk by insertion of nonmagnetic atoms. Atom-specific X-ray circular magnetic dichroism (XMCD) has become the technique of choice to investigate such and similar phenomena [682]. We discuss here in more detail only some basic phenomena.



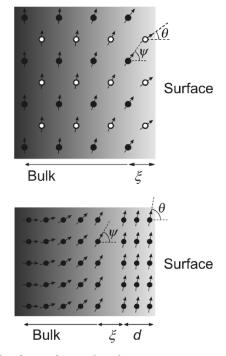


Fig. 13.17. Examples for surface induced magnetic structures in magnetic remanence. The upper picture is for the Fe(100) surface [683], with the surface plane perpendicular to the plane of the drawing, located on the right side. It is assumed that only the first layer with an expanded distance ξ is magnetically different from the bulk. The bulk of Fe is remanently magnetized upwards while the surface anisotropy K_S is perpendicular to the surface. Atoms indicated by open circles are offset out of the plane of the drawing from those shown as filled circles. The magnetization direction of the surface atoms is characterized by the angle θ , that of the second layer atoms by ψ . The lower picture shows a case that applies to 3d-4f alloys, such as FeTb. Due to the high magnetic anisotropy of Tb, the bulk is remanently magnetized perpendicular to the surface, whereas the surface layer of thickness d, consisting mainly of Fe and formed by segregation and oxidation of Tb to the outer surface (not shown), has the easy direction in-plane. Note that only the dominant 3d magnetic moments are depicted. Adapted from [684]

The surface magnetic anisotropy constant $K_{\rm S}$ may be vastly different from the bulk anisotropy $K_{\rm B}$, favoring a different direction of the magnetization and usually having much larger strength. One reason is that the orbital moment is less quenched at the surface, as discussed in Sect. 11.2. There may also be a large magnetostatic contribution to $K_{\rm S}$ if the magnetization at the surface has a perpendicular component. Hence the surface may induce special magnetic structures even if the bulk of the specimen is in a single domain state.

In Fig. 13.17, we show two examples of surface-induced magnetic structures present in magnetic remanence, that is with no external magnetic field applied. The angle θ of the surface magnetization and the angle ψ of the second layer can be determined by minimizing the sum of all energies. By including an external magnetic field in the energy balance, it is possible to calculate the surface hysteresis loop. Comparing it to the experiment yields information on the magnetic parameters of the surface layer [684]. Experimental surface hysteresis loops are obtained by measuring the surface magnetization direction, for instance by observing the spin polarization of the low-energy cascade electrons that have a probing depth of only a few atomic layers. The magnetization direction in the underlying bulk can conveniently be obtained by the magneto-optic Kerr effect, which typically has a probing depth of 15 nm in metals. If the Kerr loops and the loops from spin polarization are different, one knows that surface-induced magnetic structures are present. These structures can be a precursor to magnetic domain nucleation determining magnetic coercivity [685]. Even more dramatic consequences of $K_{\rm S}$ are revealed in the image in Fig. 13.8, recorded by spin-polarized tunneling spectroscopy.

The surface of a ferromagnet is an unavoidable magnetic defect. It may generate shorter pieces of domain walls, referred to as "embryonic domain walls", which may give rise to a reduced coercivity. It also makes the assumption of a uniform magnetization, the so called "macro-spin approximation", suspect or invalid even with a nanoscopic specimen that can not sustain a regular domain wall. Nonuniform magnetization may lead to complex switching behavior.

An interesting phenomenon due to the coupling between two different ferromagnets are "spring" magnets [686]. One of the ferromagnets is magnetically hard and the other soft, that is with a low magnetic anisotropy. In spring magnets, the magnetization of the soft magnet rotates when an external field is applied, but when this field is released, it snaps back to the previous direction given by the underlying hard magnet. The "spring" generating this elastic force is the exchange interaction between neighboring spins. The spring constant is given by the exchange stiffness A_{ex} defined in Sect. 11.3.

13.4.3 Exchange Bias

A striking consequence of exchange coupling, called *exchange bias*, arises if a thin film of a ferromagnet (FM), such as Co, has a common interface with an antiferromagnet (AFM) such as CoO. The phenomenon was discovered by Meiklejohn and Bean in 1956 [679] in the study of oxidized Co particles. They observed that the center of the magnetization loop was shifted from zero, and attributed the shift to a bias field originating from the AFM. The size of the effect could only be explained by assuming an AFM–FM *exchange* interaction. Today, the exchange bias effect has found important technological applications in magnetic sensors where it keeps the magnetization of a ferromagnetic layer, which serves as a *reference layer*, in a fixed direction in space. This effect, also

referred to as *unidirectional* exchange anisotropy, distinctly differs from the usual case of *uniaxial* ferromagnetic anisotropy discussed in Sect. 11.2, where the magnetization has two energetically equivalent orientations, either parallel or antiparallel to a direction in space called the easy axis.

The occurrence of exchange bias due to a "bias field" arising from the antiferromagnet is somewhat puzzling since we think of antiferromagnets as being magnetically neutral. Many AFMs are best described by two identical sublattices. In each sublattice, the spins are parallel generating a magnetization just like in a FM. However, the two sublattices are coupled antiparallel to each other so that the total magnetization is zero.¹ If the magnetic moments in the two sublattices are generated by the same atomic species, one speaks of an A–A antiferromagnet. This is realized in CoO or in NiO (compare Fig. 7.25). But the two different atoms may also be located in the two sublattices with a vanishing net magnetization. In that case, one speaks of an A–B antiferromagnet, MnFe being an example.

From a scientific point of view, the exchange bias phenomenon has been so fascinating because it clearly cannot be a bulk effect, but must be due to the magnetic structure near the AFM–FM interface. Because of the difficulty of experimentally determining the magnetic structure right near the interface it took nearly 50 years to unravel the exchange bias puzzle. We cannot give here an account of the large amount of work done on the subject but refer the reader to various reviews [687–692]. Instead, we shall first give a brief outline of the most important experimental observations and the terminology used in the literature and then give our present understanding of the phenomenon.

The key experimental findings and the terminology associated with exchange bias are given in Fig. 13.18. The magnetization loop of a conventional ferromagnet along the easy and hard magnetization directions is symmetric about zero external magnetic field H_{ext} , as shown in Fig. 13.18a. The anisotropy is *uniaxial* (in contrast to "unidirectional") since there are two equivalent easy magnetization directions. The uniaxial preference of the magnetization of a ferromagnet is usually due to its own magnetocrystalline anisotropy. However, if a FM is deposited on an AFM in the absence of an external field, the magnetization loop will still be symmetric and exhibit uniaxial anisotropy of the AFM and not by that of the FM itself. In order to indicate that in this case the FM anisotropy is not intrinsic but induced by exchange coupling to the AFM one often speaks of "uniaxial exchange anisotropy" or "exchange anisotropy," for short.

In contrast, when a ferromagnet is grown on an antiferromagnet in the presence of a "setting field" H_{set} , assumed to be in the *positive* field direc-

¹In a *ferrimagnet*, there are also two antiparallel coupled sublattices, but the magnetization is of different magnitude in the two sublattices. Therefore, ferrimagnets exhibit a magnetization. The most famous example of a ferrimagnet is magnetite (Fe₃O₄), discussed in Sect. 7.7.4.

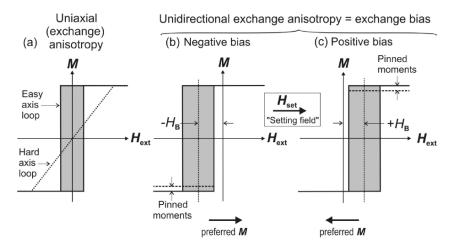


Fig. 13.18. (a): The magnetization loop of a conventional ferromagnet along the easy (solid line) and hard (dotted line) magnetization directions. The sample is said to exhibit a "uniaxial anisotropy" about the easy axis due to the magnetocrystalline anisotropy. If the easy axis in a FM is imposed by exchange-coupling and corresponds to that of an adjacent AFM, we speak of "uniaxial exchange anisotropy." In all uniaxial cases, the magnetization loop is symmetric about zero external magnetic field H_{ext} . (b) and (c) In contrast, exchange bias corresponds to the existence of a loop that is horizontally shifted by a bias field $H_{\rm B}$. In this case the magnetization in the FM prefers one direction in space, imposed by exchange coupling to "pinned moments" in an adjacent AFM. The sample is said to have a unidirectional magnetic anisotropy, which is due to exchange. If the loop shift is in the opposite direction as the "setting field" $H_{\rm set}$, applied during sample preparation, we speak of *negative* bias. In this case the preferred magnetization ${\cal M}$ of the sample is in the direction of H_{set} . If the loop shift is in the same direction as H_{set} , the bias is said to be positive and the preferred magnetization M direction is opposite to H_{set} . In some cases a vertical loop shift originating from *pinned* moments may also be observed, as explained in the text

tion, as shown, or when the system is heated above the Néel temperature and cooled in the presence of a setting field, the magnetization loop may be shifted horizontally in either the negative or positive field direction. This case corresponds to a *unidirectional magnetic anisotropy*, since the positive and negative external field directions are no longer equivalent. The sample is said to be *exchange biased* because the shift of the loop is caused by an exchange field. The more common case of *negative* exchange bias corresponds to a loop shift $-H_{\rm B}$ in the opposite direction as the setting field $H_{\rm set}$. The field $H_{\rm B}$ is called the transferred exchange field or the bias field. For negative bias $-H_{\rm B}$, the magnetization M has a preference for the positive field direction since it switches into this direction more easily. In fact, for the case shown in Fig. 13.18b, the negative loop shift is so large that the remanent magnetization direction is always positive. A *positive* bias $+H_{\rm B}$ indicates a loop shift in the

same direction as the cooling field. Now the magnetization of the system has a preference for the direction opposite to H_{set} . Another interesting finding is that in many cases exchange bias is accompanied by an increase in coercivity, as indicated by a broadening of the loop in Fig. 13.18.

We shall see later that exchange bias can be directly linked to *pinned* moments. Pinned moments are created by the setting field during the sample preparation process and they exist near the AFM–FM interface. They cannot be turned around from their preferred direction by typical external magnetic fields and, in principle, also give rise to a vertical loop shift, as indicated by dashed lines for the loops in Fig. 13.18b, c. The magnetization is slightly larger in the direction of the pinned moments since they only contribute in this direction. In practice, their number is very small and they can only be observed in special situations.

We can summarize some important points as follows.

Uniaxial exchange anisotropy refers to a preferred anisotropy axis (easy axis) in a FM that is due to the magnetocrystalline anisotropy in an adjacent AFM, transferred by exchange coupling. The magnetization loop is symmetric.

Exchange bias, also called *unidirectional exchange anisotropy*, refers to the presence of a preferred *direction* of the FM magnetization. It originates from exchange coupling of the moments in the FM to uncompensated pinned moments in the AFM. The magnetization loop is shifted along the field axis.

We shall here concentrate on the most important aspect of exchange bias, namely the origin of the effect and the factors that determine the absolute value of the bias field $H_{\rm B}$. It has long been clear that the exchange bias field $H_{\rm B}$ that locks the ferromagnet (FM) into a preferred direction must originate from uncompensated spins near the FM–AFM interface which are frozen in by the setting field. These spins must somehow be anchored in the bulk of the AFM so that they cannot be reversed by typical external magnetic fields of order 1 T. Historically, the main problem in establishing a realistic model of exchange bias has been the lack of information on the spin structure near the all-important interface. Rather than giving a historical discussion of the many models put forward over 50 years of research, which can be found in other reviews [687–692], we shall here discuss a basic model that contains all the important ingredients and is supported by the latest experimental results. In particular, starting in 2000, X-ray dichroism spectroscopy and microscopy measurements [107, 404, 405, 431, 693–695] have made key contributions to the solution of the long-standing exchange bias puzzle by providing interfacespecific magnetic information. From these and a large body of other measurements we now know the following key facts that need to be contained in a realistic model.

- 1. In the biased ground state the FM and AFM spins are aligned along the same axis.
- 2. Near the interface, there are uncompensated spins that originate from magnetic atoms in the AFM.
- 3. A fraction of the uncompensated interfacial spins are pinned. They are responsible for the existence of exchange bias and their number is proportional to the size of the bias.
- 4. The size of the bias decreases with the antiferromagnetic domain size.
- 5. The sign of the bias is determined by the sign of the exchange coupling between the pinned interfacial spins and the FM.
- 6. The interfacial pinned spins are anchored in the bulk AFM through a Bloch domain wall. The size of exchange bias is proportional to the exchange stiffness of this domain wall and the magnetocrystalline anisotropy of the bulk AFM.

Let us take a quick look at the experimental results underlying the above statements. We have already seen X-ray dichroism images of FM Co deposited on the AFMs LaFeO₃ and NiO in Sect. 10.4.3. In particular, we have seen that in both cases the Co spins are aligned either parallel or antiparallel to the AFM spin axis, illustrating point (1) [107,404].

The crux of the exchange bias problem revolves around points (2) and (3), the existence and number of uncompensated *pinned* spins at the interface. For many years scientists were misled by the notion of a well-defined layer-by-layer spin structure at the ferromagnet/antiferromagnet interface that resembled that in single crystals. For example, as shown in Fig. 7.25, for NiO all spins lie in the {111} planes with opposite spin directions in adjacent planes. So when the ferromagnet is deposited on a NiO (111) plane there will be a net exchange bias field exerted by the last NiO layer on the adjacent ferromagnet. The theory for such a "uncompensated" ideal antiferromagnet was already put forward by Meiklejohn and Bean in 1956 [679]. The problem, however, is that the size of the loop shift predicted by such an ideal model is much too large (see below).

The puzzle about the origin of uncompensated spins was solved by the experimental demonstration that real interfaces significantly differ from ideal, abrupt, single-step AFM–FM transitions between bulk-like crystal and spin structures. Furthermore it was found that not all uncompensated interfacial spins contribute in the same way. Typically, in an external magnetic field, a small fraction stays pinned while a larger fraction rotates with the ferromagnet. Only the pinned fraction creates bias while the other spins may contribute to the coercivity. In the following we illustrate these points by three key experimental observations.

When X-ray absorption spectra are recorded for a Co/NiO sandwich, one finds that the Co spectrum shows a slight oxidation of Co metal and the Ni

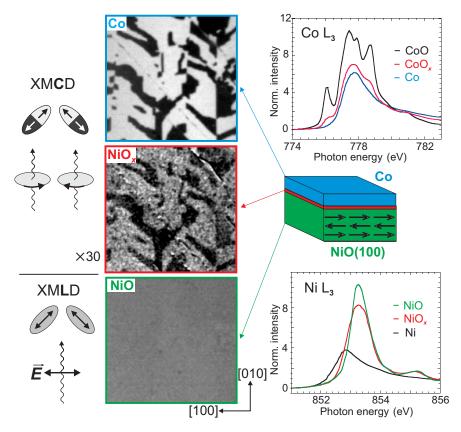


Fig. 13.19. X-PEEM images of the magnetic domain structure in a sandwich of 0.8 nm of Co deposited on NiO(100). On the *right* we show the X-ray absorption fine structure near the Co and Ni L₃ absorption edges and a schematic of the sample structure. Spectra for the actual Co/NiO sample (red) are compared to reference spectra recorded for pure metal and monoxide samples. On the *left* the sample orientation and the X-ray polarization is illustrated. In the *middle* column, element-specific XMCD PEEM images recorded at the Co (top) and Ni (middle) edges, respectively, show *ferromagnetic domain contrast*, which in the Ni case is due to uncompensated interfacial Ni spins in NiO (labeled NiO_x). The bottom XMLD image taken at the Ni edge shows no antiferromagnetic contrast due to the special sample orientation (compare Fig. 10.25)

spectrum shows a slight reduction of NiO, as illustrated on the right side Fig. 13.19. This indicates interfacial interdiffusion of oxygen, resulting in an interfacial region that is about one monolayer thick [431]. Pure NiO does not exhibit any XMCD signal because all Ni spins are completely compensated. However, the Co/NiO sandwich exhibits a ferromagnetic Ni signal, arising from Ni atoms with incomplete oxygen coordination [431,693]. One can even image the uncompensated Ni spins by means of XMCD microscopy, as shown

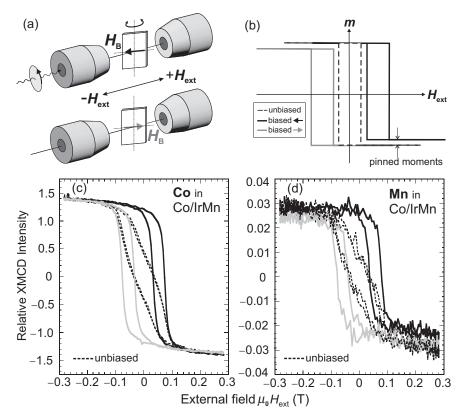


Fig. 13.20. (a) Experimental geometry for XMCD spectroscopy measurements. (b) Illustration of expected XMCD-intensity loops for the two experimental geometries in (a), assuming a small fraction of pinned moments pointing into the bias direction. (c) Element-specific Co loops for unbiased and biased samples for the two geometries in (a). (d) Element-specific Mn loops for unbiased and biased samples for the two geometries in (a)

in the middle image in Fig. 13.19. In all images in this figure the NiO substrate orientation was chosen to be at 45° with respect to the incoming X-ray direction and the *E*-vector so that no AFM contrast is seen and the ferromagnetic contrast is more clearly revealed. This image illustrates point (2) from above.

Measurements on another sample, 2 nm Co on 50 nm of $Ir_{20}Mn_{80}$, shown in Fig. 13.20, demonstrate how unpinned and pinned spins can be distinguished [694]. By use of the element-specific XMCD signal to measure the Co and Mn magnetic moments, one can measure a magnetization loop. In particular, the Mn loop is found to exhibit a horizontal as well as a vertical shift. From the vertical shift one finds that most Mn moments follow the field (and the Co FM) but a small fraction remains pinned and does not follow the field. Quantitative analysis shows that the number of uncompensated Mn moments

corresponds to 0.6 monolayer at the FM–AFM interface, and that about 7% of them are pinned. The pinned 0.04 monolayer Mn moments are responsible for exchange bias. Similar results were obtained by means of magnetic force microscopy [696] and nonlinear optical spectroscopy [697]. This illustrates point (3) from above.

Another exchange bias problem is that one finds no clear difference in the bias characteristics for spin-compensated and uncompensated antiferromagnetic single crystal surfaces and, surprisingly, the bias is typically largest for polycrystalline antiferromagnets. This points to a structure of the AFM interface that differs from that expected from a simple termination of the bulk structure. This idea was was first pursued theoretically by Malozemoff [698] in 1987. He assumed that a real AFM surface consists of different domains which may originate from imperfections. Using a random field model, he found from a statistical treatment of the AFM domain diameter d that the bias changes as 1/d. Such a behavior was indeed found in 1997 by Takano et al. [699] in a study of polycrystalline CoO/Ni₈₁Fe₁₉ films, prepared with different CoO grain sizes. The correlation of experiment and theory assumed that for AFMs, the grain size is equal to the AFM domain size. The ability to directly image small AFM domains by XMLD microscopy [106] indeed supports such a correlation. It also confirms the conjecture of a 1/d domain-size-dependent exchange bias [107,695], confirming point (4) from above. Results for the domain size dependent bias of Co on $LaFeO_3$ are shown Fig. 13.21.

The defect-based creation of AFM domains has been extended into the so-called *domain state model* by Nowak et al. [533]. By means of Monte Carlo simulations of the formation of AFM domains and their coupling to an adjacent ferromagnet, these authors demonstrated the correlation between the number of defects, the domain size, the number of uncompensated spins, and the size of the bias.

Like Co/NiO and Co/IrMn, most exchange bias systems exhibit negative bias. For these cases XMCD measurements show that the FM moments and pinned AFM moments are aligned in the same direction, hence we have J > 0 for the exchange coupling constant. In some systems, positive exchange bias has also been observed. Examples are AFM/FM systems involving transition metal fluorides [700, 701] and oxides [702, 703], as well as ferrimagnetic/ferromagnetic [704] and ferrimagnetic/ferrimagnetic [705] structures. The existence of positive bias has been suggested to arise from antiparallel coupling $(J < 0)^2$ between moments in the FM and pinned interfacial

²The case of antiparallel AFM–FM coupling (J < 0) is somewhat complicated. For "small" cooling fields the FM is aligned along $\boldsymbol{H}_{\text{set}}$ yet the pinning direction in the AFM is determined by the antiparallel exchange coupling with the ferromagnet. The combination of J < 0 and moments that are pinned antiparallel to $\boldsymbol{H}_{\text{set}}$ leads to a preferred FM alignment in the direction of $\boldsymbol{H}_{\text{set}}$, i.e., *negative* bias. In "large" cooling fields the Zeeman energy dominates and the moment directions in both the FM and AFM are aligned parallel to $\boldsymbol{H}_{\text{set}}$. When the cooling field is turned off, the moments in the AF remain frozen (parallel to $\boldsymbol{H}_{\text{set}}$) but the favored antiparallel exchange J < 0 leads to a rotation of the FM moments. The favored direction of the FM is now *antiparallel* to $\boldsymbol{H}_{\text{set}}$, which corresponds to *positive* exchange bias.

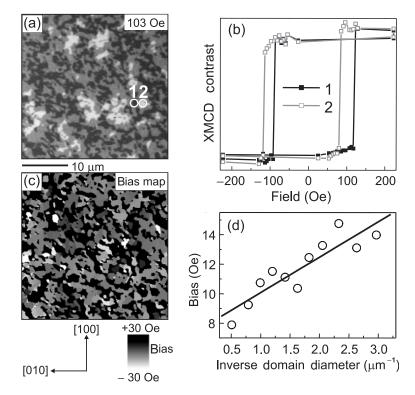


Fig. 13.21. (a) Co L-edge XMCD image of $Co(1.2nm)/LaFeO_3(40nm)/SrTiO_3(001)$, recorded with PEEM after the sample had been magnetized to 103 Oe in a field along [100] [695]. Note that half of the domains are aligned along [010] [107], and their remanent state remained unchanged (gray) after field application. (b) Local remanent magnetization loops of the two domains marked 1 and 2 in (a), showing opposite bias directions. (c) Map of the local bias field extracted from the local magnetization loops for the various domains in (a). As indicated underneath, the local bias fields have a maximum values of ± 30 Oe. Note that both positive and negative bias directions are present because no macroscopic bias was set. (d) Dependence of the bias field on the domain size, revealing an inverse linear relationship

moments in the AFM [701]. This has been verified by XMCD measurements for the Co/FeF_2 system [706] and supports our earlier point (5).

Finally, one can also investigate how the pinned spins are anchored in the AFM. This is done by rotating the FM spins with an external magnetic field and studying whether the AFM spins follow the rotation of the FM spins. This experiment was used earlier in Sect. 10.3.1 to illustrate the application of an octopole magnet and the results are shown schematically in Fig. 10.6. The real data are presented in reference [405]. They nicely demonstrate that in soft AFMs like single crystal NiO, a domain wall may be wound up in the AFM

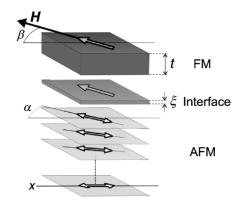


Fig. 13.22. Simple model for exchange bias. A ferromagnetic film (FM) of thickness t is separated by an interface of thickness ξ from a thick antiferromagnet (AFM) below. The uniaxial anisotropy of the AFM is along x. We assume parallel coupling between the uncompensated interfacial moments and the FM moments. The external magnetic field H is applied at an angle β with respect to x and the FM moments are aligned parallel to H. Near the interface the AFM axis is allowed to rotate and form a domain wall. The rotation of the AFM axis in the domain wall is given by $\alpha \leq \beta$

near the interface, which reduces the bias. The domain wall energy actually has two components, one due to the *exchange stiffness* of the spring, determined by the exchange coupling between the individual AFM spins, and another from the magnetocrystalline anisotropy of the bulk AFM, which determines the anchoring of the spins in the lattice. Indeed, XMLD studies show that for polycrystalline NiO, the winding up of a domain wall is suppressed, and the bias increases [707] in accord with point (6) from above.³

The simplest model that accounts for these experimental observations given by Mauri et al. [433]. The model is depicted in Fig. 13.22. In our model, the bulk uniaxial AFM is assumed to have a magnetocrystalline anisotropy favoring spin alignment along the x direction. In accordance with experimental observations we allow for an interface layer of thickness ξ (one to a few monolayers) which contains uncompensated spins. We assume an interfacial density of pinned uncompensated spins S_A , given by S_A/a^2 , where a^2 represents a unit area in the AFM, parallel to the interface. For simplicity we

³The suppression of a wound-up domain wall in polycrystalline NiO relative to single crystal NiO signifies a defect or strain "hardening" of the bulk AFM. Such a mechanism helps explain several empirical observations such as the larger bias typically observed for polycrystalline samples, the bias increase with decreasing grain size of the AFM [699] or with decreasing AFM domain size in single crystals [695], and the increased bias due to bulk "doping," e.g., by mixing MgO into NiO [708].

assume that all uncompensated spins are rigidly pinned to the AFM, as required for the occurrence of bias, and that they are aligned parallel to the AFM spin axis at the interface. The exchange coupling of the pinned interfacial spins to the FM is expressed by a Heisenberg-like coupling constant J, which in Fig. 13.22 is assumed to be positive. We assume a FM layer with thickness t and magnetization M and a magnetocrystalline anisotropy $K_{\rm F}$. Typically $K_{\rm F}$ can be assumed to be small so that, in the absence of an external magnetic field, the spins of the AFM and FM are aligned along the AFM easy axis x. If we now apply a strong magnetic field H at an angle β with respect to x, the FM moments will align along H. If the AFM is very hard, there will be no twist of the AFM axis and the uncompensated interfacial spins will remain aligned unidirectionally along x. This is the case of maximum bias. If the AFM is soft, an exchange spring will form in the AFM and the uncompensated interfacial spins will be aligned along the AFM axis at the interface, at an angle α with respect to x. Since the interfacial spins can now rotate in the field, the effective bias field will be reduced.

Mauri et al. showed that the total magnetic energy δ^* per unit interface area is given by four terms

$$\delta^* = \underbrace{E_w[1 - \cos\alpha]}_{\text{AFM wall}} + \underbrace{\frac{JS_A S_F}{a\,\xi} \left[1 - \cos(\alpha - \beta)\right]}_{\text{interface coupling}} + \underbrace{K_F \, t \, \sin^2\beta}_{\text{FM anis.}} + \underbrace{HMt \left[1 - \sin\beta\right]}_{\text{Zeeman energy}}.$$
(13.4)

The first term is the energy per unit surface area to wind up the domain wall in the AFM. The prefactor E_w corresponds to the energy of a 90° wall per unit surface area, and according to Zijlstra [709] it can be expressed in terms of the AFM exchange stiffness $A_{\rm A} = J_{\rm A}S_{\rm A}^2/a$ ($J_{\rm A}$ being the AFM exchange constant) and the AFM magnetocrystalline anisotropy energy $K_{\rm A}$ as (compare equation 11.35),

$$E_w = 2\sqrt{A_{\rm A}K_{\rm A}} \ . \tag{13.5}$$

The second term in (13.4) is the exchange coupling energy between the interfacial spins $S_{\rm A}$ (assumed to consist of uncompensated spins of the AFM) and the FM spins $S_{\rm F}$. It can be positive or negative depending on whether parallel (J > 0) or antiparallel (J < 0) coupling of the spins at the interface is favored. The third term is the intrinsic magnetocrystalline anisotropy energy in the FM with uniaxial anisotropy constant $K_{\rm F}$. We have assumed that the intrinsic FM easy axis is along x as in the AFM so that $K_{\rm F} > 0$. Finally, the last term is the Zeeman energy between the FM and the external field H. Note that all energies are per unit interface area.

If one measures the energy in units of the domain wall energy E_w , one obtains the simple formula

$$\delta = [1 - \cos \alpha] + \lambda_{\text{ex}} [1 - \cos(\alpha - \beta)] + \mu_{\text{ani}} \sin^2 \beta + \kappa [1 - \sin \beta]. \quad (13.6)$$

Magnetization curves (MCs) of the FM are calculated from (13.6) by finding the angles α_0 and β_0 for which δ is at a minimum. For $\lambda_{\text{ex}} = 0$, the ferromagnetic layer is decoupled and one finds the familiar Stoner and Wohlfarth MCs displayed in Fig. 11.15. But for $\lambda_{\text{ex}} \neq 0$, the MCs are modified by the AFM. The limiting case of negligible interfacial coupling, $\lambda_{\text{ex}} \ll 1$, is characterized by $\alpha \approx 0$ and (13.6) reduces to

$$\delta = \underbrace{\mu_{\text{ani}} \sin^2 \beta + \kappa \left[1 - \sin \beta\right]}_{\text{symmetric loop}} + \lambda_{\text{ex}} \left[1 - \cos \beta\right]. \tag{13.7}$$

The other limiting case of strong interfacial coupling, $\lambda_{ex} \gg 1$, is characterized by $(\alpha - \beta) \approx 0$ so that we have

$$\delta = \underbrace{\mu_{\text{ani}} \sin^2 \beta + \kappa \left[1 - \sin \beta\right]}_{\text{symmetric loop}} + \left[1 - \cos \beta\right]. \tag{13.8}$$

We have indicated in the above equations the part that corresponds to the energy of a uniaxial ferromagnet in an external field, described by the Stoner– Wohlfarth coherent rotation model and expressed by (11.37). The corresponding loop would be symmetric with a coercivity $2\mu_{\rm ani}$. The last terms in the two equations introduce an asymmetry in the loops since they differ for the field directions $\beta = 0^{\circ}$ and 180°. Apart from a loop shift, the model also predicts an intrinsic asymmetry of the loop shape in the reversal regions. This has been verified experimentally and the two magnetization reversals have been attributed to moment rotation and domain nucleation, respectively [710–712]. The loop shifts are due to the transferred exchange bias field $H_{\rm B}$, which is derived as

$$H_{\rm B} = -\frac{JS_{\rm A}S_{\rm F}}{a\,\xi\,t\,M} \quad \text{for} \quad \lambda_{\rm ex} \ll 1 \tag{13.9}$$

$$= -\frac{E_w}{Mt} \quad \text{for} \quad \lambda_{\text{ex}} \gg 1.$$
 (13.10)

For the last case of strong interfacial coupling, our simple model shows that the maximum bias field that one can obtain, no matter how strong the interfacial exchange coupling may be, is given by the energy it takes to form a domain wall in the antiferromagnet. This energy is calculated in much the same way as for a ferromagnet (11.36). This model is typically referred to as the *Mauri model* of exchange bias [433].

Today we know, however, that the first case $\lambda_{ex} \ll 1$ applies in most cases. Historically, the case $\lambda_{ex} \gg 1$ of weak interface coupling caused considerable consternation since one would expect that for an uncompensated AFM interface, a very large bias field should be obtainable. For example, we can estimate the bias field due to a monolayer of uncompensated interfacial spins from (13.9), using our knowledge of typical mean field values listed in Table 11.2. In particular, the exchange field expression in (13.9) is similar to that for the Weiss field in a ferromagnet given by (11.19). Since Weiss fields are of the order of 3×10^3 T, we readily see that we have a problem since the observed exchange bias fields are typically less than 0.1 T. For example, for a quick calculation we assume that due to the reduced interface coordination, Jis reduced to a typical value of 10 meV corresponding to a pair of atoms. We also assume typical spin values of $S_{\rm A} = S_{\rm B} = 1$, and an effective FM moment $a \xi t M \simeq 60 \mu_{\rm B}$. This corresponds to a Co film of t = 10 nm thickness with a magnetization of $M \simeq 1.5 \times 10^2 \mu_{\rm B}/{\rm nm}^3$ and values $a = \xi \simeq 0.2$ nm. With these numbers we obtain $H_{\rm B} \simeq 4$ T which is about two orders of magnitude too large.

The puzzle was resolved by the XMCD measurements of the fraction of pinned moments. Rather than being a full monolayer, the pinned moments amounted to only about 4% percent of a monolayer. Thus for the calculation of the field in (13.9), the effective interfacial moment density $S_A/(\xi a)$ is reduced by a factor of about 0.04. Thus the bias field is estimated to be of order 0.1 T, which is close to the value found for Co/MnIr in Fig. 13.20. Note that this value, derived under the $\lambda_{ex} \ll 1$ assumption, assumes that the interface coupling energy is smaller than the domain wall energy, so that no domain wall gets wound up in the AFM. If the two energies are comparable, then the bias field gets additionally weakened by the formation of a domain wall. This is the origin of the relatively weak bias field in NiO, which has a rather low magnetocrystalline anisotropy. As discussed earlier, field-dependent XMLD measurements for various forms (single crystal, epitaxial and polycrystalline, see footnote 3) of NiO directly reveal the correlation of the bias field and the domain wall energy given by (13.10) [405, 707].

We can summarize as follows. Relative to a AFM–FM system with a perfectly uncompensated AFM interface and a large AFM domain wall energy, the observed exchange bias field $H_{\rm B}$ in real system is reduced by about a factor of 100. This reduction is primarily due to the scarcity of pinned interfacial moments, with typical values of only a few percent of a monolayer. In addition, the formation of a domain wall further reduces the bias field value. The latter effect accounts for the difference in exchange bias between the best systems, e.g., Co/IrMn, and systems like Co/NiO where a domain wall in the AFM greatly reduces the achievable bias [405, 707].

13.4.4 Induced Magnetism in Paramagnets and Diamagnets

Another question related to the ferromagnetic interface is whether a metal that is not magnetic by itself can acquire a magnetic moment when in contact with a ferromagnet. Initially, theoretical work seemed to indicate [713, 714] that metallic magnetism can occur in very thin films even with elements that are not magnetic in three-dimensional samples. For instance, according to band structure calculations [715], V grown epitaxially on Ag(100) or Au(100) should have been ferromagnetic while bulk V is not. The magneto-optic Kerr effect [716] and spin-polarized photoemission [717] have been convenient tools

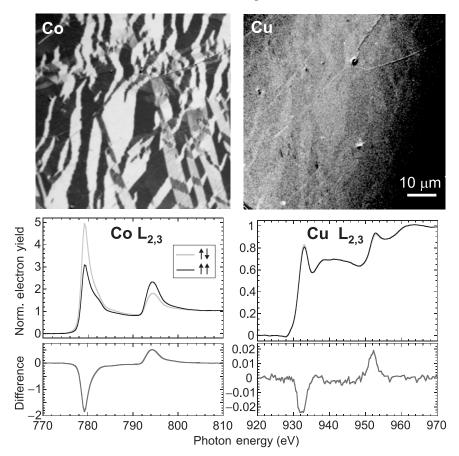


Fig. 13.23. Ferromagnetic domains in a Co layer (*left*) and XMCD signal of the Cu substrate atoms. The XMCD signal of Cu is not zero as the domains in Co appear also in the underlying Cu. The spin moment induced in the *d* shell of the interface Cu atoms by the proximity of ferromagnetic Co is $0.03\mu_{\rm B}$ per Cu atom [315].

to test such dramatic predictions, but no trustworthy evidence of ferromagnetism induced by the geometrical confinement has been found up to now.

However, elements that are not magnetic by themselves can acquire a magnetic moment when deposited on a magnetic surface. X-ray core level spectroscopy or spin-polarized Auger spectroscopy [718], as well as a number of other spin-polarized techniques, can answer the question of whether or not a magnetic moment is induced in the nonmagnetic element and also whether the magnetic moment at the interface of the substrate has been reduced by the deposition. XMCD combined with imaging in PEEM gives the most direct evidence that a magnetic moment is induced even in a noble metal by the proximity of a ferromagnet. Figure 13.23 shows that the Cu atoms below a

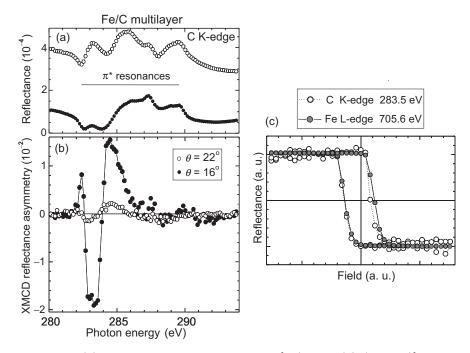


Fig. 13.24. (a) C K-edge reflectance spectra of a $[Fe(2.55 \text{ nm})/C(0.55 \text{ nm})]_{100}$ multilayer at two incidence angles θ from the surface [719]. (b) XMCD asymmetry ratio $A = (R^+ - R^-)/(R^+ + R^-)$ obtained from the reflectances R^{\pm} measured with positive and negative photon spin at the two X-ray incidence angles. (c) Element-specific magnetization loops for Fe and C atoms recorded at the indicated photon energies by monitoring the reflectance at a fixed X-ray circular polarization

ferromagnetic domain of Co acquire a magnetic moment. It turns out that this moment is a spin moment parallel to the one of Co and amounts to $0.03\mu_{\rm B}$ per interface Cu atom [315]. The Cu moment nearly disappears by the second layer away from the interface.

Another example of induced ferromagnetism is shown in Fig. 13.24. In this case, XMCD measurements for Fe/C multilayers were performed in a specular reflectance geometry at both the C K-edge and Fe L-edge [719]. The angleof-incidence dependent reflectance spectra, the dichroic asymmetry ratio and the element-specific magnetization loops are shown in three separate panels. Clearly, C is seen to be magnetic and Mertins et al. [719] estimate a magnetic moment of about $0.05\mu_{\rm B}$ per C atom. The moment is due to hybridization of C 2p and Fe 3d orbitals at the interface.

13.4.5 Coupling of Two Ferromagnets across a Nonmagnetic Spacer Layer

Layered metallic materials have become important in magnetism. For example, they can be used to enhance the surface anisotropy as illustrated in Fig. 11.11, to inject spin-polarized electrons from one ferromagnet into another, and to generate devices exhibiting giant magnetoresistance. Before discussing the latter phenomena, we investigate the equilibrium magnetic exchange coupling that exists between two ferromagnetic layers separated by a nonmagnetic spacer layer. As mentioned in Sect. 7.8, this coupling oscillates periodically between parallel (P) and antiparallel (AP) alignment of the magnetization in the two layers as the thickness of the nonmagnetic spacer layer is varied. The coupling periodicity is correlated with the existence of standing electron waves, often referred to as quantum well (QW) states in the nonmagnetic interlayer [318,720]. The QW states and their connection to magnetism have been detected by inverse photoemission [318,720] and by spin-polarized photoemission spectroscopy and other related methods [250, 274, 313, 317, 721, 722].

There is a close analogy between a standing electromagnetic wave confined by two reflecting surfaces, usually referred to as a Fabry-Pérot interferometer, and an electron captured in a square potential well, as reviewed by Himpsel et al. [250]. With electrons, potential wells have been realized in metallic thin films consisting of Au, Ag, or Cu deposited epitaxially on a metallic substrate such as Fe or Co and terminated by the vacuum interface or covered again epitaxially with some layers of the same magnetic metal. The spin-dependent band gaps at the boundary to the ferromagnetic metal generate a potential well that confines one specific spin state of the electrons. Figure 13.11 is an example of spin-dependent reflection at an Fe(001)-vacuum interface at elevated electron energies. In contrast to an optical Fabry–Pérot interferometer, electrons are strongly absorbed by the medium and the reflection at the boundary of the well is never as ideal as for an optical mirror. Yet it is experimentally confirmed that standing waves do exist for one spin state, as the spin polarization of QW states has been directly verified with spin-polarized electron spectroscopy [274, 313] and by measuring the spin asymmetry of a spin-polarized electron beam in specular reflection [721, 723].

The QW states induce a peak in the density of states at a particular wavevector $k = 2\pi/\Lambda_{\rm e}$ perpendicular to the film surface, where $\Lambda_{\rm e}$ is the wavelength of the standing electron wave. In the case that the nonmagnetic spacer layer is sandwiched between two ferromagnetic layers, the condition for a standing spin-polarized wave depends on the relative magnetization direction in the two layers. The energies $E_{\rm P}$ and $E_{\rm AP}$ connected with the density of states D(E)for parallel (P) and antiparallel (AP) alignment of the ferromagnetic layers, are responsible for the ferromagnetic coupling mediated by the nonmagnetic spacer layer. The energy density 2J of this coupling is given by:

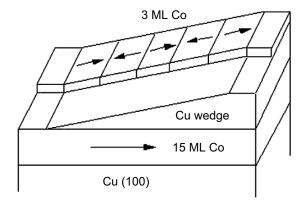


Fig. 13.25. Illustration of a sample consisting of two ferromagnetic Co layers separated by a wedge of Cu. The magnetization M in the top Co layer alternates in its direction with respect to M in the bottom Co layer as the Cu wedge changes thickness due to the presence of quantum well states. The blank part of the Cu wedge is used to determine the thickness of the wedge, while the direction of M in the top layer is measured with XMCD [722]

$$2J = E_{\rm P} - E_{\rm AP} = \int_{-\infty}^{E_{\rm F}} \left\{ D_{\rm P}(E) - D_{\rm AP}(E) \right\} E \,\mathrm{d}E, \qquad (13.11)$$

where $E_{\rm F}$ is the Fermi energy. The energy 2*J* is generated by the additional density of states introduced in one spin state by the spin-polarized QW state of the interlayer. For instance, with a Cu film sandwiched between Co films, the minority band gap of Co produces a potential well for the minority *s*, *p* electrons at $E_{\rm F}$ in the Cu interlayer, as can be seen from the respective densities of states in Fig. 12.1.

The magnetic coupling energy 2J may also be viewed as an exchange field $H_{\rm ex} = J/M_2$ transferred from layer 1 with magnetization M_1 to layer 2 with magnetization M_2 . The field $H_{\rm ex}$ has a typical value of 10^4 A m⁻¹ but can be as small as 10^2 A m⁻¹, depending on the structural quality and exact thickness of the spacer layer. The coupling, with dozens of oscillations of $H_{\rm ex}$ from positive to negative values, is detectable over ~ 100 atomic layers of the spacer layer. The range over which the coupling exists is given by the electron mean free path in the spacer layer that is it depends on temperature and on defect concentration.

The technologically most important feature of periodic exchange coupling is that the parallel alignment of two ferromagnetic films is connected with a "giant" drop of the electrical resistivity of the trilayer, usually referred to as GMR (giant magnetoresistance) and discussed in Sect. 14.1.4. In the famous GMR spin valve sensor shown in Fig. 14.3, the switching from an existing alignment to the opposite alignment of the layers is induced by an external field $H > H_{\text{ex}}$.

To calculate the thickness of the spacer layer at which the standing wave occurs, one has to examine the condition for a standing wave given by the Bohr–Sommerfeld quantization rule,

$$2k_{\rm e}(E)Nt + \Phi(E) = 2n\pi . \qquad (13.12)$$

Here the electron wave vector $k_e(E)$ depends on the electron binding energy E, N is the film thickness expressed in numbers of atomic layers, t is the thickness of one monolayer of atoms, Φ the phase shift upon reflection at the boundaries of the potential well, and n is the number of half waves that fit into the well. We encounter the familiar problem of the eigenmodes of a vibrating string or a particle in a box.

In the case of Co, the minority spin band gap provides the confinement of the minority spin Cu electrons to form the QW states. Band structure calculations indicate that the upper $(E_{\rm U})$ and lower $(E_{\rm L})$ energies of the potential well along the (100) direction of fcc Co are $E_{\rm U} = -0.58$ eV and $E_{\rm L} = -3.9$ eV, respectively. However, we know already from Sect. 12.4 that the calculated exchange splitting is usually too large, so these numbers have to be considered as an estimate. Additionally, hybridization of the Co wave functions with those of Cu is certainly present at the interface, as can be seen from the interfacial spin moments of the Cu atoms revealed in Fig. 13.23. This may further complicate the actual features of the potential well. However, according to Qiu and Smith [722], the experiments can be interpreted with the simple approach given below.

A convenient ansatz for the energy dependent phase shift $\Phi(E)$ of the electron wave function upon reflection on the ferromagnetic potential barrier is

$$\Phi(E) = 2 \arcsin \sqrt{\frac{E - E_{\rm L}}{E_{\rm U} - E_{\rm L}}} - \pi \qquad (13.13)$$

Thus the phase evolves from 0 to $-\pi$ as E is varied from the top of the potential well $E_{\rm U}$ to the bottom of the well $E_{\rm L}$. The variation of the phase shift across a band gap is related to the fact that at the completion of the band at the lower end of the gap, the electron waves are standing waves with the energetically most unfavorable location of the electrons, that is between the positively charged metal-ion cores. At the start of a new band, the electrons are localized as well, but now in the energetically most favorable position on top of the metal ions. Hence a phase shift must occur of the form assumed in (13.13) as the energy varies across the band gap. Equations (13.13) and (13.12) describe the QW states in a nonmagnetic spacer layer and the resulting P/AP coupling of the magnetization as it depends on the thickness of the spacer layer.

Still, one has to insert the relevant wave vector $k_{\rm e}$. It is ambiguous, because one can always add or subtract multiples of the lattice vector $k_{\rm BZ}$ to the electron momentum $k_{\rm e}(E)$. Angle- and energy-resolved photoemission spectroscopy on QW states turns out to be the most accurate way to measure the ratio $k(E_{\rm F})/k_{\rm BZ}$ [724], where $k(E_{\rm F})$ and $k_{\rm BZ}$ are the electron wave-vectors at the Fermi energy and at the Brillouin zone boundary, respectively. The experiments show that $k_{\rm e} = k_{\rm BZ} - k_{\rm e}(E)$. In the case of the Co/Cu/Co trilayer, one finds QW states with a periodicity of 5.88 and 2.67 monolayers of Cu. These two periods are related to $k_{\rm BZ}$ at the neck and the belly of the Cu Brillouin zone. The magnetic interlayer coupling is found to be a superposition of these two oscillation periodicities. A more complete discussion can be found in the review paper by Qiu and Smith [722].

In the pioneering imaging work on periodic exchange coupling by Unguris, Celotta, and Pierce [317], Fe layers were coupled over a wedge-shaped interlayer of Cr. The periodic changes of the magnetization in the top Fe layer with the thickness of the underlying Cr layer were imaged by scanning electron microscopy with spin polarization analysis (SEMPA), and the spectacular image arising from the periodic exchange coupling is shown in Fig. 1.9. A long and a short period of the oscillating exchange coupling were found in this case as well. The case of Cr which is the only itinerant antiferromagnet is special. It orders ferromagnetically within each (100)-layer, but the magnetization reverses with each additional layer that is added. This is due to a standing spin density wave with a wave vector $k(E_{\rm F})$ that is only 4% different from the lattice wave vector $k_{\rm BZ}$. One says that $k(E_{\rm F})$ is "nesting" in the lattice. The short period oscillations of the magnetization occurring with each added Cr layer and hence the antiferromagnetism of Cr is due to this spin density wave. The top and bottom layer of the Cr couple ferromagnetically to Fe at the interface. The top Fe layer thus changes the magnetization direction with each additional Cr layer, mirroring the direction of the Cr spins in the last layer of Cr(100). The slight mismatch between the spin density wave and the Cr lattice vector k_{BZ} leads to a phase slip and hence to an extraordinary change in the sign of the exchange coupling after 21–24 Cr layers.

The theory developed to understand the coupling of localized spins embedded in a metallic environment is usually referred to as Ruderman-Kittel-Kasuya–Yoshida (RKKY) interaction, which is discussed in Sect. 7.8 and illustrated in Fig. 7.34. The scattering of the conduction electrons on magnetic impurities is spin-dependent [725]. It induces a spin polarization in the electron gas that oscillates in sign and decays very fast in amplitude as the distance to the magnetic impurity increases. Through the RKKY interaction, dilute magnetic ions in a nonmagnetic metal may be exchange coupled at low temperatures. The coupling manifests itself by a reduction of the electrical resistivity known as the Kondo effect. This is very much in analogy to the coupling of magnetic layers via nonmagnetic spacer layers. It is therefore not astonishing that RKKY theory can also explain the periodic exchange coupling [726–728]. Yet RKKY theory, although developed in the mid 1950s, had not predicted the oscillatory exchange coupling between magnetic films. This was found more or less by chance in experiments after epitaxial metallic layers of great quality could be made.

Electron and Spin Transport

In this chapter we shall take a look at electron and spin transport across interfaces. In the first major section we discuss fundamental spin-dependent phenomena that occur during current flow from a ferromagnet to a nonmagnet and vice versa. We shall see that such flow leads to the build-up of a spin-dependent interface voltage which will be shown to directly lead to the important phenomenon of *giant magneto-resistance*.

In the second major section we discuss the injection of spin polarized currents into a ferromagnet, so-called *spin injection*. In particular, we discuss the use of spin injection to directly switch the magnetization in a nanoscale magnetic structure. This interesting phenomenon, which is based on the use of the short-range and strong exchange interaction to provide the energy and torque for switching, differs from the conventional switching method which uses long-range Oersted fields produced by current carrying wires or coils.

In the final two sections we touch on spin-dependent phenomena in semiconductors and consider the requirements for building a spin current amplifier, whose invention would revolutionize the whole field of spin dependent phenomena.

14.1 Currents Across Interfaces Between a Ferromagnet and a Nonmagnet

In this section we consider the case of an electron current flowing across an interface between a ferromagnet and a non-magnet. We assume that the current is steady, i.e., that it does not depend on time, and derive basic consequences which arise from the fact that such a current is necessarily spin polarized.

 $\mathbf{14}$

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14.1.1 The Spin Accumulation Voltage in a Transparent Metallic Contact

In the discussion of transport involving ferromagnets, one necessarily has to deal with the flow of both charge and spin. In its quantitative description it is convenient to use a thermodynamic quantity, the *chemical potential*, introduced in Sect. 12.5.1. If a system contains more than one species of particles, there is a separate chemical potential associated with each species, defined as the change in energy when the number of particles of that species is increased by one. The two types of species in a ferromagnetic metal are the majority and the minority spin electrons which can be distinguished because spin flips are very rare.

The *spin dependent chemical potential* of the majority (minority) electrons is the change in energy associated with the addition of one majority (minority) electron.

For a quantitative treatment [729], we assume that a ferromagnetic metal (F) is in contact with a nonmagnetic metal (N), and we take x to be the direction of current (positive charge) flow, *perpendicular to the interface*. If there is no electric current flowing along x, the Fermi-levels (see footnote 5 in Chap. 12) in the two metals will adjust to the same value, i.e., the chemical potential μ_0 will be constant across the interface. Also, the chemical potential for up spins will be equal to the one for down spins $\mu^{\uparrow} = \mu^{\downarrow}$, and $\mu_0 = (\mu^{\uparrow} + \mu^{\downarrow})/2$.

If now a current of density j flows from F to N along the x direction, as shown on the left side of Fig. 14.1, the validity of Ohm's law, given by (12.10), implies,

$$\frac{\partial \mu_0}{\partial x} = -\frac{e}{\sigma}j, \qquad (14.1)$$

where -e is the electron charge and σ the total conductivity. The total conductivity is determined by the conductivities of both spin-up electrons, σ^{\uparrow} , and spin-down electrons, σ^{\downarrow} , and according to the two current model, we simply have $\sigma = \sigma^{\uparrow} + \sigma^{\downarrow}$. As discussed in Sect. 12.5.2, transitions from one conductivity channel to the other require spin flips, and they are sufficiently rare that the resistivity due to crossover scattering from one spin channel to the other can be neglected at low temperatures. This is a good approximation even at room temperature since the spin flip length is about ten times longer than the (spin averaged) electron mean free path [580, 730]. It is then intuitively clear that due to the two current model interesting spin dependent phenomena must develop at the interface between a ferromagnet, characterized by preferential conduction in one spin channel, and a non-magnetic metal with equal conduction for both spins. This is indeed the case and we shall discuss the details now.

14.1 Currents Across Interfaces Between a Ferromagnet and a Nonmagnet 639

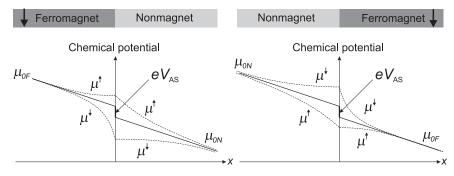


Fig. 14.1. The chemical potentials μ^{\uparrow} (majority spins) and μ^{\downarrow} at the interfaces between a ferromagnet F and a nonmagnetic metal N, with a constant electric current density flowing in the x direction, assuming $\alpha_{\rm F} > 0.5$. The magnetization direction of the ferromagnet, which is in the direction of the minority spins, is shown by an arrow. $\mu_{\rm 0F}$ and $\mu_{\rm 0N}$ are the respective spin averaged chemical potentials in F and N. The spin accumulation potential is given by $eV_{\rm AS} = \mu_{\rm 0F}(0) - \mu_{\rm 0N}(0)$. As discussed in Sect. 14.1.6 one finds $V_{\rm AS} \approx 1$ mV. The decay of the spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ with x away from the interface is discussed in Sect. 14.1.3

Charge neutrality leads to j = const across the interface. If we ignore the existence of spins, the chemical potential μ_0 is a straight line with a change in slope at the interface due to the change in σ , since $\sigma_N \neq \sigma_F$. This may be directly read from (14.1). However, this is not what happens if we consider the different behavior of the two spin states in the ferromagnetic metal F. The two current model tells us that in F we will have different conductivities for the spin-up and spin-down channels. We define

$$\sigma_{\rm F}^{\uparrow} = \alpha_{\rm F} \, \sigma_{\rm F} \quad \text{and} \quad \sigma_{\rm F}^{\downarrow} = (1 - \alpha_{\rm F}) \, \sigma_{\rm F} \, .$$
 (14.2)

Here the dimensionless factor $0 \le \alpha_{\rm F} \le 1$ accounts for the asymmetry of conduction in F. In a bulk ferromagnet, the minority spin channel has the lower conductivity and by denoting the majority spins as up spins one would have $\alpha_{\rm F} > 0.5$. Our α -dependent formulation is valid in general. For example, the case $\alpha = 0.5$ describes a nonmagnetic metal N, where there is no asymmetric conduction for the two spin states.

The special case $\alpha_{\rm F} = 1$ corresponds to a half metallic ferromagnet (HMF) in which, according to our definition of $\alpha_{\rm F}$, only the spin-up state is present at $E_{\rm F}$ so that electrical conduction occurs in one spin channel, only. Examples of HMFs are La_{0.7}Sr_{0.3}MnO₃ [731] and some ferromagnetic Heusler alloys, e.g., NiMnSb [732, 733]. In such materials the half-metallicity is typically due to the filling of the *d*-bands, and they are usually devoid of weakly polarized s-pconduction electrons. This has been discussed in Sect. 7.7.4 for the example of the HMF magnetite, Fe₃O₄, where the s-p electrons are bound by the oxygen atoms. Note, however, that the half-metallic behavior may be reduced or lost at surfaces [733], and theory seems to indicate the possibility that half-metallicity is also lost at interfaces in multilayer structures [734].

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The asymmetry of the conduction leads to asymmetric currents. We have in general

$$j^{\uparrow} = \beta j \text{ and } j^{\downarrow} = (1 - \beta) j ,$$
 (14.3)

and specifically $j^{\uparrow} = \beta_{\rm F} j$ and $j^{\downarrow} = (1 - \beta_{\rm F}) j$ in F and $j^{\uparrow} = \beta_{\rm N} j$ and $j^{\downarrow} = (1 - \beta_{\rm N}) j$ in N. Because $j = j^{\uparrow} + j^{\downarrow}$, the asymmetry parameter β for the current lies in the range $0 \le \beta \le 1$. The spin polarization P of the current is given by

$$P = \frac{j^{\uparrow} - j^{\downarrow}}{j^{\uparrow} + j^{\downarrow}} = 2\beta - 1.$$
(14.4)

As the spin polarized current from F ($\beta_{\rm F} \neq 0.5$) enters N, we will also have $\beta_{\rm N} \neq 0.5$ and $P \neq 0$ close to the interface. Because transitions between the two spin channels are rare in nonmagnetic metals it will take time or distance from the interface for the current in N to equilibrate to the value $\beta_{\rm N} = 0.5$. This fact causes a drop in voltage at the interface, called the *spin accumulation voltage*, $V_{\rm AS}$. Its value can be derived as follows. From Ohm's law for the two spin channels

$$j^{\uparrow} = -\frac{\sigma^{\uparrow}}{e} \frac{\partial \mu^{\uparrow}}{\partial x} \qquad j^{\downarrow} = -\frac{\sigma^{\downarrow}}{e} \frac{\partial \mu^{\downarrow}}{\partial x}, \qquad (14.5)$$

one obtains,

$$\frac{\partial\mu_0}{\partial x} = -\frac{e}{\sigma}j = -\frac{e}{\sigma}(j^{\uparrow} + j^{\downarrow}) = \alpha \frac{\partial\mu^{\uparrow}}{\partial x} + (1 - \alpha)\frac{\partial\mu^{\downarrow}}{\partial x} .$$
(14.6)

Integration of (14.6) yields $\mu_0 = \alpha \mu^{\uparrow} + (1 - \alpha)\mu^{\downarrow} + \text{const}$, where const = 0 because as $x \to \infty$ we have $\mu_0(x) = (\mu^{\uparrow} + \mu^{\downarrow})/2$. The spin averaged chemical potentials $\mu_{0\text{F}}$ of the ferromagnet (F) and $\mu_{0\text{N}}$ of the nonmagnetic metal (N) are then given by,

$$\mu_{0\mathrm{F}} = \alpha_{\mathrm{F}}\mu^{\uparrow} + (1 - \alpha_{\mathrm{F}})\mu^{\downarrow} \tag{14.7}$$

and

$$\mu_{0\mathrm{N}} = \frac{1}{2} \left(\mu^{\uparrow} + \mu^{\downarrow} \right) . \tag{14.8}$$

The last equation explicitly shows our assumption that $\alpha_{\rm N} = 1/2$.

At the interface, at x = 0, the chemical potentials μ^{\uparrow} and μ^{\downarrow} must be continuous since otherwise a force would act on the spins. One assumes that such a force does not exist. While the chemical potential μ_0 must be the average of μ^{\uparrow} and μ^{\downarrow} in N, it is a weighted average in F. Due to this, there must be a drop $\Delta \mu_0(0) = eV_{\rm AS}$ at the interface. This drop is the origin of the *spin accumulation voltage* $V_{\rm AS}$, and is given by

$$eV_{\rm AS} = \mu_{0\rm F}(0) - \mu_{0\rm N}(0) = \alpha_{\rm F}\mu^{\uparrow}(0) + (1 - \alpha_{\rm F})\mu^{\downarrow}(0) - \frac{1}{2} \left[\mu^{\uparrow}(0) + \mu^{\downarrow}(0)\right]$$
$$= \left[\alpha_{\rm F} - \frac{1}{2}\right] \left[\mu^{\uparrow}(0) - \mu^{\downarrow}(0)\right] . \tag{14.9}$$

The case for current flow from F to N is illustrated on the left side of Fig. 14.1, assuming $\alpha_{\rm F} > 0.5$. The reverse situation, current flow from N to F, is shown on the right side of the figure. When the two spin channels conduct equally well, that is when $\alpha_{\rm F} = 0.5$, there is no drop of the chemical potential and the spin accumulation voltage is zero, $V_{\rm AS} = 0$.

The spin accumulation voltage V_{AS} is the jump in the spin averaged chemical potentials that develops at a F–N interface. It exists if a current, that consists of separate spin-up and spin-down channels, flows across an interface between two metals with different conductivities for the channels.

The actual difference in the chemical potentials for the two spin states, or *spin voltage*, reflects the difference in the number of electrons in the two spin channels. If $\mu^{\uparrow} > \mu^{\downarrow}$ there are more up spins, and vice versa. Figure 14.1 shows that the signs of the spin accumulation and spin voltages at the F/N interface reverse with the direction of current flow. As shown in Fig. 14.1, the spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ decays with the distance x from the interface. This will be discussed in Sect. 14.1.3.

A *spin voltage* is the difference in spin-up and spin-down chemical potentials and corresponds to an unequal number of up and down spins. At a F/N interface, the *signs* of the spin voltage and spin accumulation voltage invert with the direction of current flow.

The essence of the spin accumulation voltage $V_{\rm AS}$ lies in the different conductivities associated with the two current channels. According to the Drude relation (12.13), the conductivities $\sigma = n e b$ are determined not solely by the spin polarizations of the electrons with densities n^{\uparrow} and n^{\downarrow} at the Fermisurface but also by the electron mobilities b^{\uparrow} and b^{\downarrow} which are governed by the spin selective scattering times $\tau_{\rm e}^{\uparrow} = \tau_{\rm e}^{+}$ and $\tau_{\rm e}^{\downarrow} = \tau_{\rm e}^{-}$, discussed in Sects. 8.6.2 and 12.6.1. The latter quantities are in turn related to the spin-dependent electron mean free paths $\lambda_{\rm e}^{\pm}$ according to $\tau_{\rm e}^{\pm} = \lambda_{\rm e}^{\pm}/v$, where v is the group velocity of the electrons. In our description above, we have lumped the various spin dependent contributions into a single parameter $\alpha_{\rm F}$, so that

$$\sigma_{\rm F}^{\uparrow} = n^{\uparrow} e \, b^{\uparrow} = \frac{n^{\uparrow} e^2 \tau_{\rm e}^{\uparrow}}{m_{\rm e}} = \alpha_{\rm F} \sigma_{\rm F} \quad \text{and} \quad \sigma_{\rm F}^{\downarrow} = n^{\downarrow} e \, b^{\downarrow} = \frac{n^{\downarrow} e^2 \tau_{\rm e}^{\downarrow}}{m_{\rm e}} = (1 - \alpha_{\rm F}) \sigma_{\rm F} .$$
(14.10)

The buildup of a voltage at the interface of two metals is quite a general phenomenon whenever the current flows in two separate channels with different conductivities. This effect has been known for some time. For example, in superconductors two separate channels of super-conducting Cooper pairs and normal electrons might be present. In this case, a voltage will develop at a contact to a normal metal [729].

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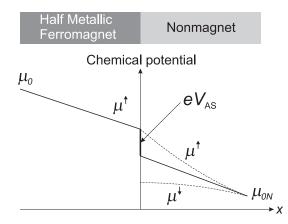


Fig. 14.2. Chemical potential near the interface between a HMF with only the spin-up channel and a paramagnet. Because μ^{\downarrow} and spin equilibration do not exist, μ^{\uparrow} is a straight line in the HMF. As discussed in the text, μ^{\downarrow} must have a horizontal tangent at $x \to 0$ on the N side

The largest spin accumulation voltage occurs at the interface between a HMF and N. In a HMF, only one spin channel, say the up-channel, conducts. In this case μ^{\downarrow} is not defined and spin equilibration at the interface is not necessary in the HMF. Therefore, $\mu_0(x) = \mu^{\uparrow}(x)$ is a straight line in the HMF. The situation is different in N. Because we have $j^{\downarrow} = 0$ at the interface, we have $\partial \mu^{\downarrow}/\partial x = 0$ at x = 0, that is, on approaching the interface from N, the quantity $\mu^{\downarrow}(x \to 0)$ must have a horizontal tangent at x = 0. The case for the HMF/N interface is illustrated in Fig. 14.2.

14.1.2 The Diffusion Equation for the Spins

In Figs. 14.1 and 14.2 we have indicated that the spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ decreases away from the interface, but so far we have not explained this fact. The *quantitative* decrease from the interface is calculated from the spin diffusion equation, which we shall derive now. It will allow us to more quantitatively define the equilibration times of the spin dependent Fermi-levels in N and F.

The differential equation governing the currents in the two spin channels is known as the *spin diffusion equation*. It was first established to understand the spreading of the spin polarization of nuclei studied by nuclear magnetic resonance, well before its application to interfaces of ferromagnets. The equation may be obtained by investigating the dependence of the density of surplus spins $n^{\uparrow}(x,t) - n^{\downarrow}(x,t)$ produced by the current as a function of the distance x from the interface. Denoting the density of atoms as $n_{\rm A}$ and the density of conduction states per atom per unit energy as D(E) one has, 14.1 Currents Across Interfaces Between a Ferromagnet and a Nonmagnet 643

$$n^{\uparrow}(x,t) - n^{\downarrow}(x,t) = n_{\rm A} \int_{\mu^{\downarrow}}^{\mu^{\uparrow}} D(E) \,\mathrm{d}E \simeq n_{\rm A} D(\bar{E}) \left[\mu^{\uparrow}(x,t) - \mu^{\downarrow}(x,t) \right] \,.$$
(14.11)

Here \overline{E} is the averaged spin-up and spin-down chemical potential or Fermi energy. In practical cases, $(\mu^{\uparrow} - \mu^{\downarrow}) \ll k_{\rm B}T$. Given a volume element of length Δx and cross-sectional area S, we have to know the electric currents flowing into the element and out of it. Fick's law says that a particle current of density dn/dt flowing *into* the volume element through the area S is given by

$$S\frac{\mathrm{d}n}{\mathrm{d}t} = S\mathcal{D}\frac{\mathrm{d}n}{\mathrm{d}x}|_x , \qquad (14.12)$$

where \mathcal{D} is the diffusion constant with dimension (area/time). The current flowing *out of* the volume element is

$$S\frac{\mathrm{d}n}{\mathrm{d}t} = S\mathcal{D}\frac{\mathrm{d}n}{\mathrm{d}x}|_{x+\Delta x} \ . \tag{14.13}$$

In our case the difference between these two currents must be equal to the equilibration rate in the spin channels $S n(x,t)/\tau_{se}$ as there can be no pile up of electrons if the current is stationary, i.e., if S j = const. Here τ_{se} is the *spin equilibration time* in the metal, also called *spin diffusion time*. This yields the *spin diffusion equation*,

$$\frac{n(x,t)}{\tau_{\rm se}} = \lim_{\Delta x \to 0} \frac{1}{\Delta x} \mathcal{D}\left[\frac{\mathrm{d}n}{\mathrm{d}x}|_{x+\Delta x} - \frac{\mathrm{d}n}{\mathrm{d}x}|_x\right] = \mathcal{D}\frac{\partial^2 n}{\partial x^2}.$$
 (14.14)

In the literature, τ_{se} is also called *spin-flip time* since the distance over which the two Fermi-levels equilibrate is related to processes that involve transitions between opposite spin states. These processes will be discussed in more detail in Sect. 14.1.3 below.

By use of (14.11), one obtains from (14.14) the desired spin diffusion equation in terms of the chemical potentials

$$\frac{\mu^{\uparrow} - \mu^{\downarrow}}{\tau_{\rm se}} = \mathcal{D} \frac{\mathrm{d}^2(\mu^{\uparrow} - \mu^{\downarrow})}{\mathrm{d}x^2} \quad (14.15)$$

The steady-state solution is

$$\mu^{\uparrow} - \mu^{\downarrow} = \left[\mu^{\uparrow}(0) - \mu^{\downarrow}(0)\right] e^{-x/\Lambda} \qquad (14.16)$$

where the characteristic exponential decay length, Λ , called the *spin diffusion* length or *spin equilibration length*, is given by

$$\Lambda = \sqrt{\mathcal{D}\,\tau_{\rm se}} \,\,. \tag{14.17}$$

The decrease of $\mu^{\uparrow} - \mu^{\downarrow}$ with the distance from the interface is determined by the characteristic equilibration time τ_{se} and equilibration distance Λ of

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the spins, linked by the diffusion constant $\mathcal{D} = \frac{1}{3}v_F\lambda_e$. Here v_F is the Fermivelocity, and λ_e the electron mean free path. Typical values for v_F and λ_e in metals are given by Ashcroft and Mermin [219]. With the values in Table 12.4 we obtain $\mathcal{D} = 2.6 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$ for Cu and $\mathcal{D} = 2.1 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ for Fe. In the nonmagnet we have for the spin averaged diffusion constant $\mathcal{D} = \mathcal{D}^{\uparrow} = \mathcal{D}^{\downarrow}$, but in the ferromagnet we have $\mathcal{D} = \alpha_F \mathcal{D}^{\uparrow} + (1 - \alpha_F) \mathcal{D}^{\downarrow}$.

The spin-dependent chemical potentials μ^{\uparrow} and μ^{\downarrow} equilibrate away from the interface over a characteristic spin equilibration length Λ and equilibration time τ_{se} .

14.1.3 Spin Equilibration Processes, Distances and Times

Because of the central role of the spin equilibration time τ_{se} and length Λ we need to take a closer look at the processes that determine them.

Nonmagnetic Metals

In N, τ_{se} is dominated by spin de-phasing processes due to spin-orbit coupling in Coulomb scattering processes on the atoms in the sample, as discussed previously in Sect. 8.6.2 in conjunction with the ballistic transmission of spin polarized electrons. Hence, in N, $\tau_{se} = \tau_2$ is related to the transverse relaxation time T_2 in magnetic resonance [735, 736]. During their different diffusive paths through the sample the individual electron spins will experience different effective magnetic fields and hence spin precessions, leading to spin randomization with, on average, equal spin up and down probabilities along any chosen quantization axis. During these scattering processes the angular momentum is directly transferred to the atoms in the lattice, as discussed in Sect. 8.6.2. The scattering may be enhanced by addition of heavy atoms such as Pt with an increased spin-obit interaction or by addition of paramagnetic impurities which lead to additional exchange scattering. Whatever the specific mechanism of the spin transitions may be, it will decrease the spin polarization of the electrons injected into N, and the spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ will tend to zero with increasing distance x from the interface.

As discussed in Sect. 14.1.5, the most reliable values for $\tau_{\rm se}$ in nonmagnetic metals are available for Cu and Al. For Cu, Jedema and collaborators find $\Lambda_{\rm N} = 1,000$ nm at 4.2 K and 350 nm at room temperature (RT) [737], while in Al the values are $\Lambda_{\rm N} = 650$ nm at 4.2 K and 350 nm at RT [738]. We have summarized various transport parameters for Cu at room temperature in Table 14.1. If we compare the spin dependent scattering lifetime $\tau_{\rm se}$ with the electron scattering life time $\tau_{\rm e}$, we find that in Cu at room temperature $\tau_{\rm se} \sim 200 \tau_{\rm e}$ so that the spin polarization disappears on average after more than 200 spin-conserving scattering events.

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Table 14.1. Transport parameters describing conduction in Cu and Co at 300 K

	$v_{\rm F} ^{\rm a} [{\rm m s}^{-1}]$	$\lambda_{\rm e}$ ^a [nm]	$\mathcal{D} = \frac{1}{3} v_{\rm F} \lambda_{\rm e} \left[{\rm m}^2 {\rm s}^{-1} \right]$	$\tau_{\rm e} ^{\rm a}$ [fs]	$\Lambda~[\rm{nm}]$	$\tau_{\rm se} = \Lambda^2 / \mathcal{D} \; [{\rm ps}]$
Cu	1.8×10^6	44	2.6×10^{-2}	25	$350^{\rm b}$	4.7
Co	1.8×10^6	5.8	3.5×10^{-3}	3.2	$38^{\rm c}$	0.4

^a From Table 12.4 for Cu. For Co we used the values $n = 18.1 \times 10^{28} \text{m}^{-3}$, $R = 6.2 \times 10^{-8} \Omega \text{m}$, and $E_{\text{F}} = 8.7 \text{eV}$

^b Ref. [737]

^c Ref. [741].

Ferromagnetic Metals

In a FM, we have to distinguish the spin polarization of the 3d electrons generating the magnetization from the spin polarization of the current due to the motion of the s electrons. As pointed out in Sect. 12.5, models for the electrical conduction in transition metals need to be based on the transport and scattering mechanism of the s-electrons, and the resistivity is in fact dominated by spin-conserving scattering of the s electrons on the hole-states in the 3d-shell. The spin polarization P of the electron current is given by (14.4), and through (14.5) and (12.13) is determined by the number of majority spins n^{\uparrow} and minority spins n^{\downarrow} at the Fermi-level, by their respective mobilities b^{\uparrow} and b^{\downarrow} and by the respective derivatives of the spin-dependent chemical potentials.

As electrons from N enter F, the spin polarization P builds up over a distance determined by *spin-conserving* s \rightarrow d electron scattering. This distance corresponds to the electron mean free path $\lambda_{\rm e} = (1/\lambda_{\rm e}^{\uparrow} + 1/\lambda_{\rm e}^{\downarrow})^{-1}$ which for a ferromagnet like Fe is about ~ 5 nm according to Table 12.4. At the interface this leads to the buildup of the spin accumulation voltage which according to (14.9) is seen to depend on $\alpha_{\rm F}$. By use of (14.10) we can write

$$\alpha_{\rm F} = \left(1 + \frac{n^{\downarrow} \tau_{\rm e}^{\downarrow}}{n^{\uparrow} \tau_{\rm e}^{\uparrow}}\right)^{-1} = \left(1 + \frac{n^{\downarrow} \lambda_{\rm e}^{\downarrow}}{n^{\uparrow} \lambda_{\rm e}^{\uparrow}}\right)^{-1} , \qquad (14.18)$$

revealing the dependence of the spin accumulation voltage $V_{\rm AS}$ on the spin dependent mean free paths $\lambda_{\rm e}^{\uparrow} = \lambda_{\rm e}^{+}$ and $\lambda_{\rm e}^{\downarrow} = \lambda_{\rm e}^{-}$. Equilibration of μ^{\uparrow} and μ^{\downarrow} away from the interface must involve tran-

Equilibration of μ^{\uparrow} and μ^{\downarrow} away from the interface must involve transitions between *opposite* spin states. Since they are much less likely than spin-conserving scattering events, as discussed in Sect. 12.7, we expect for the equilibration length $\Lambda_{\rm F} \gg \lambda_{\rm e} \sim 5$ nm. In Sect. 12.7.1 we have discussed the various processes leading to transitions between opposite spin states and also discussed their speed. For example, inelastic scattering on spin waves provides a possible mechanism for the transfer of energy and angular momentum. At room temperature energy transfers of the order of 10 meV are possible corresponding to times of about 100 fs (see Fig. 15.1 below).

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At lower temperatures electron scattering on spin waves becomes asymmetric. While spin waves can always be excited by a minority spin electron which becomes a majority spin in the process, spin wave absorption by a majority spin electron is no longer possible as spin waves cease to exist at low T.¹ At low temperatures, spin relaxation processes may still exist due to scattering at potential gradients, which according to (6.85), give rise to a spin-orbit field $B^* \propto p \times \nabla \Phi$. One would expect that such spin–orbit scattering strongly depends on the crystallographic and electronic structure of the material, and it appears that τ_{se} becomes shorter in the presence of impurities and defects [730, 739]. The details of the spin–orbit scattering mechanisms in transport still require further study. In general, τ_{se} may include loss of spin polarization by both magnon scattering and spin–orbit de-phasing, that is, contributions from τ_1 and τ_2 discussed in Sect. 8.6.2.

Experimental values for $\Lambda_{\rm F}$ have been derived from giant magneto-resistance (GMR, see Sect. 14.1.4 below) measurements on sandwich structures containing F layers in the 10–1000 nm thickness range in order to satisfy the conditions for bulk-like samples and minimize interfacial effects [739–741]. Table 14.1 gives the room temperature results for Co, obtained by Piraux et al. [741]. At room temperature, $\Lambda_{\rm F} = 38$ nm, corresponding to $\tau_{\rm se} \simeq 400$ fs. At 77 K, $\Lambda_{\rm F}$ increases to 59 nm with a spin equilibration time $\tau_{\rm se}$ of about 1 ps. Measurements on alloys give shorter values for $\Lambda_{\rm F}$, as reviewed by Bass and Pratt [740], which have been attributed to the existence of addition scattering mechanisms, similar to embedding impurities into pure metals. For example, it has been argued [739] that the scattering in permalloy, Ni₈₀Fe₂₀, resembles that for Fe impurities in Ni, explaining the measured short value of $\Lambda_{\rm F} = 4$ nm, corresponding to $\tau_{\rm se} \simeq 5$ fs.

It is interesting that the observed spin equilibration time in ferromagnets at room temperature is considerably shorter than the spin–lattice relaxation time, which is of the order of 100 ps as discussed in Sect. 15.2.2 below. This indicates that spin equilibration due to magnon excitations must only establish equilibrium within the spin system, which occurs within hundreds of femtoseconds, but not with the lattice which occurs on longer time scales. In a simple picture, an *s*-like conduction electron may flip its spin on a subpicosecond time scale by excitation of a spin wave, which corresponds to an excitation of the more localized *d*-moments. Yet the de-excitation of the excited *d*-moments, i.e., of the whole magnetization, by transfer of energy and angular momentum to the lattice takes much longer.² In the presence of a

¹Note that nonuniformities of the magnetization can also scatter spins. Strong nonuniformities like bulk or interface domain walls can be excited by spin currents even at T = 0, leading to scattering.

 $^{^{2}}$ The transfer of angular momentum from conduction electron spins to localized Mn spins and the ensuing local Mn moment de-excitation and equilibration with the lattice has been directly observed in time-dependent optical spin resonance studies of magnetic semiconductors like MnSe [742].

current, the magnetization may therefore differ from that expected from the prevailing lattice temperature.

Generalizing the results listed in Table 14.1 for Cu and Co, we can state as follows.

At room temperature, one finds typical values $\Lambda_{\rm N} \approx 500$ nm and $\tau_{\rm se} \approx 10$ ps for nonmagnetic metals, and $\Lambda_{\rm F} \approx 50$ nm and $\tau_{\rm se} \approx 1$ ps for pure ferromagnetic metals.

14.1.4 Giant Magneto-Resistance (GMR)

The potential drop at the interface between a ferromagnet F and a nonmagnetic metal N leads to a *boundary resistance*, which when properly combined at two F/N interfaces in a $F_1/N/F_2$ sandwich, leads to an effect known as *giant magneto-resistance* or GMR. GMR is extremely useful for measuring the relative magnetization directions of two ferromagnetic metals F_1 and F_2 , separated by a nonmagnetic metal N. The GMR effect is larger by almost an order of magnitude than the AMR effect discussed in Sect. 12.5.3, and it is routinely used today to detect the weak magnetic fields (stray fields) of the small domains written on magnetic recording disks. In addition, GMR detection is fast and has been used on time scales of 100 ps. Such GMR-sensors have revolutionized the reading of data from magnetic media and helped the storage industry stay on Moore's-law curve as shown in Fig. 1.15.

The principle of a GMR sensor in the form of a spin valve is illustrated in Fig. 14.3. One of the ferromagnetic layers is pinned by exchange bias (see Sect. 13.4.3) to an AFM, shown in green, and serves as a "reference" layer since it cannot be switched in typical external magnetic fields. A second ferromagnetic or "sensor" layer, decoupled by a nonmagnetic spacer layer such as Cu, may be switched in a relatively small field. Depending on its parallel or antiparallel alignment relative to the pinned reference layer, the resistance of the device changes on the order of 10%. In practice, a spin valve structure serves as a "read head" in a disk drive. As the recording disk, with its written magnetic bits rotates underneath the read head, the stray fields of the bits cause the magnetization of the sensor layer to change. The induced change in the GMR signal can therefore be used to read the bit pattern.

As illustrated in Fig. 14.3, two cases of current flow direction can be distinguished. For flow of <u>Current Perpendicular</u> to the <u>Plane (CPP)</u>, the devices are called CPP sensors. They show an approximately three-times larger GMR than sensors in which the <u>Current flows In the Plane of the interface (CIPsensors)</u>.

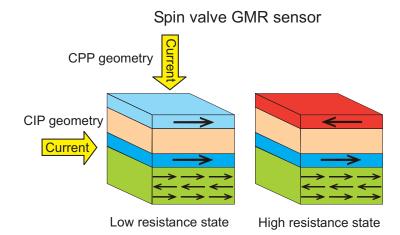


Fig. 14.3. Concept of a spin valve. The magnetization of the lower magnetic layer is fixed in direction by exchange coupling to an antiferromagnetic substrate as discussed in Sect. 13.4.3. The upper magnetic layer is separated by a nonmagnetic spacer layer and its magnetization can rotate in relatively small fields. If the spacer layer is metallic (e.g. Cu), the current typically flows in the plane of the films, called the "current in plane" or CIP geometry. When the current flows perpendicular to the plane of the films, one speaks of a "current perpendicular (to) plane" or CPP geometry. As discussed in Sect. 13.2.2 one may replace the metal spacer layer by an insulator, leading to a "tunneling spin valve" which is operated in the CPP geometry

The Concept of Boundary Resistance

In order to derive the GMR effect one first calculates the boundary resistance of a single F/N interface, defined as $R_{\rm B} = V_{\rm AS}/j(0)$ with dimension [Ohm × area]. With (14.9) one obtains,

$$R_{\rm B} = \frac{(2\alpha_{\rm F} - 1) \left[\mu^{\uparrow}(0) - \mu^{\downarrow}(0)\right]}{2 \, e \, j(0)} \ . \tag{14.19}$$

To calculate $R_{\rm B}$ from this equation, one needs to know the current j(0) flowing through the interface. By use of the ansatz $j(0) = \beta_{\rm I} j$, where $\beta_{\rm I}$ is a yet to be determined interface parameter, one may use (14.15), and approaching the interface from the side of N we have,

$$\frac{\partial \mu^{\uparrow}}{\partial x} - \frac{\partial \mu^{\downarrow}}{\partial x} = -\frac{e}{\sigma^{\uparrow}} j^{\uparrow} + \frac{e}{\sigma^{\downarrow}} j^{\downarrow} = -\frac{2(2\beta_{\rm I} - 1) ej}{\sigma_{\rm N}} = \frac{-(\mu^{\uparrow}(0) - \mu^{\downarrow}(0))}{\Lambda_{\rm N}} .$$
(14.20)

From the right-side of this equation it follows that

$$ej(0)_{\rm N} = \frac{\mu^{\uparrow}(0) - \mu^{\downarrow}(0)}{2(2\beta_{\rm I} - 1)\Lambda_{\rm N}\sigma_{\rm N}^{-1}} .$$
(14.21)

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Inserting into (14.19) gives

$$R_{\rm B} = (2\alpha_{\rm F} - 1)(2\beta_{\rm I} - 1)\Lambda_{\rm N}\sigma_{\rm N}^{-1}.$$
(14.22)

We still need to determine $(2\beta_{\rm I} - 1)$. This is done by considering the solution of (14.15) on approaching the interface $(x \to 0)$ from the side of the ferromagnet, and by realizing that the current, that is the coefficient β , must be continuous just as μ^{\uparrow} and μ^{\downarrow} must be continuous. For the ferromagnetic side of the interface we then have,

$$\frac{\partial \mu^{\uparrow}}{\partial x} - \frac{\partial \mu^{\downarrow}}{\partial x} = \frac{e}{\sigma_{\rm F}} j \frac{\alpha_{\rm F} - \beta_{\rm I}}{\alpha_{\rm F}(1 - \alpha_{\rm F})} = \frac{-(\mu^{\uparrow}(0) - \mu^{\downarrow}(0))}{\Lambda_{\rm F}} , \qquad (14.23)$$

and this yields

$$ej(0)_{\rm F} = \frac{2\alpha_{\rm F}(1-\alpha_{\rm F})}{(2\beta_{\rm I}-1)-(2\alpha_{\rm F}-1)} \frac{\mu^{\uparrow}(0)-\mu^{\downarrow}(0)}{\Lambda_{\rm F}\sigma_{\rm F}^{-1}} .$$
(14.24)

Equating (14.24) and (14.21) finally gives for the interface parameter $\beta_{\rm I}$

$$(2\beta_{\rm I} - 1) = \frac{2\alpha_{\rm F} - 1}{1 + 4\alpha_{\rm F}(1 - \alpha_{\rm F})\frac{\Lambda_{\rm N}\sigma_{\rm N}^{-1}}{\Lambda_{\rm F}\sigma_{\rm F}^{-1}}}.$$
 (14.25)

For $\alpha_{\rm F} = 0.5$ there is no asymmetric conduction and we find $\beta_{\rm I} = 0.5$, as expected. In the case of the HMF we have $\alpha_{\rm F} = 1$ and one obtains $\beta_{\rm I} = 1$. This means that the current flows in one spin channel only. The *boundary resistance* leading to the GMR effect is then obtained from (14.22) in agreement with the expression in ref. [729]. We obtain the following important result.

The boundary resistance $R_{\rm B}$ for a single interface between a bulk ferromagnet F and nonmagnet N, for current flow perpendicular to the interface and assuming that in both F and N the spin equilibration length Λ is much longer than the electron mean free path $\lambda_{\rm e}$, is given by

$$R_{\rm B} = \frac{(2\alpha_{\rm F} - 1)^2 \Lambda_{\rm N} \sigma_{\rm N}^{-1}}{1 + 4\alpha_{\rm F} (1 - \alpha_{\rm F}) \frac{\Lambda_{\rm N} \sigma_{\rm N}^{-1}}{\Lambda_{\rm F} \sigma_{\rm F}^{-1}}}.$$
 (14.26)

We see that the boundary resistance is enhanced by increasing the difference between the spin up and spin down conductivities in F, expressed by $\alpha_{\rm F} \rightarrow 1$, as expected. In our derivation we have assumed that the electric current flows perpendicular to the interface. A more detailed theory of CPP GMR has been given by Valet and Fert [730], who also treated the cases of finite layer thicknesses and multilayer structures. The more general theory of Valet and Fert was shown by the authors to reduce to our result for the case of an interface between F and N metals of thickness $t \gg \Lambda \gg \lambda_{\rm e}$. Experimental results have been reviewed by Bass and Pratt [740].

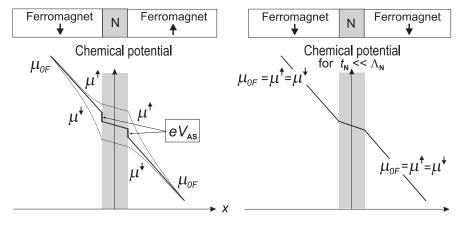


Fig. 14.4. Contact between two identical ferromagnets (FM) across a nonmagnetic metal N of good conductivity and thickness $t_{\rm N} \ll \Lambda_{\rm N}$. This corresponds to the situation in actual spin valves shown in Fig. 14.3. Left: Case of antiparallel magnetizations in the two FMs, leading to a splitting of the Fermi-levels μ^{\uparrow} and μ^{\downarrow} . At each of the two interfaces, FM/N and N/FM, the full spin accumulation voltage $V_{\rm AS}$ develops. Note that in the left ferromagnet with down magnetization, spin up refers to majority spins, while in the right ferromagnet with up magnetization spin up refers to minority spins. Right: Case of parallel magnetizations in the two FMs. With decreasing thickness $t_{\rm N}$ of N the spin accumulation voltage decreases at both interfaces, and in the limit $t_{\rm N}/\Lambda_{\rm N} \to 0$ the spin splittings of the chemical potentials vanish, as shown. The parallel coupling case has the lower voltage drop and therefore the lower resistance. The GMR effect is the difference in resistance measured between antiparallel and parallel magnetic alignments of the two ferromagnets, created by the voltage difference $2V_{\rm AS}$. Note that $V_{\rm AS}$ becomes infinitely large in the limiting case of two antiferromagnetically coupled half metallic ferromagnets

GMR of Sandwich Structures

To observe the GMR effect, one needs two ferromagnets F_1 and F_2 , connected by a nonmagnetic metal N, as shown in Fig. 14.4. In practice, N is kept thin, of order of a few nanometers, and we shall consider this case. If the thickness t_N of N is much less than the spin diffusion length, $t_N \ll \Lambda_N$, the spin relaxation in N becomes negligibly small. Note however that a finite thickness of N is required to interrupt the exchange coupling between F_1 and F_2 and to allow both parallel and antiparallel alignments of M_1 and M_2 to be stable. If N is too thin and exchange coupling exists, M_1 turns gradually into M_2 over the width of a domain wall. Depending on the spin selective scattering, the spins of the electrons will then also turn gradually into the new direction on moving from $F_1 \to F_2$ and the GMR effect is lost or greatly reduced.

Figure 14.4 shows the principle of observing GMR. In changing the orientation of the two ferromagnetic layers F_1 and F_2 from parallel to antiparallel alignment (or vice versa) one observes a different spin accumulation voltage for constant current, and hence a different boundary resistance. The change of the spin-dependent chemical potentials shown in Fig. 14.4 for antiparallel and parallel alignment of F_1 and F_2 follows from Fig. 14.1. If F_1 and F_2 are *antiparallel* the spin-dependent chemical potentials for the two interfaces are in phase, if F_1 and F_2 are *parallel*, they are out of phase and the spin accumulation tends to zero. In fact, the proper theory [730] for the *parallel case* and $t_N \ll \Lambda_N$ shows that at the interfaces, $\Delta \mu$ is reduced by a factor t_N/Λ_N relative to the "macroscopic" case $t_N \gg \Lambda_N$, treated in Sect. 14.1.1.

In fact, we can use our results for the boundary resistance given by (14.26), for the case shown in Fig. 14.4 to calculate the size of the GMR effect. To do so we make the assumption that $\Lambda_{\rm N}\sigma_{\rm N}^{-1} \gg \Lambda_{\rm F}\sigma_{\rm F}^{-1}$. Assuming that the nonmagnetic metal is Cu, this condition is *not* well satisfied for pure ferromagnetic metals such as Co, but it is a reasonable assumption for ferromagnetic alloys which have a shorter spin equilibration length $\Lambda_{\rm F} \sim 10$ nm. Indeed, today, alloys are preferentially used in practical spin valve structures. For example, using the approximate low temperature values $\Lambda_{\rm N} = 1,000$ nm and $\sigma_{\rm N}^{-1} = 2 \times 10^{-8} \ \Omega{\rm m}$ for Cu, and $\Lambda_{\rm F} \simeq 10$ nm and $\sigma_{\rm F}^{-1} \simeq 7 \times 10^{-8} \ \Omega{\rm m}$ for CoFe alloys [743], we have $(\Lambda_{\rm N}\sigma_{\rm N}^{-1})/(\Lambda_{\rm F}\sigma_{\rm F}^{-1}) \approx 30$, and therefore the second term in the denominator of (14.26) dominates. We can then write,

$$R_{\rm B} = \frac{(2\alpha_{\rm F} - 1)^2 \Lambda_{\rm F} \sigma_{\rm F}^{-1}}{4\alpha_{\rm F}(1 - \alpha_{\rm F})} .$$
(14.27)

This equation is valid, provided that each FM has a thickness $t_{\rm F} \gg \Lambda_{\rm F}$ as assumed in the derivation of (14.26). For the antiparallel case in Fig. 14.4, the full spin accumulation voltage and therefore boundary resistance $R_{\rm B}$ is obtained even for a thin spacer layer N. However, in the parallel case we have $R_{\rm B} \simeq 0$. Assuming that the thickness of layer N $t_{\rm N} \ll t_{\rm F}$, the total resistance of the structure is dominated by the two ferromagnets and amounts to $R = 2\sigma_{\rm F}^{-1}t_{\rm F}$. We obtain for the GMR signal,

$$\frac{R^{\rm AP} - R^{\rm P}}{R} = \frac{\Delta R}{R} = \frac{2R_{\rm B}}{2\sigma_{\rm F}^{-1}t_{\rm F}} = \frac{(2\alpha_{\rm F} - 1)^2}{4\alpha_{\rm F}(1 - \alpha_{\rm F})} \frac{\Lambda_{\rm F}}{t_{\rm F}} .$$
(14.28)

This particularly simple result³ is valid for a thin spacer layer $t_{\rm N} \ll \Lambda_{\rm N}$, and thick ferromagnetic layers $t_{\rm F} \gg \Lambda_{\rm F} \gg \lambda_{\rm e}$. We shall use it later in Sect. 14.1.6 to estimate the typical size of the GMR effect.

14.1.5 Measurement of Spin Diffusion Lengths in Nonmagnets

The GMR effect may be used to measure the *spin diffusion length* in nonmagnets, defined by (14.16) and (14.17) as the distance $\Lambda_{\rm N}$ over which the potential difference $\mu^{\uparrow} - \mu^{\downarrow}$ decays into the bulk of N. The principle of this experiment is based on a lateral spin valve geometry illustrated in Fig. 14.5.

³Our (14.28) is identical to (3) in ref. [739], since the parameter β in the Valet– Fert notation is related to our $\alpha_{\rm F}$ according to $\beta = 2\alpha_{\rm F} - 1$.

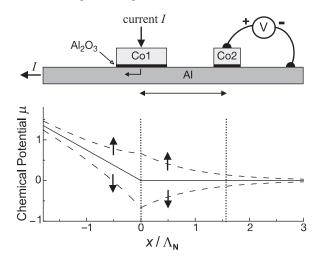


Fig. 14.5. Upper part: Design of the lateral spin valve to measure $\Lambda_{\rm N}$ in aluminum. Two Co FMs, labeled F_1 =Co1 and F_2 =Co2, with different coercivities are positioned on top of Al. The spin current I, indicated by arrows, flows from Co1 into Al and exits to the left. In the experiments with the Al-conductor shown here, a very thin Al_2O_3 layer is also inserted. The decay of $\mu^{\uparrow} - \mu^{\downarrow}$ is measured by the GMR-signal induced in Co2 positioned on top of a tunnel barrier to the right. Note that the charge current does not flow underneath Co2, thus avoiding contributions to the measured spin signal due to the Hall-effect and the anisotropic magneto-resistance. The voltage $V_{\rm AS}$ is thus solely determined by the decay of the diffusive spin current in Al, as illustrated underneath as a function of distance x in units of $\Lambda_{\rm N}$. For Al one finds $\Lambda_{\rm N} = 650$ nm at 4.2 K. Figure adapted from [738]

Using the geometry of Fig. 14.5, Jedema and collaborators [737,738] measured the voltage drop between two ferromagnets F_1 and F_2 , placed on top of either Cu or Al, and separated by variable lengths. Note that in the experiments with Cu, the thin Al₂O₃ layer shown in Fig. 14.5 was absent. If the magnetization of F_1 is switched from parallel to antiparallel relative to the magnetization in F_2 , one obtains the spin accumulation voltage V_{AS} defined in Fig. 14.4. Dividing V_{AS} by the current yields the GMR-signal, that is the resistance of the interface. The GMR signal is found to decrease exponentially with the separation between F_1 and F_2 , in agreement with the diffusion equation of the magnetization, (14.15), and thus yields the decay of the spin current due to spin relaxation and spin de-phasing in N.

The GMR decrease with the F_1-F_2 separation is governed according to Sect. 14.1.2 by the diffusion length in N, $\Lambda_N = \sqrt{\mathcal{D}\tau_{se}}$, with τ_{se} being the lifetime of the spins and \mathcal{D} the diffusion constant. The length Λ_N will depend on temperature. For Cu one finds $\Lambda_N = 1,000$ nm at 4.2 K and 350 nm at room temperature (RT) [737], while in Al the values are $\Lambda_N = 650$ nm at 4.2 K and 350 nm at RT [738]. At RT, Cu and Al seem to exhibit the same spin diffusion lengths. In later work, Jedema and coworkers [738] also detected the precession of the spin in the nonmagnetic metal Al induced by a magnetic field B_{\perp} , applied perpendicular to the injected spin polarization. The geometry for this important experiment is again that of Fig. 14.5, with the Co films magnetized in plane (perpendicular to the shown cross section in Fig. 14.5) and the field is applied in the vertical direction. In this experiment the shown thin Al₂O₃ tunnel barrier was present. It enhances the spin polarization of the injected current as discussed in Sect. 13.2.2 and also prevents re-entrance of the injected electrons into the F-electrodes which can lead to additional depolarization. Note that again the charge current does not flow through the region underneath Co2. Hence it is a purely diffusive spin current at zero charge current that is observed here.

For parallel versus antiparallel magnetization directions in Co1 and Co2, one initially observes a positive spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ in the absence of a field. As the field B_{\perp} is applied and increased, the voltage decreases to zero. This is caused by a 90° in-plane precession of the injected spins about the perpendicular field during their diffusion through N from Co1 and Co2. After further increasing the field, the spins precess by an angle of 180° and the spin voltage reverses sign and becomes negative. The experiment thus detects the precession of the spins by the measured spin voltage. As the field is further increased one would expect further precession and voltage cycles with a decrease of the voltage amplitude, indicative of spin de-phasing with time. This is not observed since even at 4.2 K the voltage already decreases drastically after only one precession cycle. This is consistent with the fact that in the relatively small fields up to 50 mT used by Jedema et al., the Larmor spin precession time is about 1 ns. During this relatively long precession time, the short-lived spin polarization with a lifetime of about 50 ps at 4.2 K in Cu and Al, has nearly completely decayed.

All-electrical detection of spin precession in metals was first reported by Johnson and Silsbee in 1985 [735], but it was difficult at the time to interpret due to the presence of the anisotropic magnetoresistance effect (see Sect. 12.5.3) and the Hall effect in the ferromagnetic contacts. In later experiments, Johnson [736] used lithographically fabricated samples and obtained the value $\tau_{se} = 17 \pm 9$ ps for Au below 65 K, close to the values for Cu obtained by Jedema [737, 738]. Over the years, the reduction of the sample size by three orders of magnitude together with the use of novel sample geometries has removed most ambiguities in the values for τ_{se} . From the arguments given in Sect. 14.1.3, τ_{se} should vary with the atomic spin–orbit interaction and one would therefore expect significant differences between Al, Cu and Au, which is inconsistent with present experimental results. This point awaits further experimental studies.

With two identical ferromagnets, the electrical resistance is lowest when the magnetizations are parallel, and increases typically by about 10% when they are antiparallel. However, this does not necessarily apply with two different ferromagnets. For example, it has been shown [744] that a sensor in which

one film is Fe and the other Fe₃O₄ exhibits a negative GMR of -5% at 300 K, that is, the resistance is lowest when the two films are magnetized *antiparallel*. Since according to Sect. 7.7.4, the electrical conduction in magnetite is entirely due to minority spins, the observed negative GMR corroborates the notion put forward in Sect. 12.2.1 that electrical conduction in Fe metal is due to majority spins.⁴ Further examples of negative GMR have been described by Bass and coworkers [743]. As discussed in Sect. 7.7.4, bulk magnetite is a half metallic ferromagnet and thus a sensor made with two Fe₃O₄ films should exhibit a huge magneto-resistance according to Fig. 14.2. This has not been verified so far.

14.1.6 Typical Values for the Spin Accumulation Voltage, Boundary Resistance and GMR Effect

Toward the end of this section we want to give some approximate values for the size of the spin accumulation voltage $V_{\rm AS}$, the boundary resistance $R_{\rm B}$ and the GMR effect $\Delta R/R$ for a ferromagnet/nonmagnet/ferromagnet sandwich in a CPP geometry. For convenience we consider the case shown in Fig. 14.4 with a thin nonmagnetic spacer layer. We furthermore assume that $\Lambda_{\rm N}\sigma_{\rm N}^{-1} \gg \Lambda_{\rm F}\sigma_{\rm F}^{-1}$ so that we can conveniently use our previously derived equations (14.27) for $R_{\rm B}$ and (14.28) for $\Delta R/R$.

We take the literature values for $\text{Co}_{0.91}Fe_{0.09}$ given by Bass and Pratt,⁵ $\alpha_{\rm F} = 0.83$, $\Lambda_{\rm F} = 12$ nm and $\sigma_{\rm F}^{-1} \simeq 70$ n Ω m [740]. By use of (14.27) we obtain $R_{\rm B} = 650 \,\Omega \text{nm}^2$ and with (14.28) $\Delta R/R = 9.3\%$. Our estimate of the GMR effect is in good accord with experimental observations in spin valve structures.

We can also calculate a value for the spin accumulation voltage using our above values. It is given by

$$V_{\rm AS} = R_{\rm B} j$$
 . (14.29)

If we assume a current density of $j = 10^{12} \text{ Am}^{-2}$, which is a typical value used in spin injection (see below), we obtain $V_{\text{AS}} \simeq 0.65 \text{ mV}$.

Finally, we can calculate the transient magnetization induced by the spin current, i.e., the difference in the number of up and down spins in the atomic volume, in both F and N. This transient moment appears only in the presence of current flow and needs to be distinguished from any intrinsic magnetic moments due to exchange splits bands. For example, the magnetic moment of an atom in F located near the interface within the spin equilibration length will be slightly different than that of an atom in F located far away from the interface, in the bulk of F. Similarly, a small transient moment due to spin accumulation will exist on atoms in N near the interface. In practice, the intrinsic magnetic moment is due to the d electrons as discussed in Sect. 12.2.2,

⁴This is also supported by measurements of spin-dependent electron mean free paths by Gurney et al. [745].

⁵The β value of Bass and Pratt is related to our $\alpha_{\rm F}$ value by $\beta = 2\alpha_{\rm F} - 1$.

while the transient moment is due to s electrons. From (14.11) we know the surplus spin density at the interface and can therefore obtain the surplus magnetization per atom in the nonmagnet, i.e., the transient magnetic moment per atom, $m_{\rm N}$, in units of $\mu_{\rm B}$, as

$$m_{\rm N} = D(E_{\rm F}) \left[\mu^{\uparrow}(0) - \mu^{\downarrow}(0) \right] \, \mu_{\rm B} = D(E_{\rm F}) \, \frac{eV_{\rm AS}}{\alpha_{\rm F} - \frac{1}{2}} \, \mu_{\rm B} \, . \tag{14.30}$$

In the last step we have used (14.9). From Fig. 12.1 we know that in nonmagnetic metals like Cu we have $D(E_{\rm F}) \simeq 0.2 \, {\rm eV^{-1} atom^{-1}}$ and with $eV_{\rm AS} \simeq 0.6 \, {\rm meV}$ we obtain $m_{\rm N} \simeq 4 \times 10^{-4} \, \mu_{\rm B}/{\rm atom}$. It may be possible in the future to measure this transient moment by XMCD.

14.1.7 The Important Role of Interfaces in GMR

So far we have made the specific assumption that the interface is *transparent* and simply separates two metals. In practice, interfaces behave differently, but the detailed understanding of interfacial effects is still a significant challenge. This is largely due to the fact that interfaces between solids are buried and their structural, electronic and magnetic properties are often not accessible experimentally. We have already encountered this problem in Sect. 13.4.3. It is clear that transport across interfaces must be influenced by several interfacial properties, and we shall briefly review them now.

One may readily list some interfacial properties which must affect the scattering of electrons and hence their transport. The *interface structure*, including effects such as roughness, compositional gradients and interface specific magnetic moments will cause deviations from idealized behavior. *Interface-specific electronic states* may exist in both the charge and spin degrees of freedom, leading to novel scattering mechanisms. In general, such effects may lead to complicated angle-dependent electron scattering cross sections, which are very sensitive to sample manufacturing techniques.

The existence of strong interfacial effects in magnetoresistance was pointed out early-on by Parkin [746], who found significant increases in spin-valve GMR by dusting the interfaces in $Ni_{81}Fe_{19}/Cu/Ni_{81}Fe_{19}$ sandwiches with Co, up to thicknesses of a few layers. Over the years, the importance of interfacial effects has become well accepted and was included into the GMR theory by Valet and Fert [730] and the analysis of experimental CPP GMR data by Bass and Pratt [740]. In such studies interface effects, included in parameterized form, typically lead to enhanced effects which may be loosely attributed to enhanced spin dependent interface scattering. It is still quite difficult to understand the microscopic origin of interfacial effects in detail.

In Sect. 13.3 we have discussed the *spin-dependent reflection* of electrons from a ferromagnetic surface. Today such spin-dependent reflection processes are thought to be at the very heart of generating spin polarized electron currents in magnetic multilayer structures. The assumption of a transparent interface is sometimes referred to as a "macroscopic" or "bulk" theory, because it is based on the different spin dependent conductivities appropriate for

bulk-like samples. Upon detailed study, this assumption has turned out to be unrealistic, and the bulk contribution amounts to only 20% of the GMR effect in practical multilayer structures consisting of thin layers of a few nanometers thickness. In such systems, the size of the measured GMR effect can only be explained by interfacial spin dependent reflection processes.

At present, reflection can be quantitatively studied only at the ferromagnetvacuum interface, as discussed in Sect. 13.3.2. This is done by preparing a spin polarized electron beam and observing the change in spin direction after the reflection, in particular, its dependence on the energy and angle of reflection. Another well documented effect of spin dependent reflection is periodic exchange coupling of two ferromagnets across a nonmagnetic spacer layer such as Cu, discussed in Sect. 13.4.5. It is important to note that spin-dependent reflection is an electronic process that proceeds on ultrafast timescales. It involves spatial separation of the two spin states as in the Stern–Gerlach experiment. Transitions between states of opposite spin are not required.

14.2 Spin-Injection into a Ferromagnet

In a trilayer $F_1/N/F_2$, such as shown in Fig. 14.4, one may transfer electrons from the first ferromagnet F_1 into the second ferromagnet F_2 by drawing an electric current. The current of electrons leaving F_1 is spin polarized. Although it is still difficult to account for the sign and degree of spin polarization,⁶ we shall simply assume here, as verified by experiments, that for a given ferromagnet the transmitted current has acquired a well defined spin polarization. We will also assume that the electrons traverse the thin nonmagnetic spacer layer by retaining most of their spin polarization P, defined in Sect. 8.4, until entering the ferromagnet F_2 , and that this holds whether the current density $j = n_e e v$ corresponds to ballistic or drift velocities v.

The total spin angular momentum vector per volume associated with the current density j of electrons, which enters the second ferromagnet F_2 , is given by

ł

$$\mathbf{S}_1 = \frac{j}{e v} \frac{\hbar}{2} \mathbf{P} \ . \tag{14.31}$$

As soon as the electrons are in F_2 , they will experience exchange coupling to the local magnetization, depending on the angle enclosed by S_1 and the magnetization M_2 . Additionally, spin selective scattering of the electrons will occur, as discussed in Sect. 12.6.4, tending to rotate S_1 into the direction S_2 of the spin density in the ferromagnet F_2 .⁷ Both phenomena lead to effective

 $^{^{6}}$ As discussed in Sect. 13.2, the degree of spin polarization and even its sign are not solely determined by the ground state magnetic properties of the source, such as the degree of spin polarization at $E_{\rm F}$.

⁷Note that minority spins which point in the same direction as M_2 (i.e., opposite direction as S_2) are preferentially scattered (see Fig. 7.6).

torques acting on M_2 (or S_2). The torques excite spin-waves and can even be strong enough to switch M_2 into the opposite easy direction. These ideas were first proposed and theoretically treated by Slonczewski [84] and Berger [85].

Spin injection is one of the most interesting developments in contemporary magnetism, testing the interaction processes of ferromagnetic spins and their dynamics and promising a host of new applications. Its quantitative understanding is still complicated by a lack of knowledge of interfacial effects on the degree and sign of the spin polarization of the injected electrons, although progress is being made [743, 747]. Also, the magnetic characteristics of the materials are insufficiently determined in practice because the samples have to be tiny to achieve the high current densities required in spin injection. Therefore nanoscale and interfacial effects are expected to play a role. A vast field of interesting research remains unexplored.

14.2.1 Origin and Properties of Spin Injection Torques

The occurrence of torques acting on the magnetization upon injecting spin polarized electrons may be viewed as a consequence of Newtonian mechanics, specifically the third law according to which *actio=reactio* in closed systems. Once an electron is injected through the interface and is inside the ferromagnet, we have a closed system with no external forces. In saying this, we have neglected the fact that the lattice of nano-magnets, of interest in our discussion, is necessarily coupled to the substrate it is fabricated on. In principle, this invalidates the assumption of a closed system as angular momentum may be transferred directly from the injected spins to the lattice and then be taken up by the substrate. However, the spin–lattice interaction is weak compared to the electron–electron interactions, and we shall neglect it for now, until we come back to it in our later discussion of the threshold value of the switching current.

With this assumption it is easy to understand in principle how spin injection works. The total angular momentum L per volume, consisting of the angular momentum density of the injected spins S_1 plus the spin angular momentum density S_2 of the magnetization in F_2 must be conserved. It follows that the angular momentum L is conserved so that dL/dt = 0. This means that the torque acting on S_1 must be equal and opposite to the torque acting on S_2 . This important result can be written in the form of the following master equation.

If a current with spin density S_1 is injected into a ferromagnet with spin density S_2 , the changes in the two spin densities, determined by the conservation of angular momentum, are related according to

$$\frac{\mathrm{d}\boldsymbol{S}_1}{\mathrm{d}t} = -\frac{\mathrm{d}\boldsymbol{S}_2}{\mathrm{d}t} \ . \tag{14.32}$$

Basic theoretical postulates discussed in Sect. 8.4 as well as experimental results of Figs. 12.22 and 12.23 show how the vector S_1 of the injected spins changes with time. It precesses about S_2 and also rotates into the direction of S_2 . According to (14.32), the motion of the vector S_1 determines the torques that are acting on the magnetization in F_2 . Yet it has not been possible so far at the electron energies relevant in spin injection to measure the change in direction and magnitude of either S_1 or S_2 as a function of the distance from the interface.

It is interesting to note that even when $S_1 = 0$ at the point of injection, it will grow to a finite magnitude through spin selective scattering as the electrons traverse F_2 , thus inducing torques on S_2 . Because the injected spin density S_1 rotates into the direction of S_2 , the torque on S_2 is directed oppositely according to (14.32), that is away from S_2 . This leads to the excitation of spin waves. Such spin waves excited by an unpolarized current have indeed been observed [748–750].

Equation (14.32) is useful for the discussion of the direction and general properties of the torques. For simplicity, we will assume in the following discussion that the injected electrons are *fully polarized*. This means that we assume that all electron spins (of magnitude $\hbar/2$) point in the same direction, given by S_1 .

Precessional Spin-Injection or NEXI Torque

Due to the exchange coupling, the injected spins $\sum \mathbf{s}_i = \mathbf{S}_1$ precess around the axis of the spins \mathbf{S}_2 if there is a finite angle Θ between \mathbf{S}_1 and \mathbf{S}_2 . This means that the injected spins are not in equilibrium with the magnetization and the torque arising from this interaction has therefore been called <u>n</u>onequilibrium <u>exchange interaction</u> or NEXI torque [751].

According to (3.31), the NEXI-torque on the *injected spins* per unit volume, $T_{\text{nex}} = dS_1/dt$, is given by,

$$T_{\rm nex} = \mid n_{\rm e} \boldsymbol{\mu}_{\rm B} \times \boldsymbol{H}_{W} \mid = \frac{n_{\rm e} \Delta \sin \Theta}{2} , \qquad (14.33)$$

where n_e is the density of the injected electrons, $n_e \mu_B$ is the magnetization of the injected electrons (antiparallel to S_1), and H_W the energy and momentum dependent molecular Weiss field. The field is responsible for the exchange splitting Δ in F₂, with a value given by $\Delta = 2\mu_B H_W$. The torque T_{nex} is directed perpendicular to S_1 and S_2 , as illustrated in Fig. 14.7, and it is largest for $\Theta = \pi/2$. The vector S_1 of the injected spins precesses about S_2 at a very fast rate due to the large exchange energy of $\Delta \approx 1 \text{ eV}$ with a cycle frequency of $\nu = \Delta/h \sim 10^{15}$ Hz. Using a Fermi velocity $v_F \simeq 10^6 \text{ m s}^{-1}$, this means that after a distance $ds = v_F dt = v_F/\nu \approx 1 \text{ nm}$ from the point of injection, S_1 has completely changed its direction.

According to (14.32) there is also a NEXI torque on the spins S_2 in the second ferromagnet. However, the NEXI torques exerted on S_2 arise from

injected electrons that travel in different k-states and their contributions will be out of phase after a short distance from the point of injection. Therefore it is difficult to imagine that a uniform motion of S_2 , possibly leading to a switching of the magnetization M_2 , can be induced by the NEXI torques. Berger has calculated the effective torque arising from NEXI and finds that its average is different from zero only if the ferromagnet F_2 is very thin, of the order of perhaps five monolayers [752]. Under most conditions, NEXI torques may contribute to the excitation of higher spin wave modes. Still, NEXI torques generate the *largest torque densities* occurring with spin currents and are certainly active in reflection of electrons from a ferromagnetic interface as discussed in Sect. 13.3.2.

Dissipative Spin-Injection or Negative Damping Torque

In addition to precessional spin motion there are dissipative electron relaxation processes. The basic process that causes a dissipative spin torque is the rotation of S_1 into the direction of S_2 . Several processes can cause this rotation and it is still unclear which ones dominate. One picture is based on spin de-phasing [84]. When spins are injected into the ferromagnet, they experience the exchange field of the ferromagnet, leading to fast precession of the spins. In the diffusive regime, the electrons have a random k-vector and this leads to de-phasing of the spins and a loss of the component perpendicular to the magnetization, as shown in Fig. 8.7c. Another model, to be discussed below, involves spin selective scattering, in analogy to what is observed in the ballistic regime, discussed in Sect. 12.6.4, and in agreement with the spin-dependent processes at N–F interfaces discussed in Sect. 14.1. From our discussion of interfacial effects in Sect. 14.1.7, the effects of "bulk" spin scattering are expected to be enhanced through interfacial spin-dependent reflection and scattering processes. Such interfacial processes are believed to greatly enhance the spin torques. For simplicity we shall not discuss them here.

Whatever the details, it is clear that angular momentum is transferred from the incident spins to the magnetization. Such angular momentum exchange within the spin system is considerably faster than any spin relaxation processes involving the lattice. Eventually the spin systems cools by equilibration with the lattice and thus the whole process cannot be time-reversed and leads to a damping-like term in the spin dynamics.

With our knowledge of the phenomenon of spin accumulation developed in Sect. 14.1 it is quite easy to see that injection of S_1 into S_2 leads to a *change in* angular momentum in S_2 . For convenience, we follow the antiparallel coupling case shown on the left side of Fig. 14.4, and choose the magnetization direction M_2 and the majority and minority spin directions to agree with those in the layer F_2 in that figure. This is illustrated in Fig. 14.6, where we compare the situation in the chemical potentials before and after current flow. Before current flow the chemical potentials for up and down spins in the ferromagnet are the same. Upon spin injection, the chemical potential of the minority

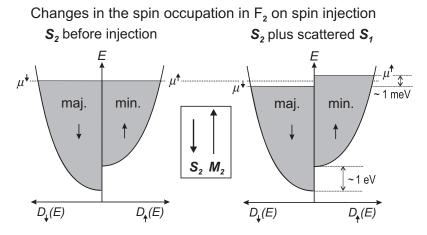


Fig. 14.6. Illustration of the changes in the majority and minority population in a ferromagnet with spin density S_2 and magnetization M_2 due to spin injection. We have chosen the magnetization direction M_2 and the majority and minority spin directions to agree with those in the layer F_2 in the antiparallel coupled trilayer in Fig. 14.4. Upon spin injection the chemical potential of the minority spins increases and majority spins decreases, and a spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ develops as in Fig. 14.4. Charge neutrality in the ferromagnet demands that the number of electrons remains unchanged and therefore the average chemical potential must remain the same as before current flow. The change in spin occupation corresponds to a *change in angular momentum* will result in a torque, as discussed in the text. We also indicate the different sizes of the exchange splitting (taken to be that of the d electrons) and the spin voltage

spins increases and the majority spins decreases, and a spin voltage $\mu^{\uparrow} - \mu^{\downarrow}$ develops as in Fig. 14.4. This spin voltage is simply the result of the different spin-dependent conductivities, in particular, the lower conductivity of the minority channel due to increased spin-dependent scattering. Note that we did not assume any "spin flip scattering", in complete agreement with our discussion in earlier sections that the spin voltage is due to spin selective transport, which in turn is determined by spin conserving scattering.

The importance of Fig. 14.6 lies in the recognition that a change in the number of spin up and down electrons corresponds to a *change in angular* momentum in F_2 . If S_1 is parallel to S_2 , the change in up and down spins in S_2 due to current flow, causes a change in the magnitude of the magnetization M_2 . Since the change in angular momentum is collinear with M_2 , there is no torque on M_2 and its direction does not change. In order to get torque we need to produce a change in angular momentum that is at an angle with respect to M_2 . This is simply achieved by orienting the incident spin density S_1 at a finite angle with respect to S_2 in F_2 . We shall discuss this situation now. Our model employs the same physical processes, namely spin dependent transport based on spin conserving scattering.

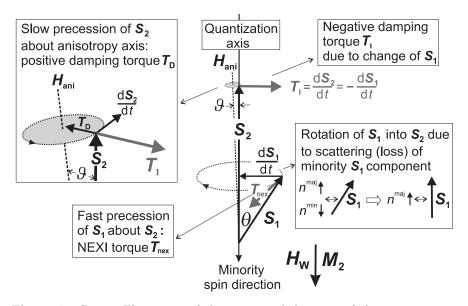


Fig. 14.7. Center: Illustration of the origin and direction of the spin injection torques T_{nex} and T_{I} that act on the spins S_{2} in the ferromagnet F_{2} on injection of spins S_1 . For reference we also show in the inset on the top left the conventional (positive) damping torque $T_{\rm D}$ and precessional torque d S_2/dt , discussed in Sect. 3.6.2, associated with the motion of S_2 relative to the anisotropy axis, labeled $H_{\text{ani.}}$ The NEXI torque T_{nex} has its origin in the precession of S_1 about S_2 , which is aligned opposite to the magnetization M_2 of the ferromagnet and the exchange field H_{W} (see bottom). The NEXI torque points in the direction $S_1 \times S_2$. The negative damping torque $T_{\rm I}$ arises from the selective scattering of injected electrons in the minority channel, as discussed in the text and schematically illustrated in the bottom right inset. The loss in the minority component due to scattering leads to a rotation of S_1 into the majority channel direction, which lies along S_2 . The associated driving torque is dS_1/dt . The torque T_1 acting on S_2 is $T_1 = -dS_1/dt$ according to (14.32). In the shown example, it is directed exactly opposite to the positive damping torque $T_{\rm D}$ associated with the conventional α -term in the LLG equation (3.39), and $T_{\rm I}$ is therefore called a *negative* damping torque. Both torques are perpendicular to S_2

Direction of the Damping Torque

In general, a torque on M_2 requires that there is an angle between the incident spin density S_1 and the spin density S_2 in F_2 . The situation is illustrated in Fig. 14.7. We will now consider how the injected spin density S_1 changes its direction. Once that is done we will also know what happens to the spins S_2 , since their motion is determined by the master equation (14.32).

We assume that the spin density S_1 of injected electrons is fully polarized. Their polarization vector $\mathbf{P} = (2ev/\hbar j)S_1$ given by (14.31) can be decomposed into minority and majority components along a quantization axis, as discussed in Sect. 8.4.3. In our case the quantization axis is naturally given

by the exchange field in the ferromagnet and therefore is parallel to S_2 , as illustrated in the center of Fig. 14.7. From Fig. 7.6 we know that the minority spins are aligned along the magnetization M_2 which points in the direction $-S_2$. Upon entering the ferromagnet the injected electrons experience preferential scattering of the minority component, known as the spin filter effect and discussed in Sect. 12.6.

Assuming that the beam is fully polarized $(|\mathbf{P}| = \text{const})$, the loss in the minority channel of S_1 corresponds to a rotation of \mathbf{P} , as illustrated in the lower-right inset of Fig. 14.7. In the extreme case when all minority electrons have been removed, the vector S_1 is aligned in the majority direction, that is along S_2 . Thus by scattering of minority electrons, S_1 rotates into S_2 , and the torque $T_{\rm I} = \mathrm{d}S_1/\mathrm{d}t$ has to be perpendicular to S_2 and points in the direction $(S_1 \times S_2) \times S_2$, as shown.

It is now easy to infer the rotation of S_2 from the master equation (14.32), since it is simply given by $dS_2/dt = -dS_1/dt$ and thus directed in the direction $S_2 \times (S_1 \times S_2)$, as shown.⁸ This rotates S_2 away from the original vertical majority direction, as shown in Fig. 14.7.

The motion of S_2 due to the dissipative torque T_I is in the direction $S_2 \times (S_1 \times S_2)$, which for the shown example in Fig. 14.7, is directed *opposite* to the *positive* (since α is positive) damping torque T_D , introduced in Sect. 3.6.2, generated in the precession of S_2 around the anisotropy axis H_{ani} in F₂. The dissipative spin injection torque T_I , which is also not invariant under time reversal, has therefore been called a *negative damping torque*.

One may also envision the origin of spin torque by considering the angular momentum transfer between the spins of injected s-like conduction electrons and d-like localized electrons in F_2 . In the first step, s-like electrons are scattered on the localized d-holes through spin conserving transitions as shown in Fig. 12.14. The change in d occupation is equivalent to an excitation of localized atomic moments responsible for the magnetization, causing a spin wave. The excitation of a spin-wave, in turn, requires a change in the conduction electron spins, in order to conserve the total angular momentum of the entire spin system. The creation of a spin wave is therefore accompanied by a conduction electron spin-flip. In the process we have taken energy and angular momentum associated with a conduction electron flip and converted it into a spin-wave excitation of the magnetization in F_2 . When sufficient angular momentum is exchanged between the conduction electrons and the localized electrons, the magnetization can be switched.

The detailed action of the dissipative torque $T_{\rm I}$ is actually complicated since it is easily seen from Fig. 14.7 that $T_{\rm I}$ may actually also point in the same direction as $T_{\rm D}$, depending on the orientation of S_1 . The important fact is that the precession angle of S_2 about the anisotropy axis is *very small*, as shown in Fig. 14.7. While the torque $T_{\rm D}$ just drives S_2 toward $H_{\rm ani}$, and

⁸One may also understand this rotation by the addition of the scattered minority component of S_1 to the density S_2 of the ferromagnet, as shown in Fig. 14.6.

becomes zero as soon as S_2 and H_{ani} are aligned, the torque T_I does not stop when S_2 and H_{ani} are parallel and therefore in all cases eventually drives S_2 away from H_{ani} . In this sense, it always has the opposite effect as the torque T_D , justifying the name "negative damping torque".

Slonczewski [84] has given the following expression for the negative damping torque $T_{\rm I}$,

$$\boldsymbol{T}_{\mathrm{I}} = g(\theta) \frac{\hbar I}{2eS_1 S_2^2} \, \boldsymbol{S}_2 \times (\boldsymbol{S}_1 \times \boldsymbol{S}_2) \,. \tag{14.34}$$

Note that the torque has the dimension of energy.⁹ Here $g(\theta)$ $(g \ge 1)$ is a dimensionless scalar function of the angle θ between S_1 and S_2 , and I is the injected electron current. The torque T_I vanishes when $\theta = 0$ or $\theta = \pi$. However, it develops as soon as S_1 or S_2 moves out of the unstable antiparallel initial configuration, for instance by thermal excitation. As the injected electrons traverse F_2 , the spins of the injected electrons again tend to come out of phase and finally the spin torque averages to zero after a characteristic length which is estimated to be ≈ 10 nm. The damping torque T_I may thus act over a somewhat larger distance compared to the NEXI-torque [752].

Berger [85] has derived an equation for the spin torque that has the same direction $S_2 \times (S_1 \times S_2)$ but specifies in detail how spin injection can induce the uniform precession mode needed for reliable deterministic switching of the magnetization in F₂. His equation for the spin-current induced torque density (see footnote 9) is,

$$\boldsymbol{T}_{\mathrm{I}} = \alpha_{\mathrm{s}}(\vartheta) \, \frac{\Delta \mu + \hbar \omega}{\hbar S_1 S_2} \, \boldsymbol{S}_2 \times (\boldsymbol{S}_1 \times \boldsymbol{S}_2) \, . \tag{14.35}$$

Here $\alpha(\vartheta) \ (> 0)$ is a dimensionless function similar to the Gilbert damping parameter α introduced in Sect. 3.6.2. It depends on the angle ϑ between S_2 and the easy direction of magnetization in F_2 , i.e., the anisotropy axis along \boldsymbol{H}_{ani} , as shown in Fig. 14.7. $\Delta \mu = \mu^{\min} - \mu^{\max}$ is the difference in the chemical potential between minority and majority spins of Sect. 14.1.1, so that $\Delta \mu$ is proportional to the current of injected minority spins.

The new additional term $\hbar \omega$ is due to the stimulation of spin flips. This term appears if we assume that minority electrons are not only preferentially absorbed but that, in addition, they may undergo spin flips to majority states. This process can be added to Fig. 14.6, as illustrated in Fig. 14.8.

In particular, an energy $\hbar\omega$ can be gained through spin-flip transitions from the minority to majority channel if $|\Delta\mu| > \hbar\omega$. It is envisioned that the shown spin flip from minority to majority states generates a spin wave that leads to the precession of S_2 about the anisotropy field of F_2 . In the reverse process a spin wave can be absorbed. Because the anisotropy field is of order

⁹ Slonczewski and Berger define the vectors S_i (i = 1, 2, 3) as spins with units $[\hbar]$, while we have defined them as spin densities with dimensions $[\hbar/\text{volume}]$. This does not matter for (14.34) but the torque in (14.35) in our case corresponds to a torque density.

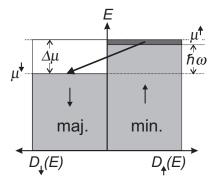


Fig. 14.8. Spin dependent density D(E) of states near the top of the filled *s*-*p*-states in a ferromagnet at T = 0, in response to the injection of minority (spin up) spins. The injected spins cause a spin dependent difference of the chemical potential as illustrated in Fig. 14.6. The minority spins may gain energy by flipping their spin as long as $|\mu^{\uparrow} - \mu^{\downarrow}| > \hbar\omega$. The shown transition generates a magnon of energy $\hbar\omega$

0.1 T, the corresponding resonant precession has a frequency of about 10^9 Hz according to (3.33), corresponding to an energy of $\hbar\omega_{\rm A} \simeq 10^{-5}$ eV. The energy gained in the spin flip is added resonantly to the precessing S_2 , thereby enlarging the angle ϑ that S_2 encloses with the easy axis of magnetization.

Berger calls this process *SWASER*, short for "spin wave amplification by stimulated emission of radiation" because it is analogous to the principle of a laser but functions with spin waves instead of photons. It can occur as soon as the injected electrons experience the exchange coupling to S_2 , that is close to the interface. The process enhances the thermally excited precession of S_2 in the uniform mode and therefore can avoid the losses in the spin torque due to excitation of the higher spin wave modes. Note that at room temperature this condition is not well defined since the thermal spread of $E_{\rm F}$ is much larger than $\hbar\omega$.

We can summarize this section as follows.

Spin injection into a ferromagnet may lead to two types of torques on the spin density S_2 of the ferromagnet:

• The NEXI torque T_{nex} originates from the precession of the injected spin density S_1 about the spin density of the ferromagnet S_2 .

• The negative damping torque T_{I} is due to preferential scattering of minority conduction electron spins S_{1} into minority *d*-states S_{2} . This initiates excitation of the magnetization M_{2} and may lead to its switching.

The two types of torques may be formally added to the precessional and dissipative terms of the LLG equation, respectively. An anatomy of spintransfer torques and unresolved controversies have been given by Stiles and Zangwill [753].

14.2.2 Switching of the Magnetization with Spin Currents: Concepts

The most interesting possible application of spin injection appears to be switching of the magnetization into the opposite direction as needed, for example, in magnetic random access memories or MRAMs. As the magnetic bits become more densely packed, the switching of selected bits by Oersted fields becomes increasingly difficult since they will also affect neighboring bits, and such "cross talk" becomes a problem. In contrast, the exchange fields activated by spin injection can be directed and confined to the exact magnetic cell location where they are needed. Also, simple scaling arguments show that because of the strong and short range exchange interaction, spin injection becomes increasingly advantageous with decreasing cell size.

The main task to achieve reliable, deterministic and energy-economic switching of the magnetization requires the avoidance of excitation of higher spin wave modes. This is illustrated in Fig. 14.9, which compares the uniform precession mode, where the spins precess in unison about the anisotropy field of the ferromagnet, with the case of a higher spin wave mode, where the magnetization becomes "fractured". The uniform precession mode conserves $|S_2|$ while the higher spin wave modes decrease the average value of $|S_2|$.

We have seen that the different spin torques are prone to come out of phase in different parts of the sample, necessarily leading to the excitation of higher spin wave modes. This might look like an increase in *spin temper*-

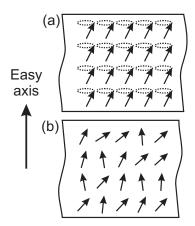


Fig. 14.9. (a) Motion of the spins in the uniform precession mode. The excitation of this mode involves only anisotropy energy. The magnetization switches direction when this mode is highly excited (see Sect. 11.5.2). (b) Snapshot of the moments in the presence of higher spin wave modes. Such modes may be due to inhomogeneous dipolar fields or to the much stronger exchange fields. The excitation of these modes requires additional energy. It also leads to a decrease of the average magnitude of the magnetization, and corresponds to spin de-phasing

ature, although one has to be aware that the spectrum of thermally excited spin waves is quite different from the spectrum of spin waves excited in spin injection. Unwanted spin waves can also be excited when the sample magnetization is not uniform due to surface or edge-induced magnetic structures such as shown in Fig. 13.17, or due to the action of the Oersted field connected with the injected current (see Sect. 15.6.3). The spin wave theory for the dynamics induced in spin injection has been studied theoretically by Rezende and coworkers [754].

Spin switching requires the injection of very high current densities, of order $j \sim 10^{12} \text{ Am}^{-2}$. We can estimate the angular velocity with which S_2 moves through the action of NEXI-torques by applying (14.32). NEXI-torques are due to the elastic exchange interaction, that is they leave the magnitude of S_1 and S_2 constant. For a fully polarized beam these magnitudes are proportional to the number density of injected spins n_e and the number density n_A of atomic spins. Denoting the angular velocity of S_1 in the exchange field by ω , we can obtain the angular change of S_2 from (14.32) according to

$$\frac{\partial \varphi}{\partial t} = -\frac{S_1}{S_2}\omega = \frac{n_{\rm e}\omega}{n_{\rm A}} \ . \tag{14.36}$$

To excite S_2 out of its equilibrium direction by a reasonable angular rate $\partial \varphi / \partial t$, we must have $n_e \approx n_A$. This obviously requires very high current densities. With $\omega / v = \overline{\varphi}$ we see that the measurement of the specific precession angle $\overline{\varphi}$ of S_1 defined as the precession angle per length of path makes it possible to determine the rate at which the homogeneous precession of S_2 is excited with NEXI-torques. By use of (14.36) we obtain [602]

$$\frac{\partial \varphi}{\partial t} = \frac{P \, j}{e \, n_{\rm A}} \,\overline{\varphi} \,. \tag{14.37}$$

Here P (= $2evS_1/\hbar j$) is the degree of polarization of the injected electrons, and the specific precession angle $\overline{\varphi}$ has been measured for Fe, Co and Ni [602]. With a current density of $j = 10^{12}$ A m⁻², just below the electro-migration limit, and with the highest possible polarization P = 1, we obtain from (14.37) a precession frequency $\partial \varphi / \partial t$ of the magnetization in F₂, which is equivalent to application of an external field of $H \sim 10^5$ A m⁻¹ (or about 1,000 Oe). This is the right order of magnitude to explain the experimental observations.

Similar motions of S_2 are expected with the effective torque T_I . However, the measurement of the motion of S_1 has only been achieved so far for ballistic electron injection at energies of 7 eV above E_F [602]. At lower electron energies applicable to solid state spin injection the exchange interactions, although not known with any certainty yet, are likely to be more favorable (see Fig. 12.18).

Finally, it is necessary to discuss that spin switching occurs only when the injected current density j surpasses a certain threshold. This limit arises in part from the spin lattice relaxation that we have neglected so far. The homogeneous precession of S_2 about the anisotropy axis induces a damping torque

 $T_{\rm D}$ according to (3.39) which is due to spin-lattice relaxation. The spin injection torque $T_{\rm I}$, which causes a rotation *away from* the easy axis can overcome the typical motion of S_2 towards the easy axis when the condition $T_{\rm I} > T_{\rm D}$ is satisfied. This establishes a threshold value for the switching current because in switching, S_2 has to move away from the easy axis.

The normal damping torque $T_{\rm D}$ can be determined in ferromagnetic resonance (FMR), typically yielding very small values for the phenomenological damping parameter $\alpha \leq 0.1$. However, in FMR the precession angle is very small, $\vartheta \leq 1^{\circ}$. For the large angles $\vartheta \sim \pi/2$ necessary for switching, α increases significantly due to coupling of the homogeneous mode with spin wave modes [754, 755], generating an additional effective damping that has to be overcome by $T_{\rm I}$. Therefore, the threshold of the switching current is affected by the excitation of higher spin wave modes in addition to the spin lattice relaxation determined in FMR. Recently, Buhrman and collaborators [756] have been able to measure directly the relaxation of M_2 after field pulse excitation by simultaneously sending a spin polarized current through the sample. The damping of the precession was found to decrease linearly with the intensity of the injected spin currents, thus verifying the basic concept, at least at the low temperature, 40 K, of the experiment. By applying higher current densities, the generation of steady state precession has been demonstrated, directly showing the existence of negative damping.

14.2.3 Excitation and Switching of the Magnetization with Spin Currents: Experiments

The high current densities that are necessary to excite the magnetization dictate the layout of the experiments. In practice, one needs lithographically manufactured strip-lines that lead the current to the nanoscale spin injection structure. Furthermore, due to the rapid de-phasing of the current induced torques, the magnetic depth over which excitation of homogeneous precession is expected is within a few nanometers of the point of injection. This has the overall consequence that spin injection experiments require magnetic samples that not only have lateral nanoscale dimensions but are very thin, as well.

Most investigators have created a nanoscale current channel either by using a fine tip that contacts a surface [121, 757] or by lithographically building a pillar structure $F_1/N/F_2$, where the layers F_i are ferromagnetic and N (e.g., Cu) is non-magnetic [758–760]. The structure of a typical spin injection sample is shown in Fig. 14.10. It consists of a lithographically manufactured pillar with a diameter around $\simeq 100$ nm that is composed of different thin layers. Of particular importance are the ferromagnetic layers, the fixed "polarizer" F_1 , and the second decoupled magnetic layer, the "sensor" F_2 . The magnetization direction of the sensor layer is manipulated by spin currents.

In principle, the small pillar diameter should help avoid magnetic domain formation and reduce the effects of the competing Oersted fields, that necessarily accompany current flow. It is important to realize that Oersted fields

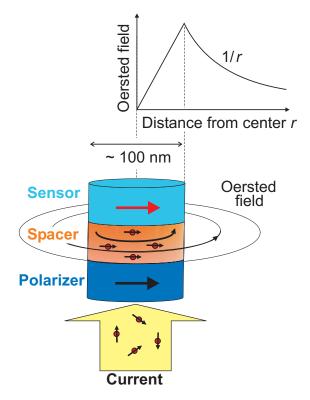


Fig. 14.10. Schematic of a typical spin injection structure and the associated spin and charge effects arising from current flow. A spin polarizing ferromagnetic layer, the "polarizer", shown in dark blue polarizes the current flowing through it. It has a fixed magnetization direction, in practice accomplished by exchange biasing. The spin polarized current then enters a second ferromagnetic layer, the "sensor", shown in light blue. The torques associated with the spin injected current can lead to a switching of the sensor layer. The spin current is accompanied by a charge current which gives rise to Oersted fields inside and outside the pillar, as indicated. The circular Oersted fields are largest at the perimeter of the pillar

do not only surround a wire on the outside but are present on the inside of the wire, as well. According to (2.7), the Oersted fields inside the wire are zero only at the center and have a maximum value at the perimeter of the wire, as illustrated in Fig. 14.10. The charge current generates circular magnetic field lines around the center. Micromagnetic computations show that even with samples as small as 100 nm, the Oersted field may play a crucial role in promoting the switching [761, 762].

Because the diameter of the pillar is so small, it cannot be seen by magnetooptical Kerr microscopy. The current induced static or dynamic changes of the magnetization in the sensor layer have therefore mostly been observed by measuring the perpendicular magneto-resistance CPP-GMR (see Sect. 14.1.4). Only recently have they been imaged by X-rays [763] which have confirmed the important effects of the Oersted fields (see Sect. 15.6.3).

In numerous experiments using CPP-GMR, the basic theoretical predictions, namely excitations of spin waves and switching of the magnetization through the injection of a spin polarized current have been verified with a variety of different metallic ferromagnets and experimental configurations [764–766]. There is no reasonable doubt that the original proposals by Slonczewski and Berger [84,85] can be put to work.

The pillar-structure shown in Fig. 14.11 is an example for a working experimental configuration. With this type of structure, reliable switching of the magnetization in the thin Co film has been induced by an electron current flowing in either direction [760]. The spectrum of spin wave oscillations excited by the injected current has been measured and analyzed in detail, as well [767].

The ferromagnetic films in this work are made of Co, which is probably in the fcc-structure as it has been deposited on a Cu substrate. Co is a favorable metal for spin switching because it exhibits a large spin selective scattering as evidenced by the failure to emit minority spins in threshold photoemission, as discussed in Sect. 13.2.1. Large spin selective scattering in turn generates a large volume density of the torque $T_{\rm I}$. The magnetization M_1 in the polarizer Co-layer F_1 is fixed in direction by a higher magnetic anisotropy while M_2 can move more readily out of its easy axis determined by a shape anisotropy created by an oval pillar shape.

Most remarkable is the fact that the magnetization in F_2 may be switched in both directions. This is evident from the hysteresis loop shown in Fig. 14.12, taken from the work of Albert et al. [760].

Starting from the lower resistance state of parallel alignment of F_1 and F_2 , one may switch F_2 into an antiparallel alignment by electron flow from F_2 to F_1 . This corresponds to a positive bias in Fig. 14.11 and positive current values

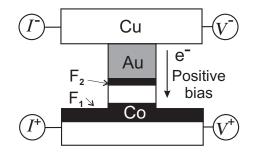


Fig. 14.11. Experimental configuration used in spin switching [760]. The thicker Co layer at the bottom is the ferromagnet F_1 serving as the source of the spin polarized current. The switching of the second Co layer F_2 , separated by a thin Cu layer, is observed by measuring the magneto-resistance of the pillar with the four-point method

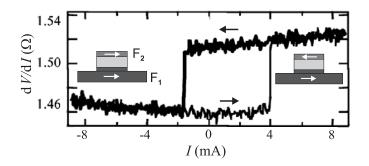


Fig. 14.12. Resistivity versus the injected current [760]. The polarizer layer F_1 and sensor layer F_2 and their magnetization directions are shown for clarity. The distinguishing feature of spin switching is the asymmetric shift of the hysteresis loop on the current axis

in Fig. 14.12. This is explained by spin dependent reflection of the electrons by the film F_1 . Preferentially, electrons whose spin direction does not match the direction favored by F_1 , will be reflected and they will lead to a reversed spin polarized current which re-enters F_2 and induces the switching of M_2 .

Starting from the higher resistance state of antiparallel alignment of F_1 and F_2 , one may switch F_2 into parallel alignment by sending electrons from F_1 to F_2 , corresponding to negative current values in Fig. 14.12. The figure shows that the threshold of the switching-current depends on the direction in which the current flows. This is expected, because $g(\theta)$ in (14.34) is larger for $\theta \cong \pi$ compared to $\theta \cong 0$, hence it is easier to switch from the anti-parallel to the parallel directions of M_1 and M_2 .

It should also be noted that perfect transmission or perfect reflection of the electrons at the N/F interface has been assumed in the derivation of (14.34). This does not correspond to reality. In fact, direct reflection experiments conducted with beams of polarized electrons demonstrate that even with total reflection, the spin may move by a large amount. Hence it changes direction even in total reflection at a band gap, as discussed in Sect. 13.3.2. Overall, we expect that a larger current must flow to induce the back-switch.

Other scenarios may be found in practice. For example, magnetostatic coupling may exist between the two layers, as illustrated in Fig. 13.16, which might favor antiparallel alignment of M_1 and M_2 . Periodic exchange coupling through the metal spacer layer may also exist but this is weak with polycrystalline samples. Any such unidirectional coupling may be detected by recording GMR hysteresis loops in an external magnetic field. The shift of these loops on the *field axis* discussed in Fig. 13.18 would reveal such coupling if present.

In the absence of coupling between F_1 and F_2 , the shift of the loop on the *current axis* is proof that a spin polarized current has been injected, because only a current of axial symmetry can prefer one magnetization direction. If the

switching was done by the ohmic heat of the current, it would not depend on the direction of the current. The Oersted field generated by the injected current averages to near zero over the plane of the sample in the CPP-geometry since it favors the generation of a closed flux structure, giving no GMR signal. Yet the effects of the Oersted field are not negligible as they seem to promote the process of switching [762, 763].

Because of the small size of the magnetic structures, thermal fluctuations also play a substantial role in their switching behavior. Most authors assume that the macrospin approximation is valid, i.e., that switching does not occur by domain wall motion. Such switching must then be described in terms of thermally activated switching over an energy barrier [541]. As a result of the thermal fluctuations, switching may depend on the time during which the current flows and, for a given time of spin injection, may occur only with a certain probability, instead of being deterministic with a sharp threshold of the switching current [760].

The degree of randomness of the switching is enhanced when higher order spin waves are excited. This amounts to an increase of the effective magnetic temperature, although one needs to use the term "temperature" with care since the spectrum of these spin waves may be quite different from the spectrum in thermal equilibrium. It has indeed been found that the "effective magnetic temperature" inferred from the switching probability over the energy barrier is higher than the lattice temperature and depends on the intensity of the injected current [768]. Even stochastic switching of the magnetization back and forth has been found with higher injected currents [768, 769]. This might be explained by the tendency of spin-torques to get out of phase over the volume of the sample combined with the fact that large angle precession of the magnetization is prone to induce self-oscillations and chaos in the magnetic excitations due to effects of nonlinear coupling discussed in Sect. 15.6.

Spin polarized electrical currents in ferromagnetic metals interact also with domain walls. The transport of spin angular momentum with the current flow can give rise to the motion of a magnetic domain wall traversed by an electric current. This long standing research topic has been revived by the observation of spin switching, with studies of the separate effects caused by the charge and spin currents. The gradual change of the magnetization direction in a domain wall, combined with relaxation of the spins into the direction of the local magnetization, results in a reduced volume density of the spintorques and renders the theoretical treatment more difficult. However, due to the experience gained from spin switching experiments, progress in the understanding of current induced domain wall motion has been made [770–774]. Current induced domain wall motion has been proposed for magnetic memory applications in which a domain wall is moved reversibly between two constrictions acting as pinning centers.

14.3 Spin Currents in Metals and Semiconductors

In semiconductors, the dynamics governing perturbations of the spin polarization is much different compared to metals. In particular, it is much slower and consequently it is understood in much more detail. We shall discuss here only some of the most basic aspects relevant to spin currents in semiconductors. For detailed discussion of electron spin relaxation in semiconductors via electron-hole and electron-nuclear spin interaction we refer the reader to [346]. Other aspects related to semiconductor based spin electronics are discussed in refs. [46, 78, 115]. The long history of the *Hall effect* and the spin contributions in the anomalous Hall effect and the spin Hall effect have been reviewed by Inoue and Ohno [775].

An electron close to the bottom of the conduction band of a semiconductor may scatter only on states introduced by doping but not with bulk band states such as the fully occupied valence states. This arises because of the presence of the energy gap. There is generally no final state available into which the conduction electron can settle once it has lost energy. The extremely fast electron-electron scattering is therefore absent with low energy electrons in the conduction bands of semiconductors. As a consequence, the lifetime of electronic states is orders of magnitude longer in semiconductors compared to metals. This has led to the possibility of coherently manipulating the spin states in the conduction states, and forms the basis of futuristic concepts such as spin and semiconductor based quantum computers [46, 78, 115]. For illustration we give in Table 14.2 some approximate numbers for the spin lifetimes τ_{se} in metals and semiconductors. Note that, in general, τ_{se} may include loss of spin polarization by both spin flip scattering and de-phasing, that is it includes contributions from the characteristic spin-flip time τ_1 and de-phasing time τ_2 , discussed in Sect. 8.6.2.

We have seen in Sect. 14.1.5 that the precession of the spins in metals can be detected electrically in lateral mesoscopic spin valves. The lifetime of the spins τ_{se} is however so short that only one cycle of the precession can be distinguished with spin currents injected into, e.g., Al [738]. In contrast,

Table 14.2. Approximate spin diffusion lengths Λ and associated spin diffusion times or lifetimes τ_{se} of electrons in metallic ferromagnets, metallic nonmagnets and semiconductors at liquid He temperature.^{\sharp}

	ferromagnet	nonmagnet	semiconductor
Λ	$50\mathrm{nm}$	$1\mu{ m m}$	$10\mu{ m m}$
$\tau_{\rm se}$	$1\mathrm{ps}$	$50\mathrm{ps}$	$10\mathrm{ns}$

^{\$}Values for ferromagnets and metallic nonmagnets are those given in Sect. 14.1.3 for Co and Cu. In semiconductors the quantities are strongly dependent on doping as discussed in the text. in semiconductors time resolved Faraday rotation (TRFR) can be used to investigate the time evolution of a spin population, and dozens of precession cycles can easily be resolved. We shall describe how the de-phasing time τ_2 of an ensemble of polarized electrons in the conduction bands of a semiconductor such as GaAs can be obtained from these experiments. The de-phasing time τ_2 is critical to applications requiring coherent manipulation of spin states such as all optical switching, see Sect. 15.6.4, or quantum computing [78].

In Sect. 13.2.2 we have discussed the experiments aiming at injection of spin polarized currents from a ferromagnetic source into a semiconductor such as GaAs. It evidently requires the presence of a tunneling barrier or the elusive half metallic ferromagnet at the interface. Let us now assume that such injection has been achieved, or alternatively that spin polarized electrons have been produced in the conduction bands of a GaAs-type semiconductor by optical pumping as explained in Sect. 8.2. In practice, measurements of τ_2 are conveniently done by generating the initial population of spin polarized electrons in the conduction bands with a circularly polarized pump pulse with the photon energy tuned to the absorption edge of the semiconductor. The pulse length is of the order of 100 fs, thus defining a sufficiently sharp moment in time when the precession of the spins starts. In spin injection, one would have to apply a sharp voltage pulse which is still difficult because of electromagnetic inertia. On the other hand, with laser excitation one knows the time zero at which an ensemble of about 10^{15} electrons/cm³ has been generated in the conduction band states with spin polarization P parallel to the beam of the pump pulse.¹⁰

The spins s of the electrons will now start to precess about the magnetic field H applied perpendicular to the pump beam as indicated in Fig. 14.13. The precession can be monitored by the time delayed probe pulse which is linearly polarized. One measures the angle φ of the plane of polarization after the probe beam has traversed the semiconductor. This is commonly called "Faraday rotation in the Voigt geometry" as opposed to regular Faraday rotation in which the light beam is parallel to the magnetic field. When the spin polarization vector P_{\perp} of the ensemble of electrons is parallel to the probe beam, the angle φ of the Faraday rotation will have one particular sign, but the sign will change when P_{\perp} has precessed by 180° and thus points into the opposite direction. The magnitude of the angle φ of rotation is proportional to P_{\perp} .¹¹ By variation of the time delay between pump and probe pulse, one will observe periodic changes in the sign of φ yielding the precession frequency $\omega = g\mu_{\rm B}H/\hbar$ where g is the g-factor of electrons in the conduction band. Due to the effective mass of the electrons in the band states, g can be quite dif-

¹⁰The optically excited spins result in a very small transient magnetization of only about 10^{-7} T or $10^{-7} \mu_{\rm B}/\text{atom}$, and it is remarkable that this can be probed by the Faraday effect.

¹¹A reduction of φ could also be due to relaxation of P into the direction antiparallel to H requiring a change in the population of the two spin states. The experimental τ_2 is thus a lower bound on τ_2 .

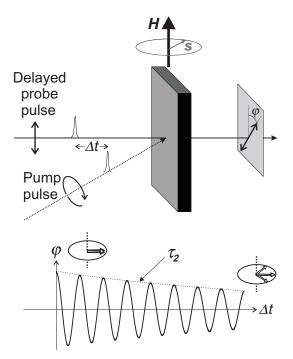


Fig. 14.13. Principle of a pump-probe experiment to measure the spin de-phasing time τ_2 in a semiconductor to which a magnetic field H is applied. The circularly polarized pump pulse generates an ensemble of electrons with spin polarization parallel or antiparallel to the pump beam, while the precession of the spin polarization is detected by measuring the angle φ of the Faraday rotation in the Voigt geometry with the time delayed linearly polarized probe pulse. The lower graph shows the decay of the TRFR amplitude with increasing delay Δt between pump and probe pulse from which the spin de-phasing time τ_2 is obtained

ferent from 2. The amplitude of φ decreases yielding the de-phasing time τ_2 according to:

$$\varphi = A e^{-\Delta t/\tau_2} \cos\left[\frac{g\mu_{\rm B} H \Delta t}{\hbar}\right] , \qquad (14.38)$$

where A is the Faraday constant. Thus fitting the data to (14.38) yields the g-factor and the de-phasing time τ_2 . The free carrier spin lifetime turns out to be generally much longer compared to metals as expected, but it also depends somewhat surprisingly in a nonmonotonic fashion on the carrier density. With n-type doped GaAs at T = 5 K and $H = 3 \times 10^6$ A m⁻¹, corresponding to B = 4 T, the largest value of $\tau_2 = 10$ ns is observed at a carrier density of $n = 10^{16}$ cm⁻³. At the same carrier density a metal-insulator transition also occurs but the correlation of the two observations is not yet understood [78]. With n-type doping of $n = 5 \times 10^{18}$ cm⁻³, the relaxation is much faster, corresponding to $\tau_2 = 40$ ps. The range in lifetimes thus spans three orders of

magnitude, depending on the doping. The dependence on doping seems to be general as the same trend is also observed with GaN and ZnSe. In addition to the variance of τ_2 with doping, a change in the precession frequency ω occurs, as well. This is due to the change in the effective mass of the electrons, hence a change of the g-factor, since the absorption band edge shifts with doping.

Faraday rotation experiments also show that clouds of spin polarized electrons can be laterally transported over distances exceeding 100 μ m without substantially disturbing their spin coherence. This is possible by applying an electric field and is due to the rather weak coupling between spin and orbital motion in the conduction bands of some semiconductors derived from *s*-like atomic orbitals, for instance *n*-type GaAs wafers doped with Si. This is the basis of the transport of coherent spin information across semiconductor devices. For more details the reader is referred to the specialized literature such as [46, 78, 115]. Spin dynamics in the magnetic metals will be the topic of Chap. 15.

It is obviously possible to treat the magnetic metals in good approximation also as spin-1/2 systems. Yet in contrast to the slow spin dynamics associated with nuclear spins or spins in semiconductors, the spin dynamics in magnetic metals is very fast. It has therefore become feasible only recently to distinguish experimentally between the two relaxation times τ_1 and τ_2 . For instance, as illustrated in Fig. 15.12 below, the relaxation of the magnetization into the direction of an external field is actually given by a change in the *occupation* of the two spin states, that is we have $\tau_{se} = \tau_1$. This important relaxation mechanism in magnetism is described by the damping torque T_D of the Landau–Lifshitz equation with the assumption that the magnitude of the magnetization remains constant.

However, it is also possible that spin waves of various frequencies are excited in magnetization precession due to the Suhl-instability [776], discussed in Sect. 15.6.1 below, or other so far unknown mechanisms. This disturbs the *phase relationship* between the precessing spins as illustrated in Fig. 14.9 and these processes are governed by τ_2 . The de-phasing is observed as a surprisingly wide distribution of the switching fields in the precessional switching mode of perpendicular high density magnetic media as discussed in Sect. 15.6.2 below. The decrease of the space-averaged magnitude of the magnetization occurs on a time scale that is different from the one of the relaxation into the field direction as quantified in the model calculation displayed in the inset of Fig. 15.26. Perhaps, as ultrafast magnetization dynamics experiments become more sophisticated, one will be able to discuss the spin dynamics in the ferromagnetic metals also in terms of τ_1 and τ_2 .

14.4 Spin-Based Transistors and Amplifiers

The first generation of spintronics devices are the GMR sensors of Sect. 14.1.4 and the Magnetic Tunnel Transistor of Sect. 12.6.2. As mentioned in the intro-

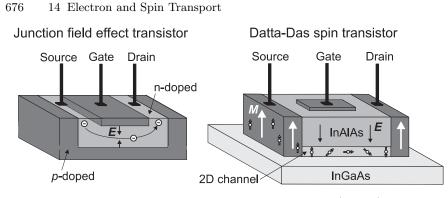


Fig. 14.14. Left: Conventional junction field effect transistor (J-FET) consisting of a channel of n-type material in a substrate of p-type material. The electron flow from the source to the drain is controlled by the charge on the gate. By increasing the negative voltage to the gate one can increasingly "pinch off" the current flow, and vice versa. Right: In the proposed Datta–Das spin transistor [116] one spin-polarizes the current by transmission through a magnetically aligned source material. The drain consists of the same material with a parallel alignment of the two magnetizations, as shown. By using a InAlAs-InGaAs heterostructure one creates a two-dimensional electron transport channel between the source and drain which, as in the J-FET, may also be controlled by a voltage on the gate. This control is possible through the Rashba effect [150-152] which is based on the fact that in the rest frame of the traveling electrons the electric field also has a magnetic field component. The magnetic field due to the applied electric field leads to a controllable change in the electron spin direction upon arrival at the drain. The transmission into the magnetized drain depends on the relative orientations of the drain magnetization and the direction of the spin polarized electrons

duction, a second generation of spintronics devices aims to couple magnetic materials with semiconductors [114, 115]. An example of such a hybrid structure is the concept of a spin-based transistor, proposed by S. Datta and B. Das in 1989 [116], which is illustrated in Fig. 14.14 together with a conventional junction field effect transistor (J-FET).

Unlike metals, semiconductors offer the opportunity to control the flow of a large number of charges by a few that are strategically placed, similar to a gatekeeper that regulates the flow of traffic. In the *junction field effect transistor* (J-FET) shown on the left of Fig. 14.14, for example, draining nelectrons from the gate may increase the flow of electrons from the source to the drain by 10 times n-that means the device has "gain". A similar effect, can in principle be obtained by the *spin transistor* shown on the right of Fig. 14.14, which makes use of the Rashba effect [150–152]. The devices are explained in the caption. Note that both the conventional J-FET and the proposed spin-transistor are *charge amplifiers*. Also, it is important to realize that the Datta–Das transistor is limited by the performance of the ferromagnetic spin filters. The development of a *spin current amplifier* has remained even more elusive than the experimental demonstration of the proposed charge-amplifying spin transistor. The spin current amplifier is a prerequisite for all semiconductor based spintronics since in practice the spin signal would severely deteriorate after only a few operations. If it could be invented, a spin current amplifier would also dramatically improve all spin polarized electron spectroscopies and microscopies.

In order to demonstrate the requirements for a spin current amplifier we define the spin current in analogy to the charge current as the spin angular momentum in units of $\hbar/2$ that flows per time interval Δt through a cross section, yielding $I_{\rm S} = PI$ where I is the charge current and P its degree of spin polarization. Let us assume an incident electron beam with intensity I_0 and with a spin polarization P_{ε}^{0} relative to a quantization direction ξ in space. With a spin current amplifier one would like to amplify the spin polarization P_{ξ}^{0} so that the output beam has a spin polarization $P_{\xi} > P_{\xi}^{0}$. However, in the process we also need to consider the transmitted number of electrons or the intensities I_0 before and I after the amplifier. It would not help us if the output would be perfectly polarized yet we had lost most of the intensity. According to (8.16) the total intensity $I = I^{\uparrow} + I^{\downarrow}$ actually enters into the definition of the spin polarization P_{ξ} , and the product $I P_{\xi} \propto n^{\uparrow} - n^{\downarrow}$ is actually what we care about since it is the difference intensity of spins polarized parallel and antiparallel to our quantization axis ξ . This shows that it does not help to simply add unpolarized electrons to the spin current since $I_{\rm S} = PI \propto n^{\uparrow} - n^{\downarrow}$ remains constant. Therefore we require for a spin current amplifier that $I P_{\xi} > I_0 P_{\xi}^0$.

There is another important requirement. If the input is mostly "spin-down" we want the output to be an enhanced "spin-down" signal and similarly for "spin-up". If the input beam is unpolarized we want it to stay that way. This is illustrated in Fig. 14.15, using three examples of a four-electron incident beam with spin polarizations $P_{\xi} = +(1/2)$, $P_{\xi} = 0$, and $P_{\xi} = -(1/2)$, respectively.

In all cases we have assumed that $I = I_0$ for simplicity, so that the action of the spin amplifier lies entirely in the enhancement of the spin polarization of the incident beam. In the middle we have shown the case where the spin polarization is zero along the vertical quantization direction, and in this case the output beam is required to stay unpolarized. This case is actually quite interesting and important. It demonstrates that we cannot use a spin filter as an amplifier since it would create a spin polarized output, as discussed in Sect. 8.4.3.

We can summarize the requirements for a spin current amplifier as follows.

A *spin current amplifier* needs to first sense the incident spin polarization, especially its sign.

It must then enhance the *spin current*, defined as the product of spin polarization and intensity.

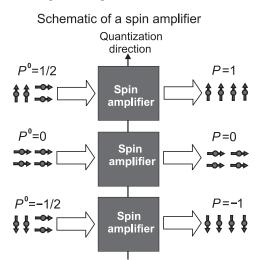


Fig. 14.15. Function of a spin current amplifier, illustrated by three simple examples of incoming beams. The amplifier, shown as a black box, needs to first sense the sign and amplitude of the incoming spin polarization relative to a quantization direction in space. It then amplifies the product of the incident intensity and spin polarization. For simplicity we have assumed that the intensity remains unchanged. If the incoming beam is unpolarized relative to the quantization axis, as shown in the middle panel, the output is required to remain unpolarized

With photons which are bosons it is possible to construct such a spin current amplifier. For instance, if one photon is brought into the resonating cavity of a laser, it can stimulate the production of more photons of exactly the same energy and polarization. With electrons, one would need a system that can be triggered by the incident spin polarization. An example is a ferromagnet just above its Curie temperature. Its moments may be induced to align into the proper magnetization direction if one could raise the Curie temperature by the incident spin polarized beam. Another example is a ferromagnet with the magnetization in the unstable hard direction. Again, the incident spin polarized electrons would trigger a switch of the ferromagnet into the desired magnetization state. Alternatively, if the production of secondary electrons depended on the spin of the primary electron, one could construct a spin current multiplier by increasing both the charge current and the spin polarization. Unfortunately, in the few relevant experiments done so far, one has only found a weak dependence of the spin polarization of secondary electrons on that of the primary electrons [609, 610].

Ultrafast Magnetization Dynamics

15.1 Introduction

The magnetization in a solid reacts to external disturbances such as changes in temperature, magnetic fields, and pressure on many time scales ranging from millions of years in geomagnetism [777] to years in magnetic storage media, milli- and microseconds in AC-transformers, and nanoseconds in magnetic data writing and reading. Magnetization changes on these various time scales and their relation to the size of magnetic structures, domains and domain walls, has been a prominent subject in magnetism because of the numerous applications [54, 778, 779].

Over the last 30 years, the development of magneto-optics with pulsed lasers has opened a new field, *ultrafast magnetization dynamics*. Typically, ultrafast studies employ pulsed lasers for both excitation of the sample and probing the ensuing changes of the magnetization, in so-called pump-probe experiments. Such experiments now have a time resolution below one picosecond (10^{-12} s) , well into the femtosecond (10^{-15} s) range [57]. The timescales in the picosecond and femtosecond range are of great interest because they naturally correspond to important magnetic energies, as illustrated in Fig. 15.1.

The plot utilizes the time–energy correlation t = h/E derived in Sect. 3.7 to link the cycle time t to a characteristic energy E. In particular, we have indicated the ranges of three important magnetic interactions for 3d systems, the magnetic anisotropy with 10^{-6} eV $\leq E \leq 10^{-3}$ eV (see Sect. 7.9), the atomic spin–orbit energy with 10^{-2} eV $\leq E \leq 10^{-1}$ eV (see Sect. 6.4.3), and the interatomic exchange energy of order $E \sim 3 \times 10^{-1}$ eV (see Sect. 11.1.4).

In order to ensure fast and homogeneous deposition of energy with a laser pulse, determined by the optical absorption length of tens of nanometers, the magnetic samples are typically films of nanoscale thickness. If a magnetic field pulse is used for excitation, the penetration depth is determined by the skin effect. Today, structures with nanoscopic dimensions in all three directions are of great interest. The lateral confinement facilitates the interpretation of the dynamics, since typically one starts from a well-characterized

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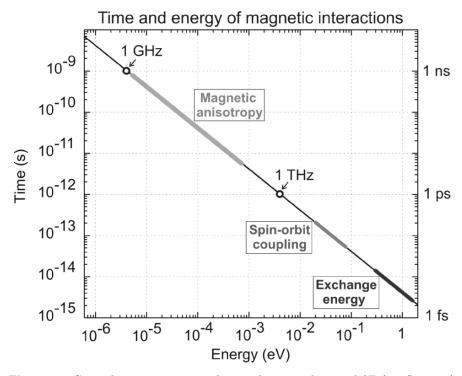


Fig. 15.1. General time–energy correlation plot given by t = h/E (see Sect. 3.7) which allows comparison of results in the frequency and time domains. On the correlation line we have indicated typical ranges for three important magnetic energies and the associated time scales found in the 3*d* transition metal systems

magnetic state such as a single domain or a magnetic vortex state. Studies of ultrafast magnetic dynamics in nanoscopic magnetic bodies have become one of the most exciting topics in contemporary magnetism. They break new ground scientifically and explore length and times scales for tomorrow's magnetic technologies. More generally, they support the demand for "smaller and faster" of our high-tech society. The future development of magnetic recording technology where the quest is for smaller magnetic bits and faster magnetic switching depends to a large extent on the outcome of this research.

While lasers and pump-probe magneto-optics have paved the way for this new field of ultrafast dynamics, the ultimate goal, namely the control of the magnetization on small length scales and short time scales, can only be fully explored by consideration of a bigger picture, illustrated in Fig. 15.2. It involves the coupling of various thermodynamic reservoirs in solids.

A ferromagnetic body can store excitation energy in three different forms: the energy of electrons, the excitation of phonons, and the change of magnetic order, that is the change of the spontaneous magnetization $M_{\rm s}(T)$. In the early laser experiments, the energy was pumped into the electron system through electronic excitations and one then attempted to probe the evolution of $M_{\rm s}$.

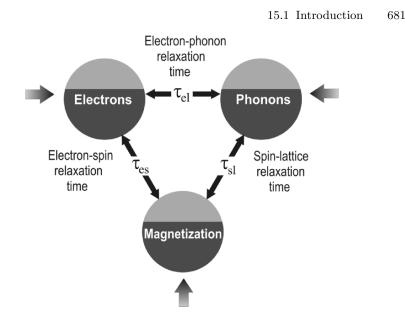


Fig. 15.2. Heat reservoirs in a ferromagnetic metal. All three reservoirs may be separately excited as indicated by *arrows*. Deposition of energy in a specific reservoir initially leads to a nonequilibrium distribution of the excitations, indicated by *two shades*. An effective temporary equilibrium temperature may or may not be reached within one reservoir before it finally equilibrates with the other reservoirs at characteristic times τ_{ij}

This is only one of three possible ways of energy deposition, as indicated by the arrows on the periphery of Fig. 15.2. For example, one may also excite phonons through a pressure or infra-red heat pulse or induce changes of the magnetization itself through a pulsed magnetic field or a spin current. It is of key importance to realize that both *energy* and *angular momentum* need to be exchanged and conserved when the magnetization reservoir is involved.

The field of *ultrafast magnetization dynamics* is concerned with changes induced in M_s as *energy* and *angular momentum* are exchanged within and between the thermodynamic reservoirs of the sample. In practice, one seeks to understand the physical processes and the time constants τ_{ij} responsible for the exchange between the reservoirs.

Of prime importance for magnetization dynamics is of course the magnetization reservoir. Since the essence of magnetization is angular momentum, the flow of angular momentum to and from the magnetization reservoir is of key importance. In particular, the magnetization can only be excited from its equilibrium *direction* and *magnitude* if angular momentum is transferred *into* the magnetization reservoir. After excitation, the magnetization searches for an equilibrium, and this process typically consists of a spiraling of the

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magnetization into the equilibrium easy axis, possibly with a change in direction from its original orientation. We have seen in Sect. 3.6.3, that this process is associated with a relaxation or damping torque so that, again, angular momentum needs to transferred in the process, in this case *out of* the magnetization reservoir.

The essence of *magnetization* is *angular momentum*. The key issues in magnetization dynamics are therefore the processes underlying the change of angular momentum.

In this chapter we will take a look at what is known about the exchange of energy and angular momentum between the three reservoirs. In particular, one may distinguish the general case of energy and angular momentum exchange between the reservoirs from the more specific and technologically important case of *magnetization switching*. The latter must be a controlled, reversible process that allows rotation of the magnetization by 180° . We shall specifically address magnetization switching in Sect. 15.6. In the following we shall start with a more general discussion.

15.2 Energy and Angular Momentum Exchange between Physical Reservoirs

In this section we shall outline the physical concepts associated with energy and angular momentum exchange between the reservoirs in Fig. 15.2. We start with a general thermodynamics discussion and then address the processes from a quantum mechanical point of view using the general energy–time concepts developed in Sect. 3.7. In later sections, experimental results will be presented that address some of the issues raised in our general discussion.

15.2.1 Thermodynamic Considerations

By exciting electron hole pairs with a femtosecond laser pulse, one deposits energy into the degenerate electron gas. Because the specific heat of the degenerate electron gas ($\propto T$) is small, the temperature reached after thermalization of the electronic excitations is high, typically >1,000 K ($\sim 0.1 \text{ eV}$). This means that the electron gas may reach temperatures $T > T_{\rm C}$ after a time of $\approx 100 \text{ fs}$ following the excitation. But the electrons cool quite rapidly to low temperatures by the excitation of lattice vibrations. Temperatures of $T < T_{\rm C}$ are then reached due to the fact that the specific heat of the metallic lattice is large, requiring the excitation of 6 degrees of freedom (DOF)¹ according to

¹A vibration of an atom in the lattice may occur in three directions, and the vibration in each direction contains kinetic as well as potential energy. This yields 6 DOF.

the rule of Dulong–Petit since one typically is above the Debye temperature of the lattice where all lattice DOF are active. It is well established that thermal equilibrium between the electron gas and the lattice is reached within ≈ 1 ps [780].

The question is now how fast can the spontaneous magnetization $M_s(T)$ follow these rapid changes in temperature. At $T < T_{\rm C}$, the magnetic moments are held in one fixed direction in space by the exchange interaction, that is the 3 DOF for the three directions of the magnetic moments in space are frozen. If the solid is heated to $T > T_{\rm C}$, these 3 DOF are activated containing each an energy $k_{\rm B}T/2$ according to the equipartition principle of thermodynamics. We therefore expect that the magnetic part $C_{\rm spont}$ of the specific heat must increase as $M_{\rm s}$ decreases. At $T = T_{\rm C}$, the increase must correspond to $(3/2)k_{\rm B}$ per spin.

In the mean field model, the Weiss molecular field $H_{\rm W}$ is given by the Ansatz $H_{\rm W} = \beta M_{\rm s}$ and the magnetic part of the specific heat $C_{\rm spont}(T)$ is readily calculated. The internal energy U of the solid due to the occurrence of $M_{\rm s}$ is given by

$$U = -\int H_{\rm W} \,\mathrm{d}M_{\rm s} = -\beta \int M_{\rm s} \,\mathrm{d}M_{\rm s} = -\frac{1}{2}\beta M_{\rm s}^2. \tag{15.1}$$

The magnetic part of the specific heat is given by

$$C_{\rm spont} = \frac{\partial U}{\partial T} = -\frac{1}{2}\beta \frac{\partial M_{\rm s}^2}{\partial T}.$$
 (15.2)

Assuming now a spin-1/2 ferromagnet, close to $T_{\rm C}$ the *T*-dependence of the order parameter $M^* = M_{\rm s}(T)/M_{\rm s}(0)$ is given by $(M^*)^2 = 3(1-T^*)$ according to 11.7, where $T^* = T/T_{\rm C}$ is the reduced temperature. Inserting $T_{\rm C}$ from 11.5 and with $M_{\rm s}(0) = N\mu_{\rm B}$ where N is the density of spins one obtains

$$C_{\rm spont} = \frac{3}{2}k_{\rm B}N\tag{15.3}$$

showing that indeed the magnetic heat must jump at $T_{\rm C}$ corresponding to the excitation of 3 DOF. We know already that the mean field cannot describe accurately the magnetic phase transition, because $M_{\rm s}$ is not reduced abruptly to zero at $T = T_{\rm C}$ due to the occurrence of critical fluctuations. Nevertheless, the magnetocaloric experiments exhibit a sizeable spike of $C_{\rm spont}$ at $T = T_{\rm C}$. This shows that heat must flow into the spin system when a sample is heated to $T_{\rm C}$.

In the classic literature on magnetism, the question of how fast thermodynamic equilibrium with respect to $M_{\rm s}$ is reached is not discussed simply because the older magnetic measurements averaged the magnetic state over times longer than 1 ns. Since it is possible today to measure $M_{\rm s}$ much faster this question has become of great interest [781].

Due to the strictly valid law of conservation of angular momentum, one cannot disorder the spin system, however, without simultaneously supplying

angular momentum to the system as well. The consideration of angular momentum transfer between the systems requires a quantum mechanical look at the problem.

15.2.2 Quantum Mechanical Considerations: The Importance of Orbital Angular Momentum

A good starting point for a quantum mechanical discussion are the processes that follow the excitation of a magnetic system by an external magnetic field pulse. When the magnetization is excited by such a pulse, which we shall assume to be strong and ultrashort (i.e., much faster than all processes that follow the excitation), the magnetization $M_{\rm s}$ moves out of equilibrium by precession about the axis defined by the *external field*. The laws of inertia are satisfied in the magnetic excitation because the source of the magnetic field pulse experiences a torque opposite and equal to the precessional torque deposited in the magnetic system. Angular momentum as well as Zeeman energy is thus directly deposited into the spin system.

After the field pulse is terminated, $M_{\rm s}$ starts a precession about the *anisotropy axis*. The damping of this precession of $M_{\rm s}$ about $H_{\rm ani}$ tells us how fast the spin system returns to its equilibrium. The flow of energy and angular momentum out of the spin system ultimately ends up in the lattice, exercising a torque on it.

The flow of energy and angular momentum out of the spin system ultimately ends up in the lattice.

From the width of the ferromagnetic resonance (FMR) line discussed in Sect. 3.6.3 one can deduce the so-called *intrinsic spin-lattice relaxation time*. It is ≈ 100 ps for ideal flat and defect-free films of Ni, Co, and Fe. This time sets a fundamental time scale for any change of the direction of the spontaneous magnetization.

In quantum mechanics one has the energy-time correlation discussed in Sect. 3.7. This allows one to predict the time scale on which processes occur. Based on this, it is not surprising that the intrinsic spin-lattice relaxation time is as long as 100 ps or so. The magnetic anisotropy energy density is given by $M_{\rm s} H_{\rm ani} \cos \gamma$ where γ is the angle between the $M_{\rm s}$ and the preferred axis. This energy holds the spin in a preferred direction in the lattice according to Sect. 11.2, and it is typically of the order of $10 \,\mu\,{\rm eV}$. The characteristic times associated with this energy are indeed in the 100 ps time range in agreement with the FMR result. For soft magnetic materials such as permalloy Ni₈₀Fe₂₀ or FeCo-alloys the magnetic anisotropy is very small leading to even longer spin lattice relaxation times of the order of 500 ps.

Phonons or lattice vibration modes have characteristic energies of meV. Since an energy of 1 meV corresponds to a time of about 1 ps, one expects that the excitation and/or annihilation of phonons by collisions with other phonons or by collision of electrons with the lattice vibrations occurs on the picosecond time scale. Thus thermal equilibrium within the phonon reservoir and also between the electron reservoir and the phonon reservoir should be established within picoseconds which again agrees with observations [780].

If we now look at spin waves, we know that they have energies of the order of meV, as well. Similar to phonons, spin waves are generated and annihilated by collisions with each other, and by collisions of electrons. However, the difference is now that each spin wave is equivalent to one reversed spin according to Sect. 11.1.5. Collisions of spin waves with each other must conserve the number of reversed spins. Similarly, as shown in Fig. 12.27, the *excitation* of a spin wave is only possible with a minority spin electron which must then make a transition to a majority spin state. Vice versa, the de-excitation of a spin wave will lead to a transition of a majority spin electron to a minority spin state. This process absorbs the spin wave. Hence the total process of excitation and annihilation of spin waves does not change the number of reversed spins, but it establishes thermal equilibrium within the spin system on a time scale of picoseconds dependent on the exact energy of the spin waves.

Phonons can scatter on spin waves as well, but if they excite or annihilate a spin wave, they must generate or annihilate the spin angular momentum connected with the spin wave. Torsional lattice modes may be able to do this, but we do not know a priori how frequent such events are. Similarly, electrons can undergo a transition to the other spin state in a scattering event with the lattice, but the spin angular momentum connected with the spin transition must then be absorbed by the lattice through magnetoelastic coupling. The events in which the spin angular momentum is transferred to the lattice constitute a bottleneck in the equilibration of $M_{\rm s}$ with the rest of the system. Let us take a look at the origin of this bottleneck.

The bottleneck in the energy and angular momentum flow between the spin system and lattice is best illustrated by assuming that no spin-orbit coupling exists. In that case, there is no coupling between the charge and spin degrees of freedom i.e., of the spin to the lattice. The atomic spins are held parallel by the exchange interaction on one side and the charges arrange themselves in an orderly array, the lattice, on the other. Without the spin-orbit interaction there is no talk between the two systems and therefore no preference direction of spins relative to the lattice. Thus although the distribution of the electrons, phonons and spin waves over the accessible energy states may change with time, the average spin polarization or the number of reversed spins of all electrons will remain the same. This is analogous to the case of singlet and triplet He shown in Fig. 6.3. Once the triplet state of He is excited by electron impact, the He-atom remains in the metastable $2^{3}S_{1}$ excited state until the spin angular momentum can be transferred out of the atom, for instance in the collision with a wall. Only then can the transition $2^{3}S_{1} \rightarrow 1^{1}S_{0}$ to the ground state take place.

Spin-orbit coupling is thus needed to couple the spin to the lattice. However, in 3d transition metals and their compounds the effective size of the spin-orbit (s-o) interaction is greatly reduced as discussed in Sect. 7.9.3 and it gives rise to the small orbital magnetic moments. The effective size of the s-o interaction is no longer given by the atomic s-o coupling constant ($\zeta \sim 10^{-1}$ 100 meV for 3d systems, see Sect. 6.4.3) but it is reduced by the quenching effect of the ligand field. For a typical LF splitting $\Delta_{\rm LF}$ this leads to a value for the effective s-o energy of order $\zeta^2/\Delta_{\rm LF}$ (see Sect. 7.9.3). We see that in a solid the effective s-o energy has a contribution from both the atomic s-o coupling, represented by ζ , and the lattice, represented by $\Delta_{\rm LF}$. This gives rise to a bottleneck in the transfer of energy and angular momentum. For the 3d transition metals we may estimate a time associated with this bottleneck from the well-known sizes of the magnetocrystalline anisotropy energies given in Table 11.3.² This energy of a few μeV corresponds to a time of about 100 ps and this value is in good accord with that derived from FMR for the spin-lattice relaxation time.

The relationship between the effective s–o energy and the spin–lattice relaxation time is indeed born out by experiments. If the effective s–o coupling is increased in 3d transition metals by addition of heavy atoms with increased s–o coupling, such as rare earth or 5d transition metal atoms, the spin–lattice relaxation time is indeed found to decrease [782,783]. With increasing effective s–o interaction one also typically finds an increased coercivity and anisotropy resulting from a locking of the orbital moment to the lattice as discussed in Sect. 7.9.3. In general, it is important, however, to distinguish the concepts of the *effective size* of the s–o coupling from the *anisotropy* of the s–o coupling, the latter corresponding to the magnetocrystalline anisotropy (see footnote 2).

So far we have ignored the direct channel from the electron to the spin system. It is least understood but we can make some general statements. This channel also does not exist without the s-o coupling and it is therefore also determined by it, as discussed by Hübner and collaborators [784–787]. The basic idea is that this channel may be ultra-fast because it involves *excited states* where the full atomic size s-o coupling is operative. From the size of the atomic s-o coupling constant $\zeta \sim 10-100$ meV for 3d systems one therefore may expect it to be of order 10–100 fs. For instance, if the electron system is excited with a laser pulse in the visible, transitions between filled and empty states take place at certain k-points in the band structure, as illustrated in Fig. 1.12. As the electron excitation energies are of the order of eV, the excitations happen on the time scale of femtoseconds. According to Hübner et al., the nonequilibrium charge distribution can induce a very large change in the

 $^{^{2}}$ As discussed in Sect. 7.9.3 the magnetocrystalline anisotropy is the difference of the spin–orbit energies along the easy and the hard axes. We assume here that the effective size of the spin–orbit energy is of the same order of magnitude as its angular dependence.

effective s-o energy which lasts as long as the electrons remain in the nonequilibrium distribution. Since in practice, the nonequilibrium distribution exists over the duration of the laser pulse, changes of the magnetization may occur over the matching timescales of 10–100 fs of the laser pulse and the characteristic s-o time. We shall discuss the processes in more detail in conjunction with the topic of all optical magnetic switching in Sect. 15.6.4.

Our discussion above also allows us to give a loose definition of "ultrafast" magnetization dynamics as those processes that are faster than about 100 ps, the intrinsic spin–lattice relaxation time. It turns out that there is another independent reason for such a definition. In many magnetic devices field pulses are created by current flow through lithographically manufactured coils. Today, the fastest such devices operate at switching times down to about 100 ps. We may therefore state as follows.

The field of **ultrafast magnetization dynamics** is particularly interested in exploring processes that are faster than $\approx 100 \text{ ps}$.

It should be stated upfront that the time of 100 ps by no means poses a general speed limit [788]. We shall see later that there are methods and processes that offer faster manipulation of the magnetization and even complete switching between two well-defined magnetic states can be accomplished much faster. Yet the understanding of the various physical processes on these faster time scales is presently incomplete and their understanding remains a challenge.

In the following chapters we shall discuss some important experiments that address ultrafast magnetization dynamics.

15.3 Spin Relaxation and the Pauli Susceptibility

Before we address time-dependent changes in the magnetization of a ferromagnet we start, as an introduction, by considering spin relaxation effects in a normal paramagnetic metal such as Cu.³ In 1927 Wolfgang Pauli treated the case of a paramagnet in an external magnetic field and discovered what is now called *Pauli spin paramagnetism* [789], already briefly discussed in Sect. 10.3.7. It turns out that the temporal evolution of this field induced magnetization is conceptually simple compared to the dynamics of the spontaneous magnetization in ferromagnets and it is for this reason that we discuss it first.

The dimensionless magnetic susceptibility is defined according to (2.12) as $\chi = M/\mu_0 H$. The part of χ which arises from the spin polarization of the metallic conduction electrons in the absence of exchange coupling is called the *Pauli susceptibility* $\chi_{\rm P}$. Contrary to Curie's law (3.20) valid for classical

 $^{^{3}\}mathrm{Cu}$ is usually called diamagnetic but all diamagnetic materials also have a paramagnetic component.

particles with a magnetic moment, Pauli showed that for conduction electrons in a metal $\chi_{\rm P}$ is independent of temperature due to the degeneracy of the electron gas [789].

Pauli spin paramagnetism refers to the small magnetic moment, of order $10^{-4}\mu_{\rm B}$ per atom, that is induced in a paramagnetic material by the presence of a magnetic field \boldsymbol{H} . It arises from an imbalance of spin up and down conduction electrons, is directed in the direction of \boldsymbol{H} , and the associated susceptibility is temperature independent.

There is also a contribution to the magnetic susceptibility stemming from the spatial motion of the electrons in the magnetic field. According to Landau, the spatial motion causes a *diamagnetic* moment directed antiparallel to H. Its magnitude is 1/3 of the paramagnetic moment induced by the spin polarization. Furthermore, one must not forget the diamagnetism of the full shells in the ionic cores, the band effects, and the electron–electron interactions. Yet, for simplicity, we confine our discussion to the dynamical aspects of Pauli spin paramagnetism.

Let us assume that we turn on a magnetic field H instantaneously to a constant value. Immediately after the field rise, two Fermi-levels will exist which we denote $E_{\rm F}^{\uparrow}$ and $E_{\rm F}^{\downarrow}$ for the two spin states as shown in Fig. 15.3.

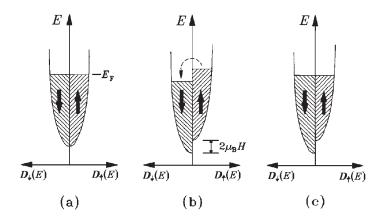


Fig. 15.3. A simple paramagnetic metal with a parabolic density of states $D_{\uparrow}(E)$ and $D_{\downarrow}(E)$ for the two spin states, (a) in the absence of a magnetic field, (b) immediately after a magnetic field has been applied, and (c) after a time $t \gg \tau_{\rm se}$. In (b), there is a large spin polarization of the states near $E_{\rm F}$ but no net average magnetization, while in (c) a magnetization has developed according to (15.4). In Cu at room temperature, $\tau_{\rm se} = 10^{-11}$ s has been determined from the decay of the spin injection voltage $V_{\rm AS}$ [737], while in Au, $\tau_{\rm se} = 4.5 \pm 0.5 \times 10^{-11}$ s is found from the decay of the magneto-optic signal after application of a field pulse [790]

The average magnetization M of the conduction electrons is still zero, but in an energy range close to $E_{\rm F}$ the spin polarization is large. Due to spin transitions, the difference between the Fermi levels of the two spin states equilibrates on the time scale of the spin equilibration time $\tau_{\rm se}$. After a time $t \gg \tau_{\rm se}$, one common $E_{\rm F}$ is established. This is illustrated in Fig. 15.3. With respect to that figure the equilibrium magnetic moment m generated by the paramagnetic spins is given by $m = \mu_{\rm B}(N^{\downarrow} - N^{\uparrow})$ where N^{\uparrow} and N^{\downarrow} are the numbers of up and down spin electrons per atom, respectively. Because the splitting $2\mu_{\rm B}H$ between the up and down spins is so small, the spin redistribution $N^{\downarrow} - N^{\uparrow}$ can simply be calculated from the density of states $D(E_{\rm F})$ at the Fermi energy according to

$$\mathbf{V}^{\downarrow} - N^{\uparrow} = 2\mu_{\mathrm{B}}H \,D(E_{\mathrm{F}}) \,. \tag{15.4}$$

For a magnetic field of $H = 10^6 \,\mathrm{A\,m^{-1}}$ and with a typical density of states of $D(E_{\rm F}) = 10^{-1} \,\mathrm{eV^{-1}}$ atom⁻¹ in an *s*, *p*-conduction band (e.g., see Fig. 12.1 for Cu), we have $N^{\downarrow} - N^{\uparrow} \simeq 10^{-4}$ and therefore the magnetic moment per atom $m = 10^{-4} \mu_{\rm B}$ is quite small. Note that with spin-polarized currents injected from a ferromagnet, one may generate an average spin polarization in the conduction bands of similar magnitude according to (14.11). With the above moments per atom we can calculate the magnetization M and the resultant Pauli susceptibility $\chi_{\rm P} = M/\mu_0 H$ is seen to be very small (<10⁻⁴). These values are in good accord with those derived for Pd from XMCD measurements, as discussed in Sect.10.3.7.

By use of the magneto-optic Kerr-effect (MOKE), Elezzabi, Freeman, and Johnson [790] have been able to detect the speed with which thermal equilibrium was established after sudden application of a field of 0.1 T. This experiment makes use of the spin polarization appearing near $E_{\rm F}$ in the unrelaxed state of the metal. The corresponding spin polarization disappears at the time scale of the *spin-lattice relaxation* while the small paramagnetic magnetization corresponding to $\chi_{\rm P}$ is generated. At room temperature, the spin-lattice relaxation time or more correctly the spin equilibration time was found to be 45 ± 5 ps in a thin film of polycrystalline Au.

In the future, the study of magnetization dynamics in nonmagnetic metals may be extended to X-rays. Figures 13.23 and 10.16 indicate that small magnetizations are also detectable in XMCD. X-ray based magnetic studies add element specificity to the magneto-optic studies which is important for alloys and interfacial systems. They furthermore can distinguish between spin and orbital moment relaxation. The physical processes involved in the transitions between the spin states in a paramagnet have been discussed in Sects. 8.6.2 and 14.1.1. Further studies would certainly help to understand these transitions in more detail.

We are now ready to look at what happens dynamically at an interface between a ferromagnet and a paramagnet. When two different metals are contacted, the electrons flow from the metal with the lower work function to the metal with the higher work function until the contact potential is

established. After that, the flow of electrical charge is in equilibrium, that is as many electrons flow from metal 1 into metal 2 or vice versa. Then, the net charge current is zero. The establishment of the charge equilibrium takes place on the time scale of the inverse plasmon frequency, that is in less than 10^{-15} s. Yet, the electrons flowing from $1 \rightarrow 2$ may have a different spin polarization compared to the electrons flowing from $2 \rightarrow 1$. In that case, one says that a spin current is flowing. The establishment of the equilibrium for the spin current takes place on the time scale of the spin equilibration time $\tau_{\rm se}$, that is about $10^{-11} - 10^{-10}$ s.

This is the time scale typical for magnetization precession in the anisotropy field. If an external magnetic field is suddenly applied to a ferromagnet, it will generate an additional paramagnetic contribution to the ferromagnetic magnetization $M_{\rm s}$. If H is parallel or antiparallel to $M_{\rm s}$, the Zeeman-energy $\mu_{\rm B} H$ adds or subtracts to the exchange energy. The equilibration time of the spins in the ferromagnet, $\tau_{\rm se}^F$ is much shorter compared to the one in the paramagnet as discussed in Sect. 14.1.1. Therefore, a spin accumulation voltage $V_{\rm AS}$ will be present at an interface between a ferromagnet and the Pauli paramagnet for some time after the application of a magnetic field leading to spin currents across the ferromagnetic interface. If $H \perp M_{\rm s}$, $M_{\rm s}$ precesses around H. This then generates a "peristaltic spin pump" according to Tserkovniak et al. [791], pumping spins across the interface as the magnetization precesses. The spin currents generate additional damping of the magnetization precession and also lead to a dynamical coupling to a second ferromagnet separated from the first one by a thin paramagnetic layer. The dynamic coupling superimposes onto the static coupling that may also exist according to Sect. 13.4. The additional damping of the precession as well as the dynamic coupling of two precessing ferromagnets have indeed been observed in ferromagnetic resonance experiments [792, 793].

In the following sections we shall discuss the excitation and relaxation of the magnetization in ferromagnets.

15.4 Probing the Magnetization after Laser Excitation

A laser pulse can induce the excitation of electron-hole pairs in a metal through the absorption of a photon with energy $\hbar\omega$. With photon energies in the range of 1.5–3 eV the characteristic excitation time is of order 1 fs according to Sect. 3.7. This is shorter than the duration of a typical laser pulse of ≈ 30 fs, used in practice. Hence we can assume that the energy of the laser pulse is deposited in the form of electron-hole pairs in a time of duration given by the length of the laser pulse.

Any changes of M_s that are induced by the pump pulse can now be probed by a pulse which enables rapid sensing of the magnetic state of the specimen at various time delays after the pump pulse. The probe pulse has to be weak in order not to deposit additional energy. The probe spot should also be laterally confined to a region equal or smaller than the region in which the excitation was induced. In all present experiments, the signal generated by a *single* probe pulse is buried in noise. To obtain useful information, one typically has to repeat the pump/probe cycle a million times. Consequently, only periodic repeatable processes can be studied so far. Stochastic events are averaged out as long as one is not able to perform single shot experiments in which one single probe pulse is enough to obtain a valid data point. Three pump–probe approaches have been used to probe the magnetization M_s .

The first, most common, technique employs *magneto-optic* effects. With the widely available laser probe pulses of near-visible light, one uses both linear [55] and nonlinear [794] magneto-optic Kerr-effects to deduce the time evolution of magnetic changes. The nonlinear magneto-optic effects such as second harmonic generation are particularly sensitive to magnetic interface properties [795].

A second way to probe M_s is to induce the emission of photoelectrons with higher-energy, ultraviolet (UV) photon pulses. The *spin polarization* P of the photoelectrons is measured with a spin detector, possibly preceded by energy analysis of the photoelectrons, as well. The time resolution of the photoemission experiment is mainly set by optical absorption, that is the excitation of an electron to an escape state from which it can surmount the surface barrier potentials. The steps subsequent to optical absorption, namely transport of the electron to the surface and then to the detector are of little concern for the intrinsic time resolution of photoemission. Therefore, the duration of the probing UV laser pulse inducing the photoemission sets the time span as in magneto-optics over which the spin polarization in the initial state in the solid is averaged.

The third method utilizes X-ray dichroism by employing tunable synchrotron radiation in the form of circularly or linearly polarized X-ray pulses. X-ray measurements are easier to interpret, have a better spatial resolution and can separately determine the evolution of the spin and orbital parts of the magnetization. However, at present, synchrotron based X-ray pulses have a duration of typically >50 ps, limiting the time resolution.

No matter which technique is used for probing, one has to carefully consider what information is contained in the measured signal. We first discuss time-resolved spin-polarized photoemission techniques.

15.4.1 Probing with Spin-Polarized Photoelectron Yield

The principle of probing the magnetization with laser-induced spin-polarized photoemission is sketched in Fig. 15.4. The question arises what information on the magnetization in a solid is contained in the measured spin polarization of photoelectrons? In fact, the measured spin polarization vector \boldsymbol{P} is directly proportional to that part of the magnetization which is generated by the initial energy states from which the spin-polarized electrons are excited [796]. Hence, as opposed to the usual magnetization measurements where one measures the

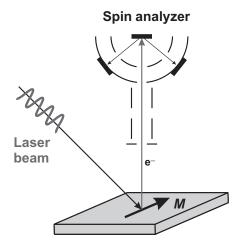


Fig. 15.4. The experimental principle for dynamical measurements of the spin polarization in photoemission with a pulsed laser or X-ray source

magnetization arising from all filled states, one obtains the contribution of selected electronic states to the spin part of the magnetization. The spin of the electronic states is measured because it remains unchanged during the photoemission process. In the dipole approximation, the electric field that is driving the excitation does not act on spin. If photoemission is induced with unpolarized light, the orbital part of the magnetization cannot contribute.⁴ If the energy of the photoelectrons is low, that is < 20 eV measured from the Fermi-energy $E_{\rm F}$, one has to consider the effects of spin filtering in the transport of the photoelectrons to the surface. The spin filtering enhances the observed spin polarization over the value in the initial electronic states from which the photoelectrons have been excited as discussed in Sect. 13.2.

To illustrate the connection of the spin polarization with the magnetization, Fig. 15.5 shows the dependence of the photoelectron spin polarization on the energy of the photon inducing photoemission as observed by Eib and Alvarado on the (100) surface of Ni [303]. There is a large variation of the degree of polarization with the energy of the photons inducing the photoemission. Only at photon energies of $\approx 10 \text{ eV}$, the expected average spin polarization of 0.07 of all the valence electrons is approached.

Clearly, it would be preferable to induce photoemission with high energy photons so that all 3*d*-states contribute with equal probability. Also, spin filtering can be neglected at higher electron energies. Under these conditions, the spin polarization of the photoelectrons would be directly related to M_s .

⁴In contrast, magnetometry based on the electromagnetic induction, the force, or the torque induced by the magnetization determine the total magnetization which includes the orbital part. Only in XMCD, orbital and spin part of the magnetization can be separated.

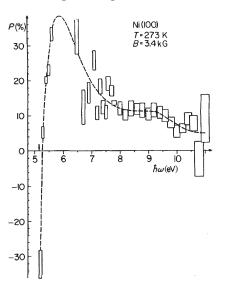


Fig. 15.5. Photoelectron spin polarization of the total yield of photoelectrons versus photon energy. The sample was a single crystal of Ni, and the photoemitting surface was (100). Magnetic saturation was induced perpendicular to the surface with a field of 0.6 T, from [303]. Data for a cesiated Ni(111)-surface are given in Fig. 13.2

The problem is that probing pulses of such UV or X-ray photons are presently not available. At present, suitable pulses of UV-photons exist only at photon energies $\leq 6 \text{ eV}$, where the spin polarization P depends strongly on photon energy. Fe is more favorable than Ni for evaluating the dynamics of $M_{\rm s}$ from the near-threshold spin polarization since it exhibits at least no change of sign and generally has a higher value of P [797].

Results for polycrystalline Fe are shown in Fig. 15.6 [798]. The pump and probe pulse were identical, that is the pulse that excites the electron hole pairs (pump-pulse) is also the pulse that probes M_s by inducing photoemission of electrons whose spin polarization is measured. Changes of M_s due to excitation of the electron-hole pairs and subsequent excitation of lattice vibrations are thus noticeable if they occur in a time shorter than t_L , the duration of the laser pulse.

The work-function of the sputter cleaned Fe-surface was lowered to 1.7 eV by deposition of Cs which made it possible to use a photon energy of 2.15 eV, delivered by an excimer laser. The spin polarization P is measured versus the total energy of the laser pulse. It is quoted relative to $P_0 = 0.55$, the degree of polarization measured with a weak pulse at room temperature along a direction \perp to the surface. A magnetic field of 0.4 T was applied in this direction to induce magnetic saturation. The energy of the laser pulse is given in units of the energy E_{ion} at which positive ions are emitted from the surface. Microscopic inspection of the focus area of the laser showed that melting

occurs at $E > E_{\rm ion}$. Photoemission from Fe probes only about three layers from the surface, and the yield is much stronger where the emission of positive ions compensates the negative space charge induced by the escaping photoelectrons in front of the surface. Hence the probing of a very thin sheet at the surface occurred in the hottest part of the laser focus.

Figure 15.6 indicates that with a laser pulse fluency strong enough to induce melting of the surface, the magnetization vanishes $(M_{\rm s} \rightarrow 0)$ at a pulse length $t_{\rm L} = 20$ ns but it remains constant $(M_{\rm s} = {\rm const})$ when the pulse length is shortened to $t_{\rm L} = 30$ ps. This agrees with the expectations based on a spin–lattice relaxation time of $30 \,{\rm ps} < \tau_{\rm sl} < 20$ ns. Molten Fe is of course paramagnetic, but when it is heated in a time span of 30 ps from an initial ferromagnetic state, the spin polarization persists above $T_{\rm C}$ far into the liquid state as $t_{\rm L}$ is too short to transfer the angular momentum to the lattice. The melting temperature of Fe is considerably higher than the Curie point, $T_{\rm melt} \approx 2T_{\rm C}$.

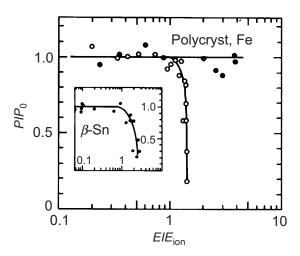


Fig. 15.6. Relative spin polarization of photoelectrons emitted from polycrystalline Fe as a function of the energy of the laser pulse [798]. Pulse duration was 30 ps (*full* circles) and 20 ns (open circles). At $E/E_{ion} \geq 1$ the sample surface melts, but the spin polarization persists with the ps-pulses. The inset shows a similar experiment with optical pumping of β -Sn. Here, the polarization does not persist upon melting

In this context, it is interesting to consider the result of a time resolved optical spin orientation experiment with a paramagnetic sample such as β -Sn⁵, shown in the inset of Fig. 15.6. With nonmagnetic samples, polarized electrons can be excited from the unpolarized ground state using circularly polarized light. This process, called *optical spin orientation*, underlies the spin

 $^{{}^{5}\}beta$ -Sn is known as "white tin."

polarized GaAs-source of electrons discussed in Sect. 8.2. The degree of spin polarization is determined by the crystal symmetry of the lattice. With molten or disordered surfaces, the spin polarization is zero [346]. In this way, spin-polarized photoemission can also detect the time scale of melting on heating with a laser pulse.

To demonstrate this, the work function of a clean β -Sn(100)-surface was lowered by deposition of Cs to 1.9 eV. This makes it possible for electrons excited with 2.7 eV circularly polarized photons to escape into vacuum. The resulting photoelectrons have a spin polarization of P = 0.04 explained by spin–orbit splitting in the involved electron states [346]. As the energy of the laser pulse becomes high enough to induce melting, i.e., $E \ge E_{\rm ion}$, the spin polarization decreases $(P \to 0)$ according to the inset of Fig. 15.6. This is independent of whether one uses long or short laser pulses. Therefore, the transfer of energy from the electrons to the lattice must occur in a time shorter than the duration of the short laser pulse. This agrees with the well-known time scale of ≈ 1 ps of electron-phonon coupling [780]. Hence we can summarize as follows.

Thermal demagnetization is limited in time by angular momentum transfer to the lattice (spin–lattice relaxation time $\tau_{\rm sl} \sim 100 \, {\rm ps}$) and is much slower than thermal melting (~1 ps).

Scholl and coworkers [86] carried out time-resolved photoemission probing with a 6 eV laser pulse at various delay times after a pump pulse with $h\nu =$ 3 eV. Both pump and probe pulses had a duration of $t_{\rm L} = 170$ fs yielding a time resolution below the ps-range. The sample was a Ni film grown on Ag(100), and $T_{\rm C}$ could be varied by growing films of different thicknesses. The incident light of both pump and probe pulse was linearly polarized \perp to the surface so that dichroic effects are excluded. The Ni films were magnetized in remanence. The experiment works like this. First, the pump pulse deposits energy by creating electron-hole pairs. Then, after a variable delay time, photoelectrons are excited by the probe pulse and their spin polarization P is measured. Figure 15.7 shows the results of the experiment.

One notices an initial fast decay of P within less than 300 fs followed by a slow decay of the order of several hundreds of ps. The slow decay of P is what one expects based on the earlier experiment shown in Fig. 15.6 while the fast decay is unexpected on the basis of an electron-phonon coupling of 1 ps or a spin–lattice relaxation of ≈ 100 ps. The time scale of the fast relaxation points to its connection with the relaxation of the electron-hole pairs.

However, whether or not electron-hole pair relaxation can generate a true demagnetization of M_s remains to be proven since care has to be exercised in the interpretation of the results. It is possible and more likely that with a photon energy of $h\nu = 6 \text{ eV}$ near the photoemission threshold, the electron-hole pairs simply generate a redistribution of the spin polarization over different

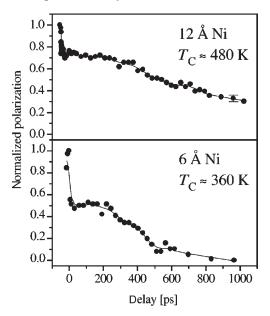


Fig. 15.7. Normalized spin polarization of electrons photoemitted with a 6 eV laser pulse at various delay times after the pump pulse with $h\nu = 3 \text{ eV}$, for two Ni films with different $T_{\rm C}$ [86]

electron states under conservation of angular momentum. This could change the spin polarization of the emitted electrons but the total magnetization may be constant. At the low photon energy, P is very sensitive to any variation in the occupied spin polarized electronic states near $E_{\rm F}$ according to Fig. 15.5. Such changes might have been induced by the pump pulse.

15.4.2 Probing with Energy Resolved Photoelectrons With or Without Spin Analysis

Rhie, Dürr, and Eberhardt [799] used time-resolved photoemission spectroscopy to probe the electron dynamics and measure the concomitant changes in the exchange splitting Δ of the spin states. The sample was a single crystalline Ni film of a few atomic layers deposited on W(110) with a Curie temperature $T_{\rm C} = 480$ K. The pump pulse of a duration of $\Delta t_1 = 85$ fs consisted of 1.5 eV photons at a fluence of $13 \,\mathrm{mJ}\,\mathrm{cm}^{-2}$. It heated the electron gas to effective temperatures $T \gg T_{\rm C}$. The pump pulse photon energy is too low to induce photoemission of electrons since the work function of the clean Ni-surface is $\approx 5 \,\mathrm{eV}$ and the pulse intensity was too weak for multiphoton photoemission. The probe pulse on the other hand side lasted $\Delta t_2 = 180$ fs and consisted of photons of 6 eV. It followed the pump pulse after various time delays up to ~10 ps. The probe pulse induces the emission of photoelectrons that are detected in a time of flight electron-spectrometer at an energy resolution of 30 meV.

The innovative feature of this experiment is that it detects not only the electrons excited from the occupied states below $E_{\rm F}$, but also the electrons excited to states above $E_{\rm F}$. This makes it possible to simultaneously determine the temporal evolution of the temperature of the electron gas and the exchange splitting Δ of the electron states.

Equation (12.7) gives the Fermi–Dirac function which is the probability that an electron state of energy E will be occupied in an electron gas in thermal equilibrium. f(E) = 1/2 when $E = \mu$ where μ is the chemical potential. At T = 0, μ is equal to the Fermi-energy $E_{\rm F}$. Figure 15.8 demonstrates that this applies approximately at temperatures of the electron gas as high as 5,000 K. The high energy tail of the distribution is that part for which $[E - \mu] \gg k_{\rm B}T$. The exponential term in the denominator of f(E) is then dominant so that we can write

$$f(E) \simeq e^{-(E-E_{\rm F})/k_{\rm B}T}$$
. (15.5)

In electron spectroscopy, $E_{\rm F}$ is determined by measuring the work function and E is obtained by high resolution energy analysis of the photoelectrons. Consequently, the occupancy of the electron states above $E_{\rm F}$ can be measured. If it shows the exponential tail according to (15.5), usually referred to as the Boltzmann-tail, we know that the electron gas is in thermal equilibrium. We

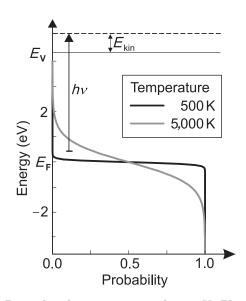


Fig. 15.8. Fermi–Dirac distribution at 500 and 5,000 K. Plotted is the probability that an electron state is occupied versus the energy in eV. The time-resolved measurement of the tail of the Fermi-function is possible with laser-induced high resolution photoelectron spectroscopy. Fermi-energy $E_{\rm F}$ and vacuum potential $E_{\rm V}$ are also indicated

can then determine its temperature from the slope of the tail in a logarithmic graph. In this way it was established that thermal equilibrium is reached in the experiment [799] at a delay time of 0.5 ps between probe and pump pulse. The highest temperature of the electron gas is thus reached 0.5 ps after excitation and it amounted to $\approx 1,000$ K. This high temperature occurs because the specific heat of the degenerate electron gas is comparatively low.

After reaching the peak temperature, the electron gas cools rapidly by heating the lattice through the excitation of phonons. The cooling of the electron gas levels off at a delay time of 2 ps indicating that the electrons are now in thermal equilibrium with the lattice. The equilibrium temperature is found to be comparatively low, namely 410 ± 30 K. This is because the lattice has a large specific heat. The effective electronic temperature remains at the lattice temperature up to the largest investigated delay times of 9 ps between pump and probe pulse. This indicates that heat conduction into the substrate is relatively slow and limits the study of magnetic phenomena to the shorter delay times. These findings are very much in agreement with prior work on electron-phonon coupling in nonmagnetic metals [780]. Yet they appear to be in conflict with a recent proposal on ultrafast demagnetization based on electron-phonon scattering [800]. We can state as follows.

The *electron-phonon relaxation time scale* for establishing the equilibrium between the electronic and lattice temperatures is independent of the magnetic state of the sample.

Of interest for the dynamics of the magnetization is the fact that the exchange splitting Δ along the $\Gamma - K$ azimuth of the Brillouin zone can be determined in this experiment as well. In Ni, the majority spin band manifests itself in a peak of the occupied d-states below $E_{\rm F}$, while the minority spin band is only partially occupied and crosses $E_{\rm F}$. The peak of the minority spin density of states is therefore not fully developed, but the peak position can be recovered by normalizing the observed energy distribution of the electrons emitted from states above $E_{\rm F}$ with the Fermi-distribution function. This technique has been applied by Greber and coworkers [567] as discussed in Sect. 12.4.2. To verify the technique employing a pulsed laser instead of the DC-He-resonance lamp, the exchange splitting was determined in the absence of a pump pulse at ambient temperature. The splitting between the majority and minority spin states turned out to be $230\pm50\,\mathrm{meV}$ in agreement with the static experiment [567]. Then, after applying the pump pulse, the exchange splitting Δ was found to collapse after 0.3 ps and to re-establish itself after 3 ps. The collapse of the exchange splitting is closely connected to the change in the occupation of the electronic *d*-states induced by the pump pulse.

It is reasonable that the exchange splitting collapses when the occupancy of the electron states near $E_{\rm F}$ is reduced by the pump pulse. After all, the main ingredient producing it might be the fact that the 3*d* levels are more

than half full. The 3d-minority spin electrons can hop from one atom to the other in the case of a more than half full 3d-shell only if the majority spins are parallel on all atoms. In this picture, the gain of kinetic energy for the 3d-electrons at $E_{\rm F}$ is then the cause of ferromagnetism in the 3d-metals. The exchange field can be reduced to zero through the electronic interactions at a fast time scale, but the collapse of the exchange field does not necessarily mean that the spin polarization of the electrons gas is also immediately reduced to zero. While it is true that the degree P of spin polarization of the electron gas will be redistributed over different energy states due to spin exchange in electronic collisions, P must remain constant at its average value of 0.07 in Ni until the angular momentum can be transferred to somewhere. At time scales where the electron gas is a closed system with internal forces only, Phas to stay constant. The electron gas cools to temperatures $T < T_{\rm C}$ in 3 ps through its interaction with the crystal lattice. Concomitantly, the exchange splitting is found to re-establish itself after 3 ps, that is to our best present knowledge before exchange of angular momentum with the lattice is possible. In the absence of the measurement of P one has no information on whether any demagnetization and subsequent remagnetization takes place at the short time scales below 3 ps. However, the new result of the experiment by Rhie, Dürr, and Eberhardt [799] is that it shows that the exchange field collapses for the duration of a few picoseconds upon exciting a large number of electronhole pairs with a fast optical laser pulse. This needs to be remembered.

The *exchange field* collapses for the duration of a few picoseconds upon exciting a large number of electron-hole pairs with a fast optical laser pulse.

An alternative approach to the question of how fast spin angular momentum is dissipated in the 3*d*-metals can be to directly measure the lifetime of a spin in a selected energy state. To first order, this lifetime is given by the spin conserving scattering active in spin filtering according to Sect. 12.6.1. Additional fast spin flip scattering would manifest itself in a further reduction of the lifetime of the spins. This was explored by Aeschlimann and coworkers [87,801] who analyzed both the spin and energy of the photoelectrons excited with a short laser pulse. This made it possible to determine the lifetime τ^{\uparrow} and τ^{\downarrow} of the two spin states of the electrons as a function of the energy $E^* - E_{\rm F}$ above the Fermi-level. In the absence of any spin flip scattering, the measured lifetimes must be equal to the ones derived from the respective spin-dependent mean free path $\lambda_{\rm e}$ of hot electrons according to $\tau = \lambda/v_{\rm G}$, where $v_{\rm G}$ is the group velocity of the electrons.

It turns out that the two experiments, measurement of the attenuation length and of the lifetime, are in qualitative agreement. They both show a longer lifetime for the majority spins. However, the ratio $\tau^{\uparrow}/\tau^{\downarrow}$ is much larger according to the more recent data shown in Fig. 12.18 compared to the direct

time-resolved measurements [87,801]. This rules out any additional mechanism reducing the lifetime of a spin beyond spin selective scattering. However, closer analysis of the experiment [801] reveals ambiguities in this first time-resolved approach.

The experiment of Aeschlimann et al. [87] involved excitation of the electrons by a first ultrashort pump laser pulse followed by a second, suitably delayed probe laser pulse which leads to photoemission of the electrons. By measuring the number of photoelectrons in the two spin states at a kinetic energy $E_{\rm kin}$ determined by the setting of the energy analyzer and as a function of the delay between the pump and the probe pulse, one obtains the spin-dependent lifetimes τ^{\uparrow} and τ^{\downarrow} in an excited state. The principle of this experiment is explained in the inset to Fig. 15.9. The pump pulse excites the electrons from their ground state to an intermediate state of energy $E^* - E_F$. The probe pulse, arriving after a variable delay, excites those electrons that are still present at energy E^* to a state above the vacuum level $E_{\rm vac}$ from where they can escape from the solid and be detected as photoelectrons. The lifetime of the electrons at E^* is obtained by measuring the photocurrent versus the delay between the two light pulses. The two pulse correlation experiment can be used to determine electron lifetimes which are much shorter compared to the duration of the laser pulses $t_{\rm L} = 40 \, \text{fs}$ because the shape of the laser pulses is known. Furthermore, the two pulses have to be linearly polarized perpendicular to each other in order to reduce the probability for the simultaneous absorption of two photons for exciting one single electron state.

Figure 15.9 displays the observed spin-integrated lifetime as it depends on the energy $E^* - E_{\rm F}$ of the excited state with Co and Ag. In the case of Co, both laser pulses had a photon energy $h\nu = 3 \,{\rm eV}$, and the work function of the surface of the fcc Co(001) film grown on Cu(001) was reduced to $\Phi = 3.5 \,{\rm eV}$ by the deposition of Cs. In the case of Ag, the laser pulses had an energy of

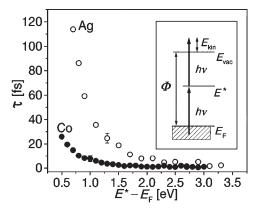


Fig. 15.9. The spin-averaged inelastic lifetime of Co and Ag in fs (10^{-15} s) versus the energy of the excited state $E^* - E_F$ [87]. The inset shows the energy levels involved in 2-photon-photoemission. Φ is the work function, adjustable by deposition of Cs

 $h\nu = 3.3 \,\mathrm{eV}$ and the work function of the Ag(111) surface was $\Phi = 4.1 \,\mathrm{eV}$. As the energy $E^* - E_{\mathrm{F}}$ is lowered, the lifetime of the electrons in Ag increases much more compared to the one in Co. This agrees with the notion that the lifetime is determined by the scattering into the hole states in the *d*band, hence must be shorter with Co compared to Ag. It is also in qualitative agreement with the results on the electron absorption coefficient in different metals shown in Fig. 12.16.

Figure 15.10 shows the spin-resolved lifetimes observed with Co. The very short relaxation times of the order of 10 fs agree with the fast relaxation of the electron gas found in reference [799]. Similar measurements have also been done with Ni and Fe [801] with qualitatively similar results. The ratio of majority to minority spin lifetimes, $\tau^{\uparrow}/\tau^{\downarrow}$, seems to decrease in all three ferromagnetic metals as the intermediate state energy approaches the Fermi energy $(E^* - E_F \rightarrow 0)$. This is contrary to the expectations based on a simple density of states interpretation. The inset to Fig. 15.10 shows the calculated density of states in fcc Co. At lower energies, the unoccupied density of mi-

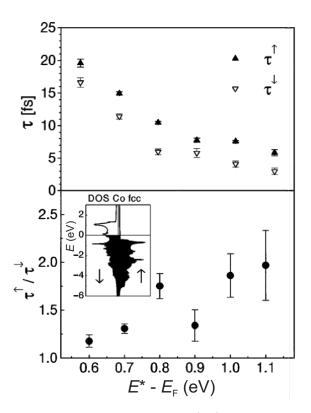


Fig. 15.10. The spin-resolved inelastic lifetime (top) and the ratio of majority to minority spin lifetimes, $\tau^{\uparrow}/\tau^{\downarrow}$, (bottom) of a cesiated 10 nm thick Co-film versus the energy of the state $E^* - E_{\rm F}$ excited with a photon energy of $h\nu = 3 \, {\rm eV}$ [87]. The inset shows the density of states of fcc Co

nority states is dominant. Therefore, the density of states model cannot be reconciled with a decrease of the ratio $\tau^{\uparrow}/\tau^{\downarrow}$ in Co, and the same applies to Ni. In Fe one expects $\tau^{\uparrow}/\tau^{\downarrow} < 1$ at $[E^* - E_{\rm F}] < 1 \, {\rm eV}$. None of this is observed in the experiments by Knorren et al. [801].

The failure to detect the effect of the majority spin holes close to $E_{\rm F}$ in Fe leading to $\tau^{\uparrow}/\tau^{\downarrow} < 1$ might be explained by the fact that this feature is not present at surfaces according to theoretical predictions shown in Fig. 12.4b. More serious is the disagreement with the results obtained with MTT's shown in Fig. 12.18. In fact, one expects that

$$\tau^{\uparrow}/\tau^{\downarrow} = \frac{\lambda^{\uparrow} v_{\rm G}^{\downarrow}}{\lambda^{\downarrow} v_{\rm G}^{\uparrow}}.$$
(15.6)

The results from attenuation measurements are thus not consistent with ratios $\tau^{\uparrow}/\tau^{\downarrow}$ close to unity observed in the direct measurements of the spindependent lifetimes at the lower electron energies. Knorren and coworkers [801] attribute this to shortcomings of the simple density of states model in explaining the lifetimes. It is proposed to adjust the Coulomb matrix elements active in electron scattering individually in Ni, Co, and Fe to obtain agreement with the experiment. However, the contradictory results of the direct measurement of the lifetimes at lower lying excited states could have more trivial reasons. The relaxation of electrons from higher lying states into the lower state whose lifetime is to be determined makes the actual lifetime appear longer. Such apparent lengthening of the observed lifetime might occur when $[E^* - E_{\rm F}] \ll h\nu$ where $h\nu$ is the photon energy of the pump pulse. The replenishing of the excited state at lower E^* by cascading electrons can therefore be at the root of the inconsistencies. Future experiments where the pump pulse has a lower energy than the probe pulse could eliminate the present uncertainty in the interpretation of the time resolved experiment [87, 801].

15.4.3 Probing with the Magneto-Optic Kerr Effect

It appears natural to investigate fast magnetization dynamics following the excitation of electron-hole pairs with the magneto-optic Kerr effect (MOKE). A pump pulse of optical photons of duration Δt_1 ps is used to excite electron hole pairs, and a second weaker probe pulse of duration Δt_2 follows at a variable delay time in order to gain information on the magnetization $M_{\rm s}$ via MOKE. The first results from such time-resolved MOKE-experiments (TRMOKE) with a time resolution below 1 ps were presented by Beaurepaire and coworkers [802] and more recently by Guidoni et al. in the same laboratory [803]. Beaurepaire et al. used laser pulses of $\Delta t_1 = \Delta t_2 = 60$ fs width with a photon energy of $h\nu = 2 \,\text{eV}$. The experiments received great attention because they seem to reveal fast demagnetization at time scales below 1 ps, contradicting expectations based on the spin–lattice relaxation time of $\approx 100 \,\text{ps}$.

Figure 15.11 shows the results of reference [802] for a polycrystalline Ni film. The rotation of the plane of polarization of the linearly polarized probe pulse in the longitudinal Kerr-effect is used to monitor the remanent magnetization $M_{\rm R}$ in the Ni film relative to the remanence $M_{\rm R}^0$ in the absence of a pump pulse. As the delay between the pump and probe pulse is varied, $M_{\rm R}$ shows first a rapid decrease at a time scale of ≈ 1 ps and then a slower recovery saturating at a plateau at about 2/3 of $M_{\rm R}^0$ at the largest measured delay times of 15 ps. The fact that one does not get the full remanence at zero delay times between pump and probe pulse is attributed to heating in the course of the experiment or to a slow motion of domain walls triggered by the pump pulse in the polycrystalline sample.

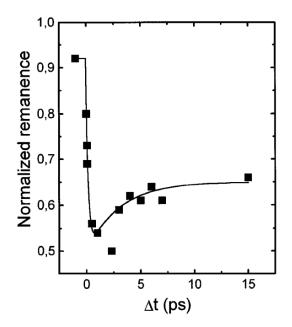


Fig. 15.11. Time-resolved magneto-optic signal (TRMOKE) from a remanently magnetized polycrystalline Ni film of 20 nm thickness on MgF₂ [802]. The fluence of the pump pulse was 7 mJ cm^{-2} at a photon energy of $h\nu = 2 \text{ eV}$. The TRMOKE signal is given relative to the MOKE-signal in the absence of a pump pulse

A number of groups have confirmed such a fast reduction of magneto-optic (MO) contrast in Ni after excitation with a fs laser pulse [804–806]. Yet Koopmans and collaborators [807] have demonstrated in more detailed TRMOKE-experiments that the fast change of the MO-signal is due at least in part to nonmagnetic changes in the electronic structure induced by the pump pulse. Kampfrath and collaborators [808] have presented experimental data showing that nonmagnetic contributions in the TRMOKE-signal are present up to 100 ps after excitation, hence it is not possible to conclusively deduce a de-

magnetization from TRMOKE. These results are corroborated by theoretical work [809] where the conclusion is reached that no information on ultrafast magnetization changes can be obtained from the Kerr-effect response.

The time-resolved spin-polarized photoemission data displayed in Fig. 15.7 exhibit in fact a similar behavior as the TRMOKE data in Fig. 15.11. But one can argue that both MOKE and photoemission do not reveal the underlying dynamics of the total $M_{\rm s}$ but rather the dynamics of the spin-polarized states that are energy selected by the photoexcitation or the photoemission process. If on the contrary one assumes that the experimental data indeed measure the magnetization, they would reveal that $M_{\rm s}$ can change even faster than the electron-phonon relaxation time of ≈ 1 ps. This in turn implies a purely electronic mechanism for the relaxation of the magnetization.

Such an ultrafast electronic spin relaxation would be in disagreement with the two current model for hot electrons discussed in Sect. 12.6.3. The model asserts that transitions of the electrons involving a change of spin state are rare in transmission of electrons through a magnetic solid. Furthermore, if the spin was unstable on the sub-ps time scale, it would be hard to imagine how spin can be transported from one ferromagnet into another as observed in ballistic spin injection experiments. It appears to be more likely that TRMOKE responds to the collapse of the exchange field [799], discussed in Sect. 15.4.2. Another channel is the blurring of the spin–orbit splitting of the electron states induced by the excitation of lattice vibrations, revealed in time-resolved optical orientation experiments during melting, discussed in conjunction with the inset of Fig. 15.6 (also see discussion later).

The direct transfer of angular momentum from the electron to the magnetization system following optical excitation, proposed by Hübner and collaborators [784,785] and discussed in Sect. 15.6.4, could explain the fast decrease of $M_{\rm s}$. So far, this mechanism does not contradict any observations. The ultrafast demagnetization could thus be due to the co-operative action of the external laser field and the internal LS-coupling. On the other hand, the recovery of the magnetization after the laser excitation must still be slow as, in the absence of the photons, it is expected to occur on the slower time scale of the spin lattice relaxation. The Hübner model thus allows a fast decrease of $M_{\rm s}$ in laser excitation, but the recovery of $M_{\rm s}$ must still be slow. This slow recovery has not been reported so far. Recently, Koopmans and collaborators [800] have proposed yet another microscopic mechanism for ultrafast magnetization dynamics based on electron phonon scattering. As the lattice heats up to temperatures close to, but still below $T_{\rm C}$, spin angular momentum can be transferred at the ps time-scale to the lattice by the spin-orbit interaction in the electron states generated by the electron-phonon scattering. This model awaits further examination.

While the experiment of Rhie, Dürr, and Eberhardt [799] establishes the ultrafast recovery of the exchange splitting within 2 ps, it does not exclude the Hübner mechanism because the experiment does not monitor the temporal evolution of the spin polarization of the electron gas. Obviously, one must distinguish between spin order and the establishment of the exchange field.

In addition to the sensitivity of magneto-optics to the occupation of the electronic states [806, 808, 809], MOKE must also depend on the lattice temperature for the following reasons. The MOKE-contrast is rooted in transitions between spin-orbit split electronic states at particular k-points in the Brillouin zone. Kerr ellipticity is caused by the difference in the absorption of right circularly (RCP) and left circularly (LCP) polarized light, while Kerr rotation is caused by the difference in the phase velocity between RCP and LCP. The transition probability between electronic states induced by photons of opposite circular polarization is equal if the electrons are not polarized. Therefore, MOKE contrast disappears if there is no spin polarization. But in ferromagnets, due to the spin polarization in the initial states, such a difference in the transition probabilities for polarized light exists and is the reason why MOKE can sense the magnetization $M_{\rm s}$. Both, Kerr ellipticity and Kerr rotation disappear when there is no spin-orbit (LS) coupling. This arises because photons can not couple directly to the spin. The LS-splitting of the electronic k-states forming a band is small in the 3d-metals and depends strongly on the location in the Brillouin zone. The LS-splitting of the electronic band states as a function of the location in the Brillouin zone can be measured with the technique of optical orientation combined with spin-polarized photoemission [346] as discussed briefly in Sect. 15.4.1. As the lattice is heated, the k-states of the crystal are increasingly blurred, and optical orientation disappears because the LS-splitting of the band states is washed out.

Experiments with optical orientation and the data for β -Sn in the inset of Fig. 15.6 show that the broadening of the electronic band-states induced by lattice disorder makes optical orientation disappear completely at the melting point or in amorphous structures [346]. Therefore one must expect that the magnitude of MOKE is reduced when lattice vibrations are excited. Then it is clear that MO depends on the lattice temperature in addition to the transition probabilities between spin-polarized electronic states.

At present, it is not possible to arrive at a final interpretation of the many existing observations on transient MOKE-contrast induced by an optical laser pulse. The reader will find a more detailed discussion in reference [810].

15.5 Dynamics Following Excitation with Magnetic Field Pulses

In Fig. 15.2 we show three distinct heat reservoirs in a ferromagnet. So far, we have discussed optical excitation where the energy is initially absorbed by the electrons in the form of electron-hole pairs, and the discussed experiments attempted to observe the subsequent temporal evolution of the magnetization $\boldsymbol{M}(t)$ as the energy distributes itself over the three reservoirs. In the present section we discuss a different approach based on exciting the magnetization

with a short magnetic field pulse. In order for the magnetization to move, the field has to exert a torque, hence the field must be an *axial* vector field as opposed to the excitation with unpolarized light which occurs mainly through interaction with the *polar* electric field. With an axial vector field, energy *and* angular momentum may be directly deposited into the spin system by moving \boldsymbol{M} out of its equilibrium direction. We now seek to understand how the energy and angular momentum dissipates out of the spin system into the lattice, either directly or via the electrons.

In order to visualize the fundamental processes underlying the dynamics following magnetic field pulse excitation, let us assume that the equilibrium direction of the magnetization M^{∞} lies along the +z-axis. The dynamics is thus started by applying a field pulse that moves M out of the +z-axis. We wish to know how fast M(t) regains its equilibrium magnitude and alignment along the easy axis, either along +z or -z.

Figure 15.12 explains the processes underlying the classical (top) and quantum mechanical (bottom) descriptions of the macrospin magnetization Massociated with a system of eight spins. We have assumed that the magnetization is initially perpendicular to the applied magnetic field H and then

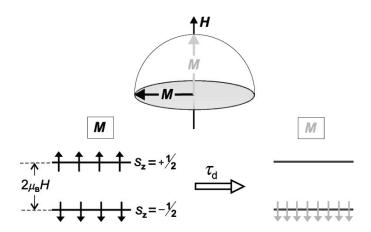


Fig. 15.12. Relaxation of the magnetization M into the equilibrium direction simulated by the field H. We assume that initially $M \perp H$. For this geometry, the spin state of each electron along H is a coherent superposition of an up-spin and a downspin wave function with an energy splitting of $2\mu_{\rm B}H$. Both spin states are equally populated. This leads to precession of the spin around the axis of H according to Sect. 3.7. As M becomes $\parallel H$, the population of the energy levels changes, and the population of the lowest spin state increases. Therefore, for M to relax into the field direction, transitions from the higher lying spin state to the lower lying spin state have to occur. The timescale on which the transitions occur is the spin relaxation time $\tau_{\rm d}$. It is related to the damping of the magnetization precession introduced in Sect. 3.6.2 and can be measured by observing the rate at which M relaxes into Haccording to (15.7)

relaxes into the direction of the field. The figures thus connects the macroscopic picture of the precession and damping of the magnetization, discussed in Sect. 3.6.2, with the quantum-mechanical description in which the damping is due to transitions between states of opposite spin, as outlined in Sect. 3.6.3.

If $M_z(t)$ is the component of the excited magnetization along the equilibrium direction and M_z^{∞} its equilibrium value then, according to one of Bloch's equations (3.41), the evolution of $M_z(t)$ with time t is given by

$$\frac{\partial M_z(t)}{\partial t} = -\frac{M_z(t) - M_z^{\infty}}{\tau_{\rm d}},\tag{15.7}$$

where $\tau_{\rm d}$ is the *spin relaxation time* related to the damping of the precession. Equation (15.7) shows that it is possible to determine $\tau_{\rm d}$ by measuring the rate $\partial M_z/\partial t$ with which \boldsymbol{M} relaxes into the field direction. If the magnitude of \boldsymbol{M} is conserved, the pathway of \boldsymbol{M} into the z-axis is a spiral with the endpoint of \boldsymbol{M} on the sphere of Poincaré, as pictured in Fig. 3.16. We will see below, however, that the magnitude of \boldsymbol{M} is not necessarily conserved, so that the uniform precession model does not always apply.

Conceptually, the excitation of the magnetization by a field pulse is much simpler than the excitation of the electron gas through generation of electronhole pairs. However, in practice, it is impeded by the difficulty of producing fast and strong magnetic field pulses which are needed in order to sharply define the time of excitation and overcome the anisotropy energy. The challenge is to generate an instantaneous field with sufficient magnitude to excite or even switch the magnetization in a small magnetic element. Several methods for the generation of magnetic field pulses have been used.

Pulse generators

Electrical pulse generators are driven by a voltage pulse which is electronically synchronized to and delayed from the trigger signal of the laser system. The fastest current pulses that can be made have a combined rise time and width ≥ 100 ps. The self-inductance of the electric circuit has to be as low as possible. It decreases with size, therefore the pulses must be guided in microwaveguides called "strip lines" of appropriate impedance made by optical lithography. The strip line can be wound into a single turn microcoil to produce a magnetic field perpendicular to the coil in the center, or one can simply use the field above or below the conductor. The strip lines have to be terminated appropriately to avoid reflection and distortion of the pulses.

Optical switches

Pulses with a shorter rise time require an optically controlled switch, provided by a so-called *Auston switch* that is located close to the sample, as illustrated in Fig. 15.13. The switch is manufactured on a GaAs crystal, typically by

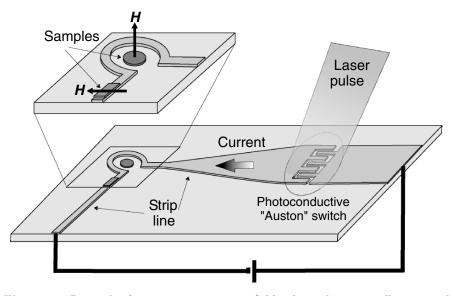


Fig. 15.13. Principle of generating a magnetic field pulse with an optically activated Auston switch. The laser pump pulse creates electron hole pairs between the metallic fingers of the Auston switch, launching a current pulse into the strip line. The sample is either located on top of the stripline where the Oersted field H is in-plane or in the center of a stripline loop where the field is out-of-plane, as shown. The sample is excited by the magnetic field pulse generated by the current pulse. The dynamic change of the magnetization is probed by a suitably delayed optical or X-ray probe pulse that is incident on the sample

means of optical lithography, by deposition of two metal lines serving as electrical contacts, one of which is also tailored into an impedance matched strip line. The metal lines meet in the actual switch region where they are electrically isolated by a meandering GaAs region. This insulating region keeps a current from flowing when a voltage is applied to the contacts, as indicated in the figure. A laser pulse incident on the switch region produces electron hole pairs in the GaAs by exciting electrons into the conduction band, thereby opening the switch. This produces a current pulse traveling down the strip line. In practice, current pulses of 100 mA have been reported producing a magnetic field of 0.1 T in the center of a single turn microcoil [790]. While the rise-time of the pulse can be few picoseconds, the decay time is ≈ 200 ps due to the intrinsic plasma recombination time in GaAs. A shorter shaped pulse can be generated by using a second Auston switch to which the opposite voltage is applied [811].

Alternatively, it is possible to use a "Schottky diode," that is a junction between a metal and a semiconductor, as the laser activated switch [812]. In practice, a metal layer is deposited on a semiconductor wafer and a voltage is applied perpendicular to the surface, from the back to the front of the diode. When a laser pulse hits the diode a current flows within the illuminated area from the back to the front of the diode. One therefore avoids the use of a strip line and one also obtains a shorter rise time. However, the current channel is limited to the size of the laser beam focus and so far the field amplitudes have been lower than those achieved with Auston switches.

Relativistic Electron Bunches

The magnetic field generated by relativistic bunches of electrons is shown in Fig. 2.4. Such pulses have an ideal Gaussian shape and combine short duration of the order of 1 ps with field strengths of ~100 Tesla near the outer edge of the electron bunch, as shown in Fig. 4.3. By passing such electron bunches through a thin film sample, the magnetic switching induced by the pulsed fields in ferromagnetic metals has been studied [788,813–815]. At distances of ~100 μ m from the beam center the field pulses have amplitudes of ~ 1 T. In metallic samples the electric field E = cB which accompanies the magnetic field B is screened after a very short lifetime ≤ 1 fs given by the plasma frequency of the metallic electrons. In insulators, the electric field is not screened and may cause damage.

Laser Heating in an Applied Field

In Sect. 15.4 we have discussed the excitation of the sample by a laser pulse. It only deposits energy into the electron gas which is then transferred to the lattice within ≈ 1 ps. One may use laser induced heating also in conjunction with a steady magnetic field. This method constitutes an indirect method of generating a magnetic field pulse. Several approaches are possible.

If the laser heats the sample to temperatures above the Curie point $T_{\rm C}$ in an external magnetic field that is set at an angle or antiparallel to the magnetization, the dynamics of the sample starts as it cools down below $T_{\rm C}$. This approach is used in *thermomagnetic Curie-point writing*. Already the first time-resolved magneto-optic Kerr (TRMOKE)-experiments [816] showed that the time scale of the dynamics is in the nanosecond range. It is dominated by the rate of cooling the sample through heat conduction into the substrate. Unless one can remove the heat quickly, the laser heating experiments thus do not tell very much about magnetization dynamics.

A related approach is based on heating a suitable sample to temperatures above the *spin reorientation transition* in which the magnetic anisotropy changes direction by 90° . Such a transition occurs for instance in thin Fe-films on Cu as mentioned in Sect. 11.2. In that case, one generates a fast magnetic anisotropy field pulse.⁶ Alternatively, on can heat a ferrimagnetic material

⁶A spin reorientation transition is said to occur when the magnetization of a thin film changes spontaneously at a material specific temperature from the in-plane direction to the perpendicular direction, or vice versa.

in an external field opposed to the magnetization to temperatures above the compensation point for the two sublattices and in that way generate a fast change of sign of the exchange field.⁷ This latter approach is used in *thermo-magnetic compensation point writing*.

Furthermore, a transferred effective magnetic field pulse may be produced in a ferromagnet by heating an exchange biased system. Rasing and collaborators [817] recently suggested that ultrafast switching of a ferromagnet is possible via laser induced reorientation of an exchange coupled antiferromagnet such as TmFeO₃. One could indeed imagine that the magnetization M of a ferromagnet exchange coupled to the AFM could be switched by precession if the anisotropy field of the AFM changes direction by 90° [817]. However, as shown in Sect. 15.6.1, the exchange bias field pulse amplitude must increase in proportion to the reduction of the duration of the pulse. This necessitates much higher effective field pulse amplitudes as commonly available in exchange biasing.

Recently, the dynamics of the antiferromagnetic to ferromagnetic phase transition that occurs in FeRh films has been studied by heating the antiferromagnetic FeRh with a laser pulse to temperatures above the temperature of ~100°C at which it becomes a ferromagnet [818,819]. In this case, a rapid increase of the ferromagnetic exchange field is generated. The direction of the developing ferromagnetic exchange field is specified by applying an external magnetic field of 4×10^4 A m⁻¹ [818]. The principle of this experiment is shown in Fig. 15.14.

Some magnetic signal appeared in the time-resolved magneto-optic Kerr effect (TRMOKE) within less than 1 ps after the fs-pump pulse. This magnetic signal saturates within ≈ 30 ps after the pump pulse. In this case, angular momentum has to be imported into the spin system rather than dissipated. Ganping Ju et al. [819] propose that the itinerant moments induced in the Rh atoms by the exchange interaction with the localized Fe moments trigger a fast phase transition, similar to that observed in Ni [799] by laser heating from the ferromagnetic to the paramagnetic phase. While it is conceivable that the exchange splitting appears on the fs-time scale, it is not obvious at all that a spin polarization can develop that fast. This latter point has been discussed already in Sect. 15.4.2. Hence TRMOKE may respond on the fs-time scale to the development of the ferromagnetic exchange splitting, but it remains open whether or not magnetic long-range order has developed as fast as the authors propose.

The special feature of *axial* magnetic fields that were assumed to be present in our discussion earlier, is that they provide a unique direction which the magnetization of the sample responds to. Since an unpolarized or linearly

⁷A compensation point $T_{\rm comp}$ may exist in ferrimagnetic materials when the sublattice magnetizations $M_{\rm A}$ and $M_{\rm B}$ change at different rates with temperature. The net magnetization $M = M_{\rm A} - M_{\rm B}$ vanishes at $T = T_{\rm comp}$. M must then switch direction on going through $T_{\rm comp}$.

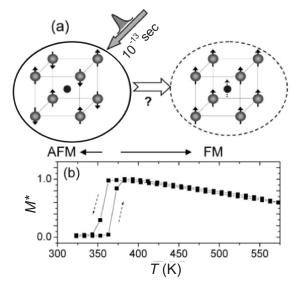


Fig. 15.14. (a) A laser pulse supplies energy in the form of electron-hole pairs which induces an antiferromagnetic to ferromagnetic phase transition in FeRh. (b) Dependence of the magnetic order parameter M^* on the temperature T in thermodynamic equilibrium, taken from reference [819]. The phase transition in equilibrium occurs at different T for heating and cooling cycles

polarized laser beam interacts with the solid predominantly via the *polar* electric field, it does not specify a unique direction. It is very interesting to consider whether switching of the magnetization by means of controlled laser pulses alone is feasible as reviewed by Rasing and collaborators [521]. We will come back to this problem in Sect. 15.6.4. There we shall also discuss the case of antiferromagnets, where the reorientation of the spins is possible on much faster time scales since the conservation of angular momentum does not affect the dynamical properties [787, 820].

Spin Injection

Another highly interesting way to excite dynamics is to generate a sudden exchange field by injecting a pulse of spin polarized electrons into a magnetic sample. Such experiments utilize structures similar to the one shown in Fig. 14.11. It is best to pin the magnetization M_1 of the reference layer used to define the spin polarization by exchange bias and orient the equilibrium magnetization M_2 of the layer to be excited or switched at a finite angle with respect to M_1 . This may conveniently be accomplished by an oval shape of the pillar where the shape anisotropy aligns M_2 along the long axis.

The relative *average* angle between M_1 and M_2 may be detected by the change in the electrical resistance probed through the giant magneto-

resistance (GMR) effect [756]. In order to achieve an adequate signal-to-noise ratio signal averaging is required. Today it is also possible to directly image the time dependent magnetization M_2 by element specific XMCD microscopy [763]. In this way the detailed magnetic structure of the layer of interest can be observed and effects hidden in transport experiments are revealed, like the presence of nonuniformities such as curls. Details of the various experiments on the time dependence of the spin injection process will be discussed in Sect. 15.6.3.

15.5.1 Excitation with Weak Magnetic Field Pulses

A short magnetic field pulse as generated with an Auston switch, exerts a torque on the magnetization M which in turn will start a damped precessional motion discussed in Sect. 3.6.2. This motion evolves on the time scale of the precession frequency in the effective magnetic field present in the sample. Freeman and collaborators [821] have imaged the motion of M by scanning magneto-optic Kerr microscopy in the sub-ps time domain with a spatial resolution of $\sim 1 \mu$ m. This was accomplished even when the amplitude of the variation oscillations is very close to the ferromagnetic resonance (FMR) frequency, but departures due to non-uniform response became evident as well. The damping of the oscillations is found to agree with expectations based on FMR experiments.

Today, experiments of this type have become well established and they have revealed a wealth of interesting details about excitations of the magnetization in small magnetic structures. In general, they corroborate the findings from techniques in the frequency domain such as FMR, Brillouin scattering, the measurement of the dynamic susceptibility or numerous other techniques. The developments are reviewed in the book by Hillebrands and Ounadjela [56,57]. Essential to the dynamics is the initial magnetic state of the sample. In Fig. 15.15 some examples of stable magnetic states in small thin film elements are given.

The magnetization dynamics in submicron sized thin film elements are of particular interest. Such elements may be used to store information in nonvolatile, magnetic random access memories (MRAMs). Typically, magnetic thin film elements consist of soft magnetic materials that are several nanometers thick and have lateral dimensions up to a few hundred nanometers. In order to write, read and store information in the elements, the magnetization is switched between two stable states. It is often tacitly assumed that the macrospin approximation is valid, i.e., that these two states are single domain states of opposite magnetization direction. However, it turns out that the magnetic structure is often inhomogeneous. In fact, it may be argued that a single domain state in which the macrospin approximation is strictly valid cannot exist in ultra-small structures since the surface spins become increasingly im-

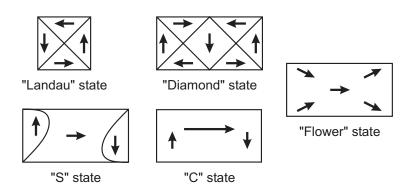


Fig. 15.15. Examples of magnetization patterns in small (submicrometer) thin-film elements and the corresponding names

portant. They are known to possess different primary magnetic properties, as illustrated in Fig. 13.17.

One important multidomain state of a small thin-film element is the Landau state, shown in Fig. 15.15. Here, four in-plane magnetic domains form a flux-closed structure in which the magnetostatic energy is minimized. In the center of the Landau state, a magnetic vortex may exist in which the magnetization points in a direction perpendicular to the film plane. This "vortex core" costs a large magnetostatic energy and is therefore very small, of the order of $\approx 10 \text{ nm}$ [542].

There are four basic vortex structures as shown in Fig. 15.16. The handedness of a vortex is determined by aligning the thumb into the direction of the out-of-plane magnetization of the core, as shown, and then matching the directions of the fingers of the right or left hand with the in-plane curl direction of the Landau state. The magnetic vortex structure is special in that it combines the basic symmetry properties of *inversion* and *time reversal* discussed in Sects. 2.7.1 and 2.7.2. This is seen by inspection of Fig. 15.16. The four basic structures correspond to the two types of handedness, which are transformed into each other by the parity operation, and the two magnetization directions of the core, which are transformed into each other by the time-reversal operation, since the magnetization is an axial vector. The symmetry properties raise the interesting question whether a vortex can be switched [822, 823].

However, the Landau state and its even more complex relative, the diamond state, possess in fact a composite magnetic character in which three different magnetic substructures exist: domains, domain walls, and the vortex core. These three different substructures differ in their dynamic behavior and are mutually coupled, yet are generally simultaneously excited with a magnetic field pulse. This leads to an overall very complex dynamic behavior of the Landau state.

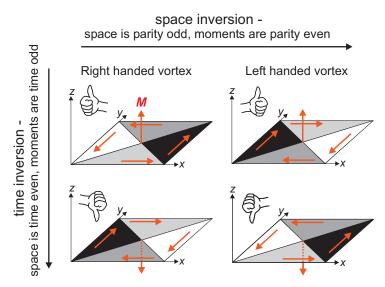
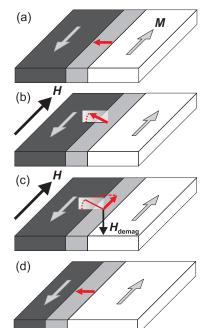


Fig. 15.16. The four basic magnetic vortices, classified by their handedness and out-of-plane direction of the core. A magnetic vortex combines the concepts of hand-edness and time-reversal and the four basic structures are transformed into each other by either the time reversal or inversion operations discussed in Sect. 2.7.1, as illustrated

Within one of the four magnetic domains of the Landau state, the spontaneous magnetization M_s is constant and the dynamics are dominated by precession and damping of M_s in the anisotropy fields. The vortex itself is dominated by the exchange energy and quite different as we will see, yet its motion is necessarily strongly coupled to the one of the domain walls. The walls taken by themselves are intermediate between domains and vortex with contributions from both exchange and magnetostatic energy.

A large literature exists on the dynamics of magnetic domain walls [54], while comparatively little was known until quite recently on magnetic vortex dynamics in metals because the metallic vortex is a 10 nm object requiring high resolution, nondestructive imaging hardly available with the classical techniques [522]. Therefore we will discuss in more detail the excitation of a magnetic vortex structure by a weak magnetic field pulse, but we need to include some basic facts about domain wall dynamics as well in order to understand the dynamics of the composite Landau state.

In Fig. 15.17 it is shown that a domain wall moves in the direction perpendicular to an applied magnetic field \boldsymbol{H} . While \boldsymbol{H} does not generate a torque on the magnetization \boldsymbol{M} within the domains, a torque exists within the domain wall. This torque generates a demagnetizing field perpendicular to the film plane which is the actual cause of the domain wall motion. As the maximum demagnetizing field is given by $H_{\text{demag}}^{\text{max}} = -M/\mu_0$, we see that there is a maximum speed with which a domain wall can move. However, in real life, domain wall dynamics is more complex due to wall pinning at impurities and the more complicated architecture of real domain walls [54].



Motion of a Néel wall in a field

Fig. 15.17. (a) Illustration of a thin film containing two magnetic domains with magnetization M in opposite directions, separated by a Néel wall (see Fig. 11.13). (b) Under application of an external magnetic field H, as shown, the torque vanishes in the domains because H and M are parallel or antiparallel. In the domain wall the torque does not vanish and moves M out of the plane of the film in the direction $H \times M$ (see (3.31)), thereby creating a demagnetizing field H_{demag} which is perpendicular to the plane of the film and rotates M. (c) The torque on M in the domain wall rotates M into the direction of H. Note that both torques caused by H_{demag} and H get weaker as M approaches the direction of H. (d) The domain with M in the direction of H becomes enlarged and the Néel wall moves in a direction perpendicular to H

15.5.2 Excitation of a Magnetic Vortex

If one reduces the thickness and lateral dimensions of a magnetic film from macroscopic dimensions one encounters the vortex as a stable magnetic structure for lateral dimensions below the micrometer range before a "single domain" state is favored at smaller dimensions. For example, in self-organized Fe films on W(001), uniform single domain, simple vortex, and distorted vortex states have been observed with spin-polarized scanning tunneling spectroscopy [824]. Magnetic vortices become stable over the single domain state at larger film thicknesses ≥ 10 nm and for lateral dimensions $\geq \approx 200$ nm [824]. However, it has been found that magnetization states in small structures may be bistable, e.g., depending on its magnetic history, a sample may exhibit either a vortex state or a uniform magnetized state [825].

Early studies imaged vortex structures occurring in garnets [826]. More recently, vortex excitations have been imaged in real time in magnetic microstructures by means of magneto-optical Kerr microscopy [537, 827] or Xray magnetic circular dichroism microscopy [538, 828–830]. In the frequency domain, vortex excitations in microstructures have been detected by means of microwave reflection in a nearby coplanar waveguide [831]. The exciting magnetic field can be in the plane of the film or perpendicular to it. Below we shall discuss both cases of in-plane and out-of-plane excitation of a vortex structure.

In-Plane Field Excitation of a Magnetic Vortex

Before we discuss experiments let us illustrate the torque exerted by an inplane magnetic field onto the magnetization of a vortex. This will guide us in what is expected for the instantaneous response of the vortex structure to a magnetic field pulse. As an example we show in Fig. 15.18 the magnetic structure of a left handed magnetic vortex with emphasis on the out-of-plane structure along the y direction.

The direction of motion of the vortex core induced by an in-plane magnetic field \boldsymbol{H} is determined by the direction of the torque on the magnetization along the line of the magnetic field. For a left handed vortex with the core along +z and a magnetic field applied in the y direction, illustrated in Fig. 15.18, the equation of motion is given by (3.31), i.e., $d\boldsymbol{M}/dt \propto -\boldsymbol{m} \times \boldsymbol{H}$. Thus the magnetization \boldsymbol{M} located at a negative y position moves out of the film

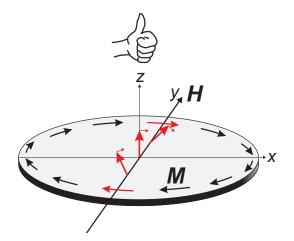


Fig. 15.18. Left handed magnetic vortex structure near the center of a Landau state. The magnetization M rotates out of the x-y-plane into the z direction. In a magnetic field $H \parallel y$, the location where M is \perp moves toward -y, that is the vortex core moves opposite to H. If the vortex is right handed the vortex core moves into the direction H

plane and M located at a positive y position moves toward the film plane, as indicated by little arrows. In this case the vortex core, defined by $M \parallel +z$, thus moves opposite to the direction of the magnetic field H. By inspections of the torques for the four basic vortex structures one finds the following rules.

For an in-plane magnetic field H, the center of a *left handed vortex* always moves in the direction -H, while the center of a *right handed vortex* always moves into the direction +H.

Dynamic images of the Landau-state have been obtained by the XMCD-PEEM technique by Choe and collaborators [538] and by Raabe and collaborators [828], and in transmission X-ray microscopy by Stoll and collaborators [829]. The principle of time resolved PEEM is shown in Fig. 15.19. The time resolution is limited mainly by the width of the synchrotron radiation X-ray pulses emitted by individual bunches in the electron storage ring. De-

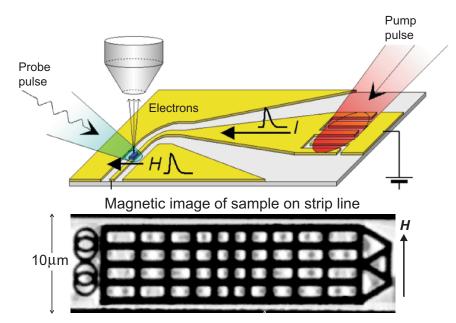


Fig. 15.19. Principle of time dependent PEEM microscopy of magnetic samples [538]. The pump pulse is launched by a laser activated Auston switch into a lithographically manufactured strip line. Magnetic samples of various sizes are manufactured on top of the strip line, and are shown in the magnetic PEEM image in the lower part of the figure. They experience the in-plane magnetic field of the current pulse. The circularly polarized X-ray probe pulses emitted by individual bunches in the electron storage ring, are synchronized with the laser pump pulses at a variable delay. Also shown is the objective lens of the PEEM electron optics into which the electrons emerging from the sample are accelerated

pending on the operating conditions of the storage ring the pulse length varies from about 30 to 100 ps. The PEEM spatial resolution is well below 100 nm, as discussed in Sect. 10.4.1. Choe et al. simultaneously probed the dynamics of magnetic structures of different sizes and shapes positioned on top of the strip line. This is possible because PEEM is a direct imaging method that simultaneously images all structures within the field of view of the instrument (about $30 \,\mu$ m). A representative magnetic image of various micromagnetic sample on a strip line is shown at the bottom of Fig. 15.19.

PEEM images with XMCD magnetic contrast were recorded by pumpprobe techniques as a function of delay time between the Auston switch triggered pump pulse and the X-ray probe pulse. Figure 15.20 shows magnetic images of two adjacent $1 \times 1.5 \,\mu\text{m}^2$ samples that were patterned by focused ion beam milling into a 20 nm CoFe film deposited onto the Cu waveguide. The images clearly show the Landau states of the two samples. Differential images of the same samples that highlight the regions of contrast changes in the original images are also shown later. The differential images facilitate the determination of the vortex center without resolving its actual size.

By pump-probe technique one can now record a sequence of images as a function of the delay time of the X-ray probe pulse relative to the laser pump pulse. When the magnetizations which in the ground state of the two samples form similar Landau patterns is excited by the horizontal field H in the shown direction, the initial directions of motion of the vortex centers and the ensuing

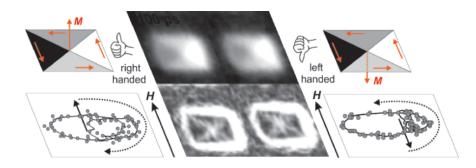


Fig. 15.20. Center: Magnetic images of two adjacent $1 \times 1.5 \,\mu\text{m}^2$ CoFe rectangles, patterned into a 20 nm thick film with in-plane easy axis [538]. The original images recorded by PEEM using XMCD magnetic contrast are shown on top, and differential images that highlight changes in contrast in white are shown below. The time evolution of the vortex center is indicated by dots in the *lower left* and *right* insets. The points represent sequential vortex positions (in 100-ps steps) up to 8 ns and the lines represent the time-averaged positions. When the magnetization in the two samples is excited by a horizontal field H, the initial directions of motion of the vortex center (*straight arrows*) and the ensuing gyrotropic motions (*dotted curved arrows*) are found to be in opposite directions. This indicates that the two vortices have opposite handedness, as illustrated on the top left and right

gyrotropic motions, both indicated by arrows, are found to be in opposite directions. As discussed in conjunction with Fig. 15.18, this indicates that the two vortices have opposite handedness. After the vortex is initially shifted from its equilibrium position, the imbalance of the in-plane magnetization creates magnetostatic fields driving the vortex into a spiraling motion back to its equilibrium position. A stable motion on a circular path may be induced by suitably interspaced periodic magnetic field pulses. The speed with which the vortex moves can be determined quite accurately. It turns out that the core velocity is an order of magnitude higher than expected from the static susceptibility of the vortex. This points to a much higher internal field near the vortex core than calculated from the static susceptibility.

The gyrotropic motion of the vortex on a circular path has thus been observed via the motion of the center of the Landau state with square samples of 1 μ m side length, and with stroboscopic pump and probe techniques, that is with a periodic excitation repeated every 8 ns [538, 829]. With larger squares of 6 μ m, the domain wall motion becomes dominant over the vortex motion, that is the center of the Landau state defined as the crossing of the Néel walls moves perpendicular to the magnetic field and relaxes without showing a circular orbit [828]. In the latter experiment, the exciting magnetic field pulses were wider spaced at 16 ns intervals. All three excitations expected from the constituent elements of the Landau state can then be found as revealed by Fourier analysis of the complex total spectrum.

The results of these experiment demonstrate that handedness plays an important role in the dynamics of microscopic magnets. Vortices, hidden to most imaging techniques, are often present in domain walls and can change the dynamics in an unexpected way [827].

Out-of-Plane Excitation of a Magnetic Vortex

If the magnetic field is applied perpendicular to the Landau state, it is parallel or antiparallel to the magnetization direction in the vortex core in the center. Hence the core experiences no torque and consequently the vortex does not change position in this case. But oscillations of M are excited in the inplane closed-flux magnetic structure surrounding the core. We will see that these oscillations are analogous to the familiar eigenmodes of a thin elastic platelet or membrane excited with a drumstick. The domain walls of the Landau state of a quadratic platelet are in fact the node-lines of the lowest magnetic eigenmode. In the case of elastic eigenmodes the node-lines can be made visible by putting sand on the platelet. The sand will collect in the nodes of the oscillations and thus reveal the node-lines of the excited eigenmode. The resulting beautiful sand patterns are known as *Chladni-figures* [832].

The elastic eigenmodes and the magnetic eigenmodes possess similar frequencies owing to similar phase velocities of phonons and magnons and, interestingly, but not surprisingly are coupled by magnetoelastic interactions in the case of a ferromagnetic platelet. With thin ferromagnetic disks it has

been shown that the frequency and damping of the elastic eigenmodes depend on the direction of the magnetization with respect to the node-lines, producing magnetomechanic Chladni-figures [833].

The external magnetic field pulse triggers the motion of the magnetization M. The field is applied perpendicular to the film plane. Thus, it causes an initial motion of M in the film plane. This launches the time-dependent motion which consists of an elliptical precession around the axis given by the equilibrium position of M. The amplitude of this precession decreases in time due to the damping of the precession. The path of the precession is elliptical rather than circular because as soon as M moves out of the plane of the film, a strong demagnetizing field appears making the out-of-plane amplitude smaller compared to the in-plane amplitude. Figure 15.21 illustrates the precessional motion of M induced by a magnetic field pulse applied perpendicular to the plane of the film that carries the vortex structure.



Fig. 15.21. The precessional motion of M excited by a perpendicular magnetic field pulse in a circular platelet that is initially in a vortex state. The magnetization M is pinned at the edge and in the center of the magnetic platelet

To calculate the precession frequency in the simplest possible model, let us assume that the ground state magnetization forms an ideal vortex. Rather than studying the magnetic eigenmodes of a square platelet which would be the Landau state, we now investigate the simpler case of a circular magnetic platelet. The magnetization in cylindrical coordinates is $\boldsymbol{M} = (M_r, M_{\phi}, M_z)$, and in the ideal case the remanent magnetization is then given by $\boldsymbol{M}_{\rm R} =$ $(0, M_{\rm s}, 0)$. Neglecting the crystalline anisotropy, the frequency ω of precession is calculated from [138]:

$$\omega = \gamma M_{\rm s} \sqrt{N_r N_z} \tag{15.8}$$

where N_r and N_z are the local demagnetizing factors. As discussed in Sect. 2.5, $N_z = 1/\mu_0$ is constant over the whole disk, changing only when the position r is close the edge of the disk, within a range comparable to the thickness of the disk. On the other hand, N_r , defined by $N_r = \mu_0(\partial H_r/\partial M_r)$ reaches a minimum at r = R/2 and diverges near the center at r = 0 and near the edge at r = R, where R is the radius of the disk. N_r depends somewhat on the mode, but this will be neglected in the following. Due to this large demagnetizing field in the r-direction, the eigenmodes of the oscillations of M must have a node in the center and at the edge of the disk.

Experimental results for a polycrystalline Co-disc, 20 nm thick and 6 μ m in diameter, are shown in Fig. 15.22 [537]. Displayed is the M_z component only, which is related to the M_r -component by the precession. The M_z -component gives the largest signal in the longitudinal Kerr-effect, but it has been shown by Acremann et al. [537] that one can measure all three components of M_s with TRMOKE simultaneously, leading to vectorial scanning TRMOKE. With this, one can construct time-resolved pictures of the magnetization as a function of position with a spatial resolution of somewhat below 1 μ m.

The spatial resolution in the TRMOKE experiments is not sufficient to resolve the oscillations near the pole in the center, but the node at the outer edge is clearly visible. The fact that there is a node of the eigenmodes at r = R came as a surprise at first glance, because one had always assumed that spin waves should have an antinode at the surface which was believed to be a free

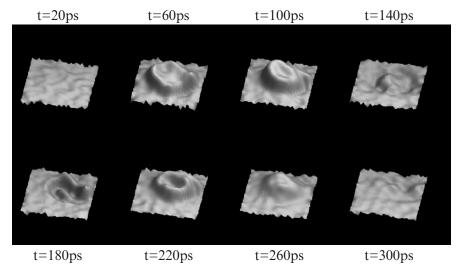


Fig. 15.22. Magnetization dynamics observed with scanning vectorial TRMOKE in a circular Co disk, placed inside a single turn coil that produced a magnetic field pulse in the direction perpendicular to the disk plane. The picture shows a square area that is larger than the circular disk. The size of the magnetic disk corresponds to the outer edge of the crater in the picture for a delay time of 60 ps. The 3D contrast corresponds to the magnitude and sign of the magnetization component M_z , perpendicular to the disk surface at specific delay times of the probing pulse. The Co disk is 20 nm thick and has a diameter of $\approx 6 \,\mu$ m. Figure courtesy of Yves Acremann [537]

end. We see that this is not true in cases where the oscillations of M generate a large demagnetizing field.

For small amplitudes of the oscillations, the motion of M is described by the superposition of the eigenmodes of a thin elastic disk with a node at r = 0and r = R according to [834]

$$M_r(t,r) = \sum_n a_n \sin(\omega_n t) M_n(r), \qquad (15.9)$$

where n is the mode number, ω_n its frequency, and a_n the amplitude with which it is excited by the field pulse. We need to remember that the eigenmodes of a membrane or platelet are not harmonic, i.e., the frequency of a higher mode is not an integer of the lowest mode frequency ω_0 . As a consequence, the oscillations of M_r are not stationary in time. All modes have antinodes at the center and at r = R, but the higher modes have additional circular antinodes at irrational values of r/R. They can be calculated in the simplified linearized model without further assumptions from the differential equation describing the elastic vibrations of a circular platelet. This approach containing reasonable assumptions but no adjustable parameters reproduces the essential features of the observed spatiotemporal evolution of the vortex spin excitation with an in-plane magnetic field. In fact, one only has to superimpose the first four eigenmodes with the appropriate amplitudes to arrive at a satisfactory description of the observations. A more complete study using Fourier transform imaging of spin vortex eigenmodes shows the presence of the higher modes as well [835].

However, there are differences of the magnetic eigenmodes compared to the elastic ones. In the elastic case, adding a circular or a diametric node always produces an increase of the vibrational frequency, as a consequence of the positive dispersion of sound waves in elastic media. Now, in the case of the magnetic oscillations, the frequency of the modes is found to decrease with the number of diametric nodes. The negative dispersion of the spin waves involved in this case explains this unusual behavior and can be explained with the magnetostatic energy generated by the demagnetizing fields [836].

At finite temperature, the magnetic eigenmodes are automatically excited. This has been detected with microfocus Brillouin light scattering spectroscopy [837]. Hence at finite temperature, a magnetic platelet generates magnetic frequencies, which, if made audible, would generate a bell-like sound. A magnetic platelet might thus be called a magnetic Boltzmann-harp in analogy to the audible eigenmodes of an elastic body excited by the wind, known as Aeolian harp.

In the sequence of images of $M_z(r)$ shown in Fig. 15.22 taken at successive times, we are able to follow the buildup and evolution of the nonuniform precessional mode. Precession starts closer to the boundary of the disc and appears to propagate into the center where it becomes active after 100 ps. Then, after 140 ps, the precessional mode reverses sign and moves back to the boundary where, after 220 ps, it reverses sign again to positive values and the whole cycle repeats. The amplitude of the oscillations decay with a time constant of 330 ps, in agreement with what one would expect from the FMR line width for small amplitude oscillations. This behavior is understood from the superposition of the eigenmodes according to (15.9). In particular, the displacement of the maximum amplitude M_z is not a consequence of the propagation of a spin wave to and from the center, but it is understood as a consequence of the inhomogeneous precession frequency rooted in the superposition of the nonharmonic eigenmodes of the "magnetic membrane."

The merits of this experiment are that it reveals the quenching of the spatially uniform mode of precession and the reversal of the sign of the excitation upon reflection as a direct consequence of magnetization pinning at the center and at the border of the disc. While the magnetostatic interaction opposes the appearance of a radial component M_r at the border, the stiffness of the exchange interaction favors the appearance of M_r at the border if $M_r \neq 0$ inside.

Although the experiment shows that M is pinned at the border, we are not sure why this is so. In general, the boundary conditions become more complicated as the exchange interaction becomes relevant. This is the case for the excitation of higher modes in technologically interesting nanoscale elements. Then, the boundary conditions are expected to depend on the length scale of the excitations. Thus, requiring pinning of M at the surface or setting its surface normal derivative to zero is only a practical way to arrive at some degree of understanding. It is interesting to compare the vortex excitations observed in the time domain by Pescia and coworkers [537] to the excitations observed in the frequency domain by Brillouin light-scattering [837,838]. The findings of both approaches agree in that the observed modes are identified as spin excitations dominated by the magnetostatic interaction. Yet the actual motion of M at a boundary awaits exploration by time-resolved X-ray microscopy with higher spatial resolution.

15.6 Switching of the Magnetization

Magnetic switching is the process by which the magnetization of a specimen is changed from one stable direction into another. In practice it involves a rotation of the magnetization by 180° , from one orientation along the easy axis to the opposite orientation, and this process is therefore referred to as *magnetization reversal*. It is important to realize that in today's technological applications the magnetization is typically not read immediately after its switching is initiated or completed. Therefore in technology, the relevant time for the "writing" process is only the time that it takes to put the system into a state from which it will reliably move into the new desired magnetization direction. It is acceptable to have a longer "settling down" phase, as long as it is deterministic. Magnetic switching can be achieved by the following methods.

Application of an Oersted field H

This is the traditional well-known method to reverse the magnetization. One applies the field H in the direction opposite to M. However, such a field does not exert a torque on M and switching can only proceed after thermal excitations have caused M to move out of the easy axis so that a finite torque exists. Then M may change direction in a complicated process that involves precession of the magnetization about the external and various internal fields with a final damping process that leads to its alignment along the opposite direction along the easy axis. Since the change of the angle between H and M involves angular momentum transfer to the lattice, it is of the order of 100 ps, limited by the spin–lattice relaxation time.

Ultrafast switching occurs if the magnetic field H is applied perpendicular to M. In that case, the torque is directly delivered by the external magnetic field and one avoids the bottleneck of the spin-lattice relation [605]. If the field is pulsed, the switching time may be determined by the precession time or the inverse Larmor frequency of M about H, provided that the magnetization acts like a macrospin. For a field of 1 T, for example, the pulse length has to be matched to the 180° precession time of about 20 ps. The only limit for the speed is the strength of the magnetic field pulse and its correct duration. If the pulse lasts too long, M switches back. Also, M switches each time one applies a field pulse, in contrast to the case $H \parallel M$ where switching occurs only if Hand M are antiparallel. "Precessional switching" or "ballistic switching" with $H \perp M$ therefore requires precisely timed pulses and a different read–write logic as used today.

In practice, one often uses a combination of the above two methods. The field H is applied at a finite angle with respect to M. This increases the switching speed considerably by avoiding the initial "dead time" where the torque is zero.

Switching by spin injection

In this case the angular momentum for the change of the magnetization M is provided by injection of a spin-polarized current, as discussed in Sect. 14.2.2. By alignment of the injected spin polarization relative to the magnetization to achieve optimum torque, in theory, the switching speed is determined only by the duration and amplitude of the spin injection pulse. In this case the transfer of the angular momentum should be possible directly from the incident spinpolarized beam to the magnetic moments of the sample, i.e., by avoiding the spin–lattice relaxation bottleneck. This would lead to fast switching times on the femtosecond time scale. In practice, however, such fast switching times which require optimum angles between injected spins and the magnetization in conjunction with ultrashort current pulses have not yet been achieved. Also, since faster switching requires higher spin-polarized currents one runs into limitations set either by power considerations or even by electromigration associated with high current densities. The exploration of the ultimate speed of spin injection switching remains an important research topic.

All optical switching

This (so-far) hypothetical method first proposed by Hübner and collaborators [784–787] is based on the application of a well-shaped ultrashort laser pulse of correct frequency, polarization and duration, and it potentially works on the femtosecond time scale. It involves the excitation of the system from the ground state to a well-defined final state where the magnetization is manipulated so that it decays into a new ground state with opposite magnetization direction. We shall see however, that this is quite difficult to accomplish in metals, where electron-electron scattering appears to make coherent manipulation of the magnetization difficult if not impossible. One can imagine, however, that laser manipulation produces a partial ultrafast reduction of the magnitude of M which would facilitate switching in an applied field. Namely, if |M| is reduced, the anisotropy barrier $M \cdot H_{ani}$ is lowered and switching could be initiated with a smaller field pulse amplitude.

15.6.1 Precessional Switching of the In-Plane Magnetization

In this section we shall discuss all three methods, realizing that so far, only the first method is being used in technology. Spin injection and especially alloptical switching are still the subject of forefront research. Whether they will ever replace conventional switching with Oersted fields remains to be seen. In general, however, the topic of fast magnetic switching is of great scientific and technological interest. It not only challenges us to understand fundamental physical processes but it also forms the basis for improved magnetic recording and magnetic memory applications and underlies the whole field of spin-electronics.

It is again necessary to limit our discussion to thin films, because spectroscopic observation of the switching is only possible at or near the surface, and only in specimens that are thin compared to the exchange length can one assume that the dynamics at the surface is related in a tractable way to the dynamics in the interior. We shall discuss both extended and laterally confined magnetic structures because both are important in applications. We start with a discussion of Oersted switching of samples, first with an in-plane and then with an out-of-plane easy axis. We will place particular emphasis on coherent precessional switching with ultrafast Oersted fields as the most realistic avenue toward fast magnetization reversal. We shall then discuss results on the time dependence of switching by spin injection. Finally we discuss the theoretical concepts underlying the method of all-optical switching.

The term "precessional switching" is sometimes used for two somewhat different switching processes: Freeman and coworkers [839] use it to describe the coherent precessional switching that might occur when the magnetic field

is applied antiparallel or nearly antiparallel to the initial direction of the magnetization. In that case, the magnetization spirals into the opposite direction via the damping of the precessional motion. Such reversal relying on damping to move M into the direction of H, although employed in present devices, is wasteful in time and energy compared to the process in which the field is applied perpendicular to the magnetization to maximize the torque acting on M.

In the fastest and most economical precessional switching mode, the magnetic field is applied perpendicular to the direction of the magnetization, along the hard axis of the specimen [811, 815, 840, 841]. In this case, the process of switching depends critically on the duration of the field pulse, and the magnetization might be switched back with the same pulse without changing the polarity of the magnetic field.

Precessional switching in the latter definition can be divided into the three steps outlined in Fig. 15.23. With the longer field pulses [811, 840, 841] produced with pulse generators or Auston switches, step (a) and (b) are not separated, that is they occur simultaneously. But with the short and strong pulses produced by passing through the sample relativistic electron bunches, the separation is clean in most cases and makes the process of reversal more transparent as will be shown below.

We define the coordinate system so that the x-y plane is the film plane, and the x axis is parallel to the easy axis along which M is assumed to be oriented prior to the arrival of the field pulse. The z-axis is perpendicular to the plane of the film and the external field pulse H_{ext} is applied in the direction -y. In the first step (a), the magnetic moments m precesses out of the film plane,

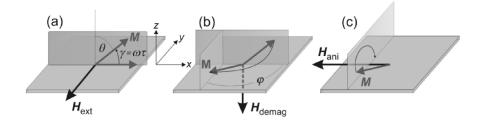


Fig. 15.23. Three-step model of precessional magnetization reversal with an inplane, homogeneously magnetized, uniaxial thin film magnetic element. (a) The magnetic field is applied in the hard direction perpendicular to \boldsymbol{M} whereby \boldsymbol{M} precesses out of the in-plane easy axis of the film by an angle $\gamma = \omega \tau$, where τ is the duration of the field pulse. (b) \boldsymbol{M} precesses by an in-plane angle φ about the demagnetizing field $\boldsymbol{H}_{\text{demag}}$ which is generated by the perpendicular component of \boldsymbol{M} , perpendicular to the film plane. (c) \boldsymbol{M} relaxes into the new direction, spiraling around the anisotropy field $\boldsymbol{H}_{\text{ani}}$ of the sample. With the fastest conventional magnetic field pulses of $\approx 10^4 \,\mathrm{A \,m^{-1}}$ amplitude and 100 ps duration, step (a) and step (b) occur simultaneously leading to a complex motion of \boldsymbol{M}

caused by the torque according to the right hand rule, as shown. The angle of precession $\gamma = \omega \tau$ away from the easy axis is given by the duration of the pulse τ and the angular frequency of the precession $\omega = (e/m_e)\mu_0 H_{\text{ext}}$. The anisotropy energy density for a thin film is given by (11.31), where γ is the direction of \boldsymbol{M} with a "unique axis," which we have chosen to lie along the in-plane easy axis, as shown in Fig. 15.23. The polar angle between the surface normal and \boldsymbol{M} is denoted $\theta = 90^{\circ} - \gamma$. The anisotropy energy density deposited by the field pulse in the film is then given by

$$E = K_{\perp} \sin^2 \gamma , \qquad (15.10)$$

where K_{\perp} is the energy density of the total perpendicular anisotropy and γ is defined in Fig. 15.23. Higher order anisotropies have been neglected as they are usually much smaller.

In step (b), starting at the end of the field pulse, \boldsymbol{M} precesses about the demagnetization field $\boldsymbol{H}_{\text{demag}}$ along the z-axis that has been generated by the out of plane motion of \boldsymbol{M} during excitation with the field pulse. As γ is quite small in practice, in the experiment discussed below $10^{\circ} < \gamma < 25^{\circ}$, a large polar angle $\theta = 90^{\circ} - \gamma$ is enclosed between \boldsymbol{M} and $\boldsymbol{H}_{\text{demag}}$. This distinguishes the precession leading to switching from that in ferromagnetic resonance (FMR) where θ is very small.

In the large angle precession, the in-plane component M_x oscillates periodically between the two easy directions. Owing to the damping of the precession, M spirals back into the plane of the film until it no longer can overcome the anisotropy barrier imposed by the uniaxial, in-plane crystalline anisotropy energy K_u . At this point, the energy consuming steps of the switching are terminated and step (c) starts, in which M oscillates about the in-plane uniaxial anisotropy $H_{\rm ani} = 2K_u/M$ until it comes to rest in the new or the old direction, depending on the in-plane precession angle φ between M_x and the *x*-axis at the end of step (b), as shown in Fig. 15.23.

Ultrafast Switching with a Relativistic Electron Beam

By passing relativistic electron bunches of high energy through metallic samples, the shortest and strongest magnetic field pulses may be generated as illustrated in Fig. 2.4. As the electron bunch passes through the thin film magnetic sample along the film normal parallel to the z-direction, a magnetic field is generated in the x-y-plane, that is the plane of the film, which resembles the field of a straight current-carrying wire. The vector of the magnetic field during the pulse is then given by $\mathbf{H} = I[y/r, x/r, 0]/(2\pi r)$. If $\mathbf{M} = [M_s, 0, 0]$, that is if the saturation magnetization M_s has been set parallel to the xaxis prior to the arrival of the field pulse, the torque/volume acting on \mathbf{M} is $T = MH_y$. Thus, the lines of constant torque are also the lines of constant excitation energy of the spin system given in (15.10). The angle γ by which \mathbf{M} precesses out of the film plane is calculated from

$$\gamma = \int_{-\infty}^{+\infty} \omega \,\mathrm{d}t = \frac{e\mu_o x}{m_e 2\pi r^2} \int_{-\infty}^{+\infty} I \,\mathrm{d}t = \frac{e^2 N}{m_e} \frac{\mu_o}{2\pi} \frac{x}{r^2} , \qquad (15.11)$$

where N is the number of electrons in the bunch. During the strong and short field pulse, the precession of M about the intrinsic anisotropies can be neglected. It is apparent that in this approximation and assuming uniform precession of M, the lines of constant excitation energy do not depend on pulse shape and on pulse duration, only on the total electrical charge of the electron bunch. The contour lines E = const are then calculated from the condition $\gamma \propto x/r^2 = \text{const}$ yielding:

$$\left(\frac{x-a_{\nu}}{a_{\nu}}\right)^2 + \left(\frac{y}{a_{\nu}}\right)^2 = 1 , \qquad (15.12)$$

The contour lines are thus circles with radius $R = a_{\nu}$ with the respective centers lying on the x axis at $x = \pm a_{\nu}$, as shown in Fig. 15.24.

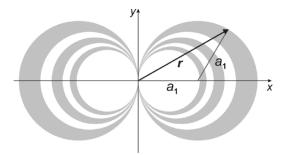


Fig. 15.24. Lines of constant torque or energy of excitation, given by (15.12), with a uniaxial magnetic film, originally magnetized in the x direction, after one electron bunch has passed through the origin, perpendicular to the figure plane. Gray regions designate the areas where M has switched to the opposite easy direction

The first switch or reversal of M to the opposite easy direction requires the energy $K_{\rm u}$ to overcome the hard axis plus the energy lost in the precession toward the hard axis which requires precession by an angle $\varphi = 90^{\circ}$. After that, M relaxes into the new direction in step (c) of the switching without further consumption of energy. This first reversal must occur along a line given by a constant a_1 . One more switch reverses M back to the starting direction. It requires the same energy as the first switch plus the damping loss in the precession by an additional angle $\Delta \varphi = 180^{\circ}$. It therefore occurs along a line of constant excitation energy $E(\gamma_2) > E(\gamma_1)$ that is at a switching radius $a_2 < a_1$. Higher order switches n require K_u plus precession by the angle $\varphi_n = 90^\circ + (n-1)180^\circ$ and occur along lines of constant excitation characterized by n constants a_n , with $a_n < a_{n-1} < \cdots < a_1$. The energy increment ΔE for each additional switch can thus be determined from the magnetic pattern and yields the energy consumed in the precession by the angle $\Delta \varphi = 180^{\circ}$, a truly ideal situation for measuring the damping loss in large angle precession.

If one starts with a uniaxial and homogeneously magnetized thin film, exposes it to one electron bunch and then produces a magnetic image which shows the regions where M has switched, one expects therefore to see a pattern like the one shown in Fig. 15.24.

This shape of the switching pattern, in particular the circular boundaries of the switching, is a feature that occurs only if the three-step model Fig. 15.23 applies. If the magnetization precesses appreciably already during the field pulse, the circles (15.12) are not lines of constant torque. This case has been observed and discussed by Back and collaborators [815].

Figure 15.25 shows the magnetic pattern that has been observed with an epitaxial model film of bcc-Fe grown on GaAs(110), consisting of 15 monolayers (ML) of Fe [842]. It clearly exhibits the pattern expected from (15.12) and Fig. 15.24. In the pattern, imaged several weeks after exposure to the electron bunch and after sputtering away the capping Au-layers, M is either parallel (light gray) or antiparallel (black) to the horizontal easy direction. The sample has been characterized by ferromagnetic resonance (FMR) yield-ing the gyromagnetic ratio g = 2.09 which turns out to be the same as in bulk Fe [792,843]. The width of the FMR resonance is found to be independent of film thickness, and increases linearly with FMR frequency from 9 to 70 GHz. This indicates that the FMR-width can be interpreted as due to intrinsic spin lattice relaxation with a Gilbert type damping $\alpha = 0.004$.

The anisotropy constants are obtained from FMR as well, yielding for 15 Fe-ML $H_{\rm ani} = 2K_{\rm u}/M = 4.72 \times 10^4 \,\mathrm{A \, m^{-1}}$ and $H_{demag} = 2K_{\perp}/M =$ $128 \times 10^4 \,\mathrm{A \, m^{-1}}$. The pattern has been produced with an electron bunch charge of 1.73 nC. Up to 10 switches of M induced by one single electron

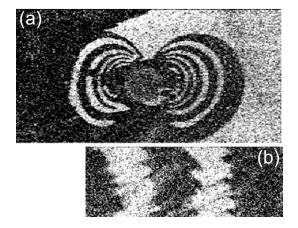


Fig. 15.25. (a) Experimental magnetic switching pattern obtained with a single crystalline bcc Fe-film of 15 atomic layers deposited onto a GaAs(110) template [842]. In the dark regions, M has reversed to the opposite easy direction. The picture was taken with SEMPA after sputtering off 10 capping layers of Au at the surface. It covers an area of $869 \,\mu\text{m} \times 432 \,\mu\text{m}$. (b) Enlarged region showing characteristic zig-zag domains

bunch can be distinguished in some locations of the pattern Fig. 15.25. The constants a_{ν} are obtained by fitting circles to the pattern. With 15 Fe-ML, 8 transitions with circle diameters $2a_1, \ldots, 2a_8$ of 325, 270, 238, 209, 185, 167, 152, 139 µm, respectively, have been determined [842]. The accuracy with which the $2a_{\nu}$ are obtained is estimated to be $\pm 1 \,\mu$ m. It is not possible to quantify the location of the higher switches that are certainly present but appear to be fragmented.

One type of problem encountered in determining the contour lines (15.12) is due to rugged transitions between regions of opposite M. Higher magnification of the switching boundaries, shown in Fig. 15.25b reveals the familiar zig-zag-domains near the x-axis that are known to occur by relaxation of the so called "head-on" configuration of M [54]. The switching leads initially to the unfavorable "head-on" position of M when a contour line runs perpendicular to the x-axis. The head on-transitions relax later into the longer, but more favorable zig-zag domain walls [815]. The location of the switching transition is the average over the zig-zag-walls.

A second type of uncertainty arises from the fact that the ultrathin film samples are soft-magnetic with a coercivity of $1-2 \text{ kA m}^{-1}$ only. This means that domains may easily shift in accidental magnetic fields. Apparently, domain wall motions occurred after exposure and deformed the left side of the pattern of Fig. 15.25 while on the right side, the pattern appears to be undisturbed.

A third problem is the damage caused by the high energy electron bunch in the sample. With the semiconducting GaAs substrate larger damage is observed compared to metallic buffer-layer substrates used in other experiments [788, 815]. The damage can be attributed to the electric field pulse $E^{\rm p} = cB^{\rm p}$, running perpendicular the magnetic field $B^{\rm p}$ of the pulse. $E^{\rm p}$ is not rapidly screened in a semiconductor, resulting in electrostrictive deformation of the GaAs-template responsible for the uniaxial magnetic anisotropy of the Fe-film. The permanent beam damage is delineated by a halo around the location of beam impact at $r \leq 50 \,\mu$ m. Although the halo is below the distances of the measurable switching events, it cannot be excluded that the magnetic anisotropy is affected transiently even at larger distances by the electrostrictive shock of the GaAs-template.

If the energy (15.10) required for the onset of a new switch is plotted in units of K_u versus the angle φ of precession of M_x , one obtains the universal switching diagram shown in Fig. 15.26. It displays data with 10 and 15 bcc Fe-ML on GaAs [842]. The switching diagram is independent of the different magnetic anisotropies of the films, but depends somewhat on film thickness as apparent with increasing number of switches. The first switch requires the reduced energy $E \approx 1$, compatible with the small damping observed in FMR. The small precessional damping contribution in the first switch explains the difficulty to determine it with conventional magnetic field pulses inducing only one switch. Yet already with the second switch, the additional precession by the angle $\varphi = 180^{\circ}$ requires much more energy than what results from FMR damping. The loss in the higher switches is nearly an order of magnitude larger than the dissipation expected from FMR.

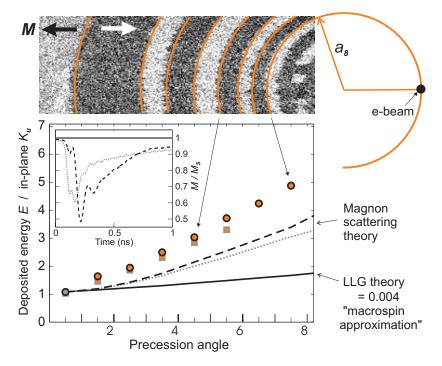


Fig. 15.26. Energy deposited in the spin system by an ultrafast magnetic field pulse versus the precession angle φ of M_x [842]. The energy is measured in units of the uniaxial in-plane anisotropy constant K_u of the sample, producing a universal switching diagram. Data points are for 10 Fe-ML(squares) and 15 Fe-ML(circles) on a GaAs template. The simulations are with the FMR Gilbert damping $\alpha =$ 0.004 and no magnon scattering (—), and for 10 Fe-ML (···) and 15 Fe-ML (--) including magnon scattering. The inset shows the relative saturation magnetization $M(t)/M_s(0)$ where t is the time after an exciting field pulse of amplitude 0.24 × 10⁶ A m⁻¹ for 10 Fe-ML (···) and 0.175 × 10⁶ A m⁻¹ for 15 Fe-ML (--). But without magnon scattering(—), $M(t)/M_s = 1$

Figure 15.26 also shows that precessional switching requires very little energy. For example, for an element of volume V corresponding to a film thickness of 1 nm and a diameter of 1 µm, we have $K_{\rm u}V \approx 10^{-15}$ J. With well-shaped magnetic field pulses inducing what has been termed ballistic precessional reversal [844], all three steps of the precessional reversal are accomplished within a time that depends on the length of the magnetic field pulse only. Hence precessional switching is fastest and most energy economic. Experiments conducted with field pulses produced by a photoelectric switch or in a pulse generator [840, 841, 844, 845] are compatible with the FMR derived dissipation and with what is found in Fig. 15.26 with one single switch induced by relativistic electron bunches. Up to 10 switches can be induced by one single pulse in the latter case. This makes it possible to detect the increase of the damping as the angle φ of precession grows.

A fundamental question in spintronics research is the existence of fast processes for the dissipation of spin angular momentum, resulting in temporary energy and angular momentum storage before their ultimate dissipation to the lattice. Two such processes have been considered. One is the dissipation within the spin system itself [839] due to the *Suhl instability* discussed later, the other the transfer of angular momentum from the spin to the orbital degrees of freedom [784, 785]. The latter process is active only in pulsed laser excitation. The multiple precessions of M after the excitation with the field pulse show that ultrafast relaxation is indeed not present here as expected.

The increase of the energy loss after the first switch shows that dissipation of spin angular momentum increases with time. The knowledge of the switching time comes from the fact that the exciting magnetic field pulse sets in motion the internal precessional clock from which the end of step 2 can be determined using the Landau–Lifshitz equation. We have seen that the magnetization precesses about the field $H_z = 2K_{\perp} \cos \theta / M$ after the magnetic field pulse.

The delayed dissipation is characteristic for the Suhl instability [776], which is the transfer of energy from the uniform precession mode with wavevector k = 0 to higher spin wave modes with $k \neq 0$. The transfer of energy, induced by nonlinear interactions owing to H_{demag} and H_{ani} , takes time because the numbers of excited nonuniform spin waves grow exponentially with time. A quantitative theory for the dissipation caused by the Suhl instability has been developed recently by Dobin and Victora [755]. The inset of Fig. 15.26 shows simulations for an area of $1 \,\mu\text{m} \times 1 \,\mu\text{m}$ of the 10 and 15 ML-Fe-film with a respective pulse amplitude that completes the first switch. It demonstrates one important consequence of the generation of nonuniform spin wave modes, namely the decrease of the space-averaged order parameter M/M_s with time.

It is seen that M/M_s decreases sharply ≈ 50 ps after the field pulse, and recovers slowly through spin lattice relaxation of the spin waves. Now, from the time t_{ν} after the field pulse at which the last change of sign of M_x occurs, we know the moment in time at which the energy-consuming part of the switch ν is terminated. With 15 ML-Fe these times are $t_1, \ldots, t_8 = 40, 115,$ 155, 195, 235, 270, 310, 360 ps, respectively. Large dissipation is observed only *after* the first switch. This agrees with the 50 ps delay seen in the development of spin wave scattering. Furthermore, as the angle of precession grows, the fluctuations of M/M_s in time and space can induce randomness in the switching, explaining the fragmentation of the higher switches.

Another characteristic of the Suhl instability concerns the film thickness. To conserve energy and momentum, the effective scattering of the uniform mode requires the excitation of *low* energy spin waves. The phase space for such low energy, long wavelength modes decreases with film thickness, and this explains why smaller dissipation is observed in agreement with the simulations as the film thickness is reduced. Hence there is no reasonable doubt that the Suhl instability contributes significantly to the dissipation observed in the experiment.

However, as apparent from Fig. 15.26, the simulations fall short by a factor 2 to fully account for the observed damping. Surface roughness is known to contribute to the damping. However, the detailed analysis based on the work of Dobin and Victora [846] shows that the surface roughness measured on the present films [792] is not enough to explain the observations. Furthermore, surface roughness should increase the damping in FMR as well. One therefore has to conclude that additional, so far unknown relaxation mechanisms must be active in large angle precession of the magnetization.

15.6.2 Precessional Switching of the Magnetization for Perpendicular Recording Media

As we have seen, precessional magnetization switching is interesting because it is faster by an order of magnitude and, according to Fig. 15.26, also uses much less energy to reverse the magnetization compared to the traditional methods of switching. This is of particular interest in magnetic memory devices where the logical bits are recorded by selectively setting M either up or down. We have also seen that in precessional switching, M may be switched back without changing the polarity of the magnetic field pulse, simply by applying the same pulse again. This last point must be examined specifically as it will be important for applications that the switching be deterministic, that is that it occurs with certainty whenever a magnetic field pulse is applied.

Magnetic recording with the highest bit density is achieved with granular magnetic recording media of the CoCrPt-type [847]. The media are thin films of ≈ 15 nm thickness consisting of isolated magnetic grains with the easy direction of magnetization aligned *perpendicular* to the film plane. The main condition for high density recording is that the grains are exchange decoupled so that the media can sustain narrow transitions between up and down bits. The decoupling of the grains occurs in the manufacture of the media through segregation of Cr to the grain boundaries induced by deposition at elevated temperatures.

The quest for long term thermal stability of magnetic bits requires a high value of the uniaxial magnetic anisotropy $K_{\rm u}$ which has to have a positive sign to favor the perpendicular direction of M, that is $K_{\rm u} \ge K_{\rm s}$ where $K_{\rm s}$ is the shape anisotropy. This in turn necessitates high magnetic fields to switch the magnetization in the process of writing the bits [443]. In order to achieve the high perpendicular switching fields with the tiny electromagnet used for the writing, a soft magnetic underlayer (SUL) is positioned under the magnetic medium providing flux closure for the field of the horse shoe electromagnet used in writing the bits. Figure 15.27 shows that the SUL also stabilizes the bits by reducing the demagnetizing field on the lower side. On the upper side of the structure, the stray fields emerge and are used for reading the bits. The principle of this approach is similar to the synthetic antiferromagnetic structure used to stabilize the bits with in-plane magnetic media illustrated in

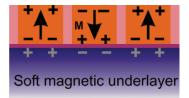


Fig. 15.27. Schematic cross-section through a perpendicular magnetic recording medium illustrating the effect of the soft magnetic underlayer (SUL) on the magnetic stray field of the bits. The bits are typically ≈ 40 nm wide, hence contain several magnetic grains

Fig. 2.10. One might suspect that SUL has some influence on the precessional switching as well. Therefore, one needs to test media with and without SUL.

The diameter D of the magnetic grains constituting the magnetic bits ranges from 10 to 20 nm. The grain size is small enough to consider the magnetic field produced by, e.g., an electron bunch at a distance $R = 20 \,\mu\text{m}$ to be homogeneous over the grain diameter as $D/R = 10^{-3}$. Hence the switching of a grain induced by the magnetic field pulse of an electron bunch occurs in a homogeneous applied magnetic field. With the grains magnetized perpendicular to the film plane, the magnetic field H_p produced by an electron bunch traversing the films along the normal to the film lies in the magnetically hard plane and is orthogonal to M everywhere. This is the optimum geometry to induce a precessional motion of M about H_p . Once M has precessed about H_p by an angle $\geq \pi/2$ to cross the hard equatorial plane, it will continue to spiral by itself into the opposite direction. This motion of M is shown in Fig. 15.28.

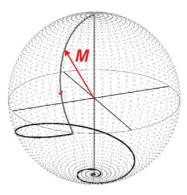


Fig. 15.28. The motion of the magnetization M on the sphere of Poincaré in the process of precessional switching of a perpendicular magnetic grain. For a switch to occur, M has to precess around the field and cross the hard equatorial plane during the field pulse. After that, it spirals by itself into the other easy direction

If, however, $\boldsymbol{H}_{\rm p}$ ceases to exist before \boldsymbol{M} has reached the hard plane, \boldsymbol{M} is expected to relax back to its original perpendicular direction, hence no switch has occurred. The condition for switching is that the angle $\gamma = \omega \tau \geq \pi/2$. By the same reasoning applied to derive (15.12), the lines of constant magnetic excitation are thus circles with radius R about the origin:

$$\left(\frac{x}{R}\right)^2 + \left(\frac{y}{R}\right)^2 = 1. \tag{15.13}$$

Ultrafast Switching with a Relativistic Electron Beam

We now discuss switching patterns obtained with granular CoCrPt recording media as an example [788]. The grain size was determined by X-ray diffraction and amounted to 20 ± 5 nm in this material. The effective magnetic anisotropy field $H_{\rm ani}^{\rm eff}$ is the crystalline anisotropy minus the shape anisotropy field. The product $M_{\rm s}H_{\rm ani}^{\rm eff}$ must be large compared to the Boltzmann factor $k_{\rm B}T$ in order to stabilize the magnetization direction over a sufficient length of time as discussed in Sect. 11.5.2. Three similar types of materials were investigated: CoCrPt I with $H_{\rm ani}^{\rm eff} = 648 \,\mathrm{kA} \,\mathrm{m}^{-1}$, and CoCrPt II and CoCrPt III with $H_{\rm ani}^{\rm eff} = 398 \,\mathrm{kA} \,\mathrm{m}^{-1}$, each, but CoCrPt II had no SUL while CoCrPt III did. Otherwise the three materials were identical. The high magnetic anisotropy makes it impossible to induce magnetic switching with the weaker field pulses such as produced for instance by Auston switches. The only way known so far to induce precessional switching in this type of media is to use the field pulses produced by high energy electron bunches [788, 813, 814].

To study precessional switching in these CoCrPt magnetic recording media sustaining very high bit densities [788], relativistic electron bunches of energy 28 GeV were focused to a cross-section of $10.8 \times 7.4 \,\mu\text{m}$ in the x-y plane of the films. The electron beam propagates along the z-axis perpendicular to the film plane. Along the z-axis, the electron distribution is Gaussian with a variance of 0.7 mm in the laboratory frame, yielding the variance of the Gaussian field pulse in the time domain $\tau = 2.3 \times 10^{-12}$ s. The maximum amplitude of the field pulse was $\mu_0 H_p = B_p = 54.7/R$ where R is measured in μ m to obtain B_p in Tesla.

The top left panel of Fig. 15.29 displays contour lines of constant B_p in the x-y plane of the films. The dark central spot indicates the size of the electron beam focus close to which no data can be obtained owing to beam damage caused in the sample. The actual magnetic switching patterns are displayed in the remaining panels of Fig. 15.29. The shape of all patterns is circular as expected from (15.13), in contrast to the case with the initial position of M in-plane, where the switching patterns have a figure 8 shape according to Sect. 15.6.1.

Before exposure, the magnetization of the grains had been aligned perpendicular to the film plane into what we shall call the "up" direction. Patterns

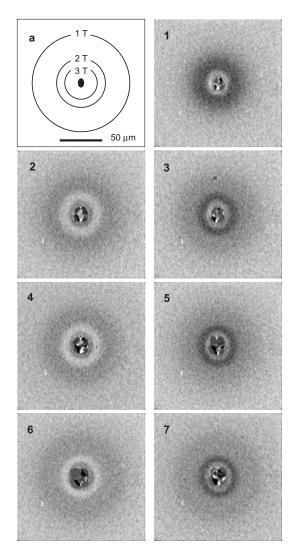


Fig. 15.29. Magneto-optic patterns of the magnetization in a perpendicular granular magnetic recording medium, called CoCrPt I in the text, obtained by sending one or several relativistic electron bunches through the film [788]. Diagram at top left shows contour lines of constant magnetic field $B_{\rm p} = \mu_0 H_{\rm p}$ with the area of the electron bunch shown in the *center*. The numbers on subsequent panels indicate the number of electron bunches that passed through the sample. The gray contrast in the image is set so that the outer light region corresponds to M in the initial "up" state. As darkening intensifies, M has switched increasingly to the opposite "down" direction. The contrast in the central region at $r < 10 \,\mu$ m is due to beam damage

generated by one electron bunch, and patterns generated by up to seven consecutive electron bunches passing through the same focus on the sample are analyzed. The time separation of the consecutive electron bunches was 1 s. In this way, the aforementioned reversibility of precessional switching can be tested. If the grains are magnetically decoupled, as they must be in high density recording, a subsequent magnetic field pulse should restore what the first pulse has generated. Three weeks after exposure, the perpendicular component of M was imaged by polar MOKE. Hence one images only those switching events that have been retained over 3 weeks, a minimal requirement for a magnetic memory.

A set of magnetic patterns exposed to one or multiple magnetic field pulses is shown in Fig. 15.29 panel 1–7. The spatial resolution of Kerr microscopy (MOKE) used to image the patterns is 1 µm, so that the integral over 2,500 grains constitutes one pixel. The spot in the center is due to beam damage in the material. It extends to roughly twice the beam focus. The increase of the damaged area with the number of shots is due to beam jitter, estimated at $\pm 2 \,\mu$ m per shot. The gray scale of the images indicates the magnetic order parameter $M^* = M/M_s$ where M_s is the saturation magnetization \perp to the film plane. The light gray regions near the edge of the frames correspond to the initial "up" state. Darkening indicates that particles have increasingly switched to the down state.

It is evident that the magnetic order parameter M^* changes gradually over tens of micrometers rather than abruptly. The switching is not reversible, because the second magnetic field pulse does not return M to the initial "up" direction. For odd numbers of field pulses, the dark ring where M has switched from "up" to "down" narrows with increasing number of pulses, whereas the outer gray zone corresponding to partially switched M expands. With an increasing number of even pulses, the central light ring narrows and the outer gray zone expands. Such a switching behavior is characteristic of a stochastic process. Starting with a homogeneous magnetic "up" state, it takes only seven magnetic field pulses to create a random distribution of the magnetization direction throughout the large grey zone where $M^* = +1$ in some grains but $M^* = -1$ in others.

Let us first discuss the mean switching field strength B_0 at which the magnetic order parameter vanishes after the first magnetic field pulse. Figure 15.28 shows in fact the mean path followed by the magnetization with a field amplitude B_p close to B_0 . Using $B_p = 54.7/R$ derived from the Biot–Savart law (4.19), B_0 corresponds to the radius R_0 of the circle along which $M_1^* = 0$. This radius can be calculated with the Landau–Lifshitz–Gilbert (LLG) equation, assuming coherent precession and inserting the magnetic anisotropy field H_A and fitting the Gilbert damping constant α to reproduce the data. But in the limit $H_A = 0$ and $\alpha = 0$, one can calculate by hand the largest possible radius R_0^{\max} at which $M^* = 0$. One simply needs to know that R_0^{\max} is given by the condition that the precession angle $\gamma = \pi/2$. Using the same Ansatz as in

(15.11), one obtains

$$R_0^{\max} = \mu_0 \frac{gNe^2}{2\pi^2 m_{\rm e}}.$$
(15.14)

If we assume for the grains the g-factor, g = 2.2, for bulk Co, we obtain $R_0^{\text{max}} = 41 \,\mu\text{m}$ with the experimental number N of electrons per bunch. Figure 15.30 shows the order parameter $M^*(R)$ actually observed with the three different magnetic media [788].

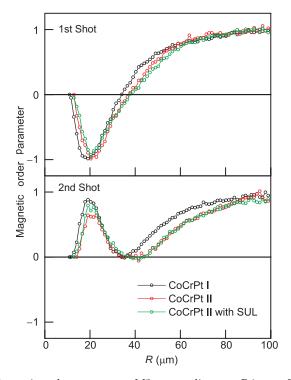


Fig. 15.30. Magnetic order parameter M^* versus distance R in µm from the center for three different materials. The graphs shows the magneto-optically determined order parameter $M_1^*(R)$ (upper graph) and $M_2^*(R)$ (lower graph) after one and two magnetic field pulses, respectively [848]. It is evident that the switching transition extends over large distances rather than occurring at one sharply defined radius, translating into a broad range of switching field amplitudes B_p for the grains. Furthermore, the switching is irreversible as the second switch does not restore the initial uniform order $M_0^* \equiv +1$. For CoCrPt I with the larger $H_{\text{ani}}^{\text{eff}}$, the zero intercept $M_1^* = 0$ occurs somewhat closer to the center compared to CoCrPt II and III with the smaller $H_{\text{ani}}^{\text{eff}}$. Note, that $M^*(R)$ is identical for CoCrPt II and CoPt III which means that SUL does not affect precessional switching

The condition $M^* = 0$ occurs in all cases at $R_0 < R_0^{\max}$, meaning that in reality magnetic field pulses of higher amplitude are needed to induce a switch. This is due to the combined action of the magnetic anisotropy and the damping. The precession in the anisotropy field, so far neglected during the field pulse, induces lengthening of the pathway of M towards the equator of the sphere of Poincaré thereby reducing R_0 , while the damping is expected to reduce R_0 by slowing down the angular velocity ω of the precession.

Since the magnetic anisotropy is well known from other experiments [847], R_0 can be calculated rigorously with this anisotropy using the LLG-equation discussed in Sect. 3.6.2. It turns out that the damping constant α of the precession during the field pulse has to be as high as $\alpha = 0.35$, to obtain the observed R_0 for all three samples. A damping of this magnitude is considerably larger than the typical intrinsic damping.

The strong damping of the precession revealed in the experiment signals that the torque exercised by the magnetic field pulse is lost at a very high rate, presumably by deposition into the spin system.

CoCrPt I, which generated the magnetic patterns of Fig. 15.29, possesses the largest $H_{\text{ani}}^{\text{eff}} = 684 \,\text{kA} \,\text{m}^{-1}$, and exhibits $M^* = 0$ at the smallest R_0 . CoCrPt II and CoCrPt III both have by a factor 0.56 lower $H_{\text{ani}}^{\text{eff}} = 398 \,\text{kA} \,\text{m}^{-1}$ compared to CoCrPt I. They both exhibit $M^* = 0$ at larger, but identical R_0 . The fact that R_0 as well as the overall shape of $M^*(R)$ is the same in CoCrPt II and III is surprising because CoCrPt III sits on a soft magnetic underlayer (SUL) while CoCrPt II does not. This indicates that the SUL has no influence on precessional switching.

Let us lastly analyze the irreversibility of the switching in more detail by considering the precession of the magnetization M of a magnetic particle for a time τ in a magnetic field B. If the precession angle $\gamma \propto B\tau$ due to the field pulse is less than $\pi/2$ needed to rotate the magnetization into the hard plane, the sample will not switch unless random torques or random initial conditions supply the lacking precessional angle. We now assume that the probability p of such stochastic events is Gaussian (see Appendix A.10) and can be expressed as the probability of an additional magnetic field Γ :

$$p(\Gamma) = \frac{1}{\Delta B \sqrt{2\pi}} \exp\left(-\frac{\Gamma^2}{2(\Delta B)^2}\right), \qquad (15.15)$$

The magnetic order parameter $M^*(B)$ is given by the fraction of particles that switch minus the fraction of particles that do not switch in a single pulse of amplitude B:

$$M^{*}(B) = \int_{-\infty}^{B_{0}-B} p(\Gamma) \,\mathrm{d}\Gamma - \int_{B_{0}-B}^{\infty} p(\Gamma) \,\mathrm{d}\Gamma \,, \qquad (15.16)$$

We can now choose the average switching field amplitude B_0 and its variance ΔB to fit the observed dependence of the order parameter on distance

 $R \ M_1^*(R)$ after the first field pulse. $M_1^*(B)$ is calculated from (15.16) for $R > 20 \,\mu\text{m}$ with the choice $B_0 = 1.7 \text{ T}$ and $\Delta B = 0.59 \text{ T}$. After substituting the variable B by R, one obtains $M_1^*(R)$ which is plotted in Fig. 15.31 panel 1 on top of the experimental data. It reproduces the observed $M_1(R)$ for CoCrPt I after the first field pulse in a perfect way.

CoCrPt II and III require both the same but lower field value $B_0 = 1.55$ T and slightly different $\Delta B = 0.57$ and 0.51 T, respectively, to reproduce the observed $M_1(R)$. The lowering of the average switching field B_0 in CoCrPt II and III is understood with the help of the LLG equation using the identical damping parameter $\alpha \approx 0.35$. It is interesting to note that $H_{\text{ani}}^{\text{eff}}$ which is almost 2 times lower in the latter samples compared to CoCrPt I plays a relatively insignificant role in precessional switching. This is in contrast to the quasistatic Stoner–Wohlfarth switching discussed in Sect. 11.5, where the field strength necessary for switching scales with the anisotropy field. The increase of M_1^* at $R \leq 20 \,\mu\text{m}$ indicates the onset of the second precessional switch. It cannot be quantitatively analyzed because the beam damage area is too close.

Strikingly, the order parameters $M_2^*(R), M_3^*(R), ..., M_n^*(R)$ are obtained from $M_1^*(R)$ by multiplication:

$$M_n^*(R) = [M_1^*(R)]^n, (15.17)$$

This accounts very well for the features observed in the experimental data, shown as points in Fig. 15.31, panel 1–6, on top of the calculated distributions. Of course, any experimental errors are enhanced by raising $M_1^*(R)$ to the *n*th power. Such experimental errors may be caused by beam jitter, and the uncertainty in extrapolating $M_1^*(R) \to +1$. At any rate, multiplicative probabilities are the signature of a random variable. Therefore, the analysis of the multiple pulse experiments reveals that the switching is dominated by a memory-less, or Markov uniform stochastic process. Stochastic switching has been observed in many cases. It is usually modeled by inserting a probability distribution of random magnetic fields into the LLG equation. We see here that the strong and short magnetic field pulses make it possible to actually determine the probability distribution of the magnetic field (15.15) by experiment.

What one now wants to know are the sources of the randomness. It turns out that the causes are not known with certainty. However, one can exclude certain phenomena that come to mind. Two theoretical results based on model calculations with the LLG equation are shown in panels (a) and (b) of Fig. 15.31. Panel (a) demonstrates that static dispersion of the easy axis of magnetization in the decoupled single grains cannot produce anything but deterministic switching. Such switching reverses M_1^* to the original $M_0^* = +1$ in the second shot. This is in gross contradiction to the experiment.

Panel (b) explores thermal excitation of the uniform precession mode. This mode determines the long-term stability of the grain magnetization as discussed in Sect. 11.5. The degree to which the uniform mode is excited is

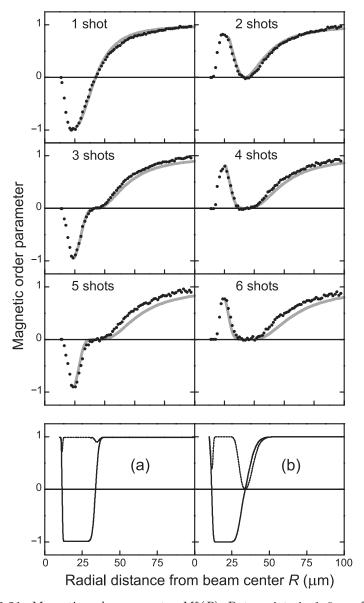


Fig. 15.31. Magnetic order parameter $M_n^*(R)$. Data points in 1–6 are from radial cuts of the magneto-optic patterns in Fig. 15.29, setting $M_1^*(100 \,\mu\text{m}) = +1$ and $M_1^*(20 \,\mu\text{m}) = -1$. The gray lines are generated from $M_n^*(R) = [M_1^*(R)]^n$. (a) Calculated $M_1^*(R)$ (full line) and $M_2^*(R)$ (dashed line) with the observed easy axis dispersion of 5.5° FWHM [847] showing $M_2(R) \equiv M_0 = +1$ in stark contrast to the experiment. (b) Calculated $M_1^*(R)$ (full line) and $M_2^*(R)$ (dashed line) assuming the excitation of the uniform precession mode corresponding to the observed long term stability of the bits, from [788]

known from the long-term stability of the bits [443]. The uniform mode introduces randomness in the direction of M at the point in time when the magnetic field pulse hits. In this way, the uniform mode indeed generates dispersion of $M_1^*(R)$, but the dispersion is much too small to explain the data. To reproduce the observations, one would have to assume that the uniform mode is excited to the extent that the magnetization direction of the bits has a lifetime of only 1 μ s according to (11.40). This is again in stark contradiction to the fact that the data have been taken 3 weeks (1.8×10^6 s) after exposure, and in fact were designed to be stable for years. Therefore, the magnetization in the grains must have a substantial lifetime. This in turn proves that the uniform precession mode is not excited to the extent necessary to explain the observed randomness.

The effect of heating the sample by the electron bunch can be asserted without calculation. The supersonic heat wave that might emerge from the point of impact of the electron bunch requires 10^{-9} s to travel 1 µm. However, the motion of M is already completed at that moment in time. Similarly, magnetostatic coupling between the grains cannot explain the variance of the switching fields. This coupling favors antiparallel alignment of neighboring bits in the case of perpendicular M, but parallel alignment in the case of in-plane M. Hence it changes sign just at the moment in time when the magnetization precesses toward the hard plane of the films. Therefore, magnetostatic coupling has a complicated, but generally small influence on the process of switching. SUL changes the magnetostatic coupling significantly. Therefore, if it was an important player in the process of precessional switching with the short field pulses, $M^*(R)$ of grains with and without SUL should be different which it is not, according to Fig. 15.30.

Figure 15.32 compares simulated and observed magnetization patterns for a CoCrPt sample with perpendicular anisotropy, after one and seven field pulses, respectively. The samples were originally magnetized perpendicular to the film plane in the "up" direction, indicated by a light color and a white arrow. The theoretical images were calculated by means of the LLG equation using all known magnetic parameters of the sample as input, including static and thermal disorder. The center regions of the simulations are shown black and correspond to the regions of beam damage in the experimental patterns. The first light-colored rings around the centers correspond to regions where the magnetization has rotated by 360° upon beam exposure and is thus again in the up direction. In the larger dark rings the magnetization direction has rotated 180° from up to down. In the outermost region the magnetization has remained unchanged in the initial up direction.

The important part of the comparison between experiment and theory is the relative sharpness of the rings in the theoretical simulations, in contrast to the wide and diffuse rings seen experimentally. In particular, the magnetic pattern for seven shots observed experimentally shows a broad halo around a narrow dark ring. This halo region consists of an equal number of small

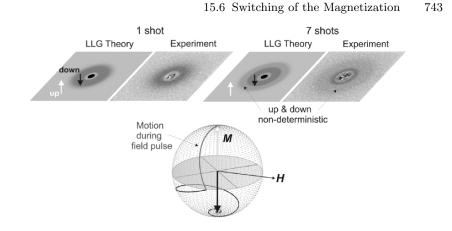


Fig. 15.32. Top: Comparison of simulated and observed magnetization patterns for a CoCrPt sample with perpendicular anisotropy, after one and seven field pulses, respectively. The central region is shown black in the simulations and it corresponds to the region of beam damage in the experimental patterns. The gray-scale contrast in the patterns indicates the direction of the magnetization directions in different sample regions. Light contrast means the magnetization direction is out-of-plane in the "up" direction and dark contrast indicates a "down" magnetization direction, also indicated by arrows. The simulation was done by solving the LLG equation using all known magnetic parameters of the sample as input. Note the sharp ring structures in the simulations and the more diffuse rings in the experimental images, as discussed in the text. *Bottom*: Magnetization reversal process from "up" to "down" during a field pulse in the direction H that rotates the magnetization M just past the hard equatorial plane

regions with up and down magnetization directions, respectively, and thus indicates nondeterministic switching. The broadening of this region in the seven-shot image is reflected in Fig. 15.31 by increasing regions of near-zero intensity with increasing number of shots. At the bottom of Fig. 15.32 we illustrate the motion of the magnetization M during (gray) and after (black) a field pulse in the direction H, that has the proper amplitude and duration to rotate M just across the hard equatorial plane and thus initiates the switch of the magnetization no longer reliably moves across the equator into the opposite direction, resulting in the diffuse halo region without a well-defined magnetization direction.

The puzzle of the origin of the nondeterministic switching may be resolved by realizing that the thermal fluctuations within a grain at ambient temperature also include higher spin wave modes. As illustrated in Fig. 14.9 in such modes the spins are not parallel to each other as in the uniform mode. The higher spin wave modes have a small amplitude before the arrival of the field pulse. Kashuba [849] has given spin wave equations describing the nonequilibrium precessional state of a ferromagnetic system, which reveal a new

type of spin wave instability. Numerical simulations reveal a non-stationary picture of domain chaos as this instability develops. Such spin wave instabilities can explain the observations of stochastic switching in precessional magnetization reversal.

The extremely large value of the damping constant α inferred from the average switching pulse amplitude B_0 indicates that the torque of the magnetic field pulse is lost at a high rate to the spin system. This must result in excitation of higher spin wave modes. At the end of the field pulse, the nonequilibrium modes can exert the random torques postulated in the ansatz (15.15). For a theoretical analysis of the dynamics of magnetization reversal in single magnetic grains, the reader is also referred to the work of Safonov and Bertram [850].

15.6.3 Switching by Spin Injection and its Dynamics

The dynamics following a spin injection pulse leading to magnetization switching has been studied by several groups. Buhrman and collaborators [756] used an experimental arrangement similar to the one shown in Fig. 14.11, except that the magnetic films are made of Ni_{.80}Fe_{.20} permalloy instead of Co, and the magnetization M_1 of the fixed layer source of the spin-polarized current is pinned by exchange bias to an IrMn-antiferromagnet. The easy axis of the magnetization M_2 of the free sensor layer is determined by the shape anisotropy. The relative angle between M_1 and M_2 is detected by the change in the electrical resistance due to the giant magnetoresistance (GMR) effect. In order to achieve an adequate signal-to-noise ratio signal averaging had to be employed. A voltage step with 65 ps rise time was applied to the pillar, causing a step of the current which in turn induced oscillations of the GMR-signal caused by magnetization precession. The oscillatory signal was extracted by subtracting the background.

With periodic signals, the phase of the oscillations has to be the same in each trace or else the oscillations are averaged out. This imposes strict initial conditions, namely M_1 and M_2 cannot be parallel or antiparallel when the spin-polarized current pulse is injected. For such a zero-torque initial condition the start time of the precession would be determined by thermal fluctuations. To avoid random starting conditions of the precession, the initial angle enclosed by M_1 and M_2 was set at 30° and fluctuations were reduced by cooling the sample (40 K in Ref. [756]). Under these conditions one can directly observe GMR oscillations due to magnetization precession. From the damping of the oscillations, the damping of the magnetization precession in the presence of a spin current can be determined. Buhrman and collaborators found that the *total* Gilbert-type damping of the precession of M_2 decreases linearly with increasing spin-current present during precession. This is taken as proof that the *negative* spin-injection induced damping torque increases linearly with the injected current to compensate for the *positive* but constant Gilbert damping due to spin-lattice relaxation. Such behavior is expected from the simple

model of spin injection discussed in Sect. 14.2.3. At a certain spin injection current, both positive and negative damping terms compensate, leading to an effectively undamped precession, or to a steady-state precessional motion of the magnetization M. Buhrman and collaborators [756] indeed observed a steady-state mode of M, showing that the damping of the precession can be controlled electrically. Furthermore, the time needed to switch the magnetization could be chosen to be <1 ns and the switching was deterministic, i.e., it occurred at a well-defined magnitude of the injected spin current.

These experiments are not consistent with models in which the dominant spin transfer mechanism is due to spin wave excitation which would lead to a more chaotic rather than a uniform motion of M. The notion of uniform precession over the whole volume of the sample is also in disagreement with X-ray imaging results discussed later which show that the curly Oersted field generated by the charge current cannot be neglected. Obviously, the dynamics are of key importance for understanding the torques operating when a spin-polarized current is injected. Whatever the final picture may be, the fast switching times <1 ns indicates that spin injection is a highly interesting new concept for magnetic memory applications.

Tulapurkar et al. [851,852] have demonstrated magnetization switching by spin injection at time scales even considerably below 1 ns. They also point out that the energy consumed in pulsed spin injection switching is very low, making the switching promising for applications in magnetic random access memories (MRAMs). The required switching current can be reduced even further by using materials with lower saturation magnetization [852]. These authors applied current pulses of various amplitudes, polarities and durations ranging from 100 ps to 10 ns to pillar-shaped CoFe/Cu/CoFe trilayers. The bottom CoFe-layer is larger and thicker and therefore acts as the pinned layer, thus the sample structure is basically the same as in Fig. 14.11. GMR measurements were again used to reveal the relative magnetization direction in the two layers. It was found that the switching from a parallel direction of M_1 and \boldsymbol{M}_2 to the antiparallel direction (P \rightarrow AP), is independent of temperature from 150 to 240 K, needs a higher current density, and proceeds comparatively slowly. The switching $AP \rightarrow P$ on the other hand takes less current and less time. It also becomes *faster* at low temperatures. The authors define the switching speed as the inverse of the time required for achieving 90%switching probability.

The acceleration of the switching speed on lowering the temperature is surprising. Thermal activation of the uniform precession mode is too small to explain any of these observations, even the trend is wrong. This applies also to more elaborate macrospin models for thermal activation [853, 854]. In references [851, 852] it is then concluded that the sample needs to be in a coherently uniform micromagnetic state in order to be most susceptible to the spin injection torques. At higher temperatures, the population of nonuniform

spin wave modes increases compared to the uniform mode, hence overall, the system is in a less well-defined state. Thus on the basis of this reasoning high temperatures are expected to inhibit the switching of the sample.

Devolder and collaborators [855] carried out a detailed interpretation of the measured results I(R) in references [851, 852], where I is the injected current and R the GMR resistivity of the pillar. Experimentally it is found that the curvature of I(R), which is mainly determined by the deposition of Joule's heat, shows an anomaly in that it depends on the sign of the injected current. By a somewhat complex analysis, Devolder et al. suggest non-uniform magnetic structures, so called C-states. The structure in the fixed layer is assumed to be uniform but deforms temporarily at the edges by the action of the Oersted field coming with the injected charge current which, as opposed to the heat, depends on the direction of the current I(R). Since the GMR signal is the difference between the magnetic structure of the fixed relative to the free layer, this is suggested to explain the dependence of I(R) on the current direction. We shall see below that this analysis is indeed confirmed by X-ray imaging. On the other hand, Fukushima and collaborators [856] interpreted the same experimental data by assuming that there is a uniquely large Peltiereffect with the submicron metallic junctions that leads to cooling of the pillar for one and heating for the other current direction. In principle, this behavior can also explain the dependence of the curvature of I(R) on the direction of the injected current.

This all goes to show how important it is for the understanding of spin injection to actually image the evolution of the magnetic structure in the free layer, independently of temperature and the magnetic state of the fixed layer. This has indeed been accomplished recently by use of X-ray microscopy [763]. Such studies allow the observation of the detailed magnetic orientation of a sensor layer, buried inside a pillar, resulting from spin injection and even during the spin injection process itself. While GMR transport measurements can detect the presence of different magnetic configurations between the polarizing and sensing layers in the spin injection device, the detailed nature of the states remains hidden. As discussed in Sect. 14.2.3 and shown in Fig. 14.10 spin injection is accompanied by Oersted fields consisting of circular magnetic field lines. Micromagnetic computations have indicated that these Oersted fields may indeed play a crucial role in the switching process [748, 749, 761], even in samples as small as 100 nm. The X-ray imaging results reveal a rather interesting phenomenon, namely that the curly Oersted field induces a vortex state which in the switching process is displaced in different directions by the spin current. Thus the vortex state, discussed in Sect. 15.5.2 is far more than an academic curiosity. Similar to a vortex-like hurricane that moves across an island, a magnetic vortex that moves across a small magnetic island will cause a considerable change. We shall now discuss this in more detail.

The sample geometry and the experimental arrangement for the X-ray microscopy measurements by means of STXM are shown in Fig. 15.33. The figure also illustrates the pump-probe scheme used for the measurements. The central part of the spin injection sample was a pillar of oval cross-section and a size of 100 nm \times 150 nm. A 17.5 nm thick antiferromagnetic PtMn layer (green) was used to pin the lowest 1.8 nm thick Co_{0.86}Fe_{0.14} FM layer (blue) by exchange bias. This FM layer was coupled antiferromagnetically through a 0.8 nm thick Ru spacer layer to a second 2.0 nm thick Co_{0.86}Fe_{0.14} FM layer. This AFM coupling between the two FM layers reduced stray fields on the light blue sensor layer. The spin polarization of the injected current flowing through the pillar is determined by the magnetization (red arrow) of the second FM, the "polarizer." It then flows through a 3.5 nm thick Cu spacer layer and enters the 4.0 nm thick Co_{0.86}Fe_{0.14} sensor layer (light blue), whose magnetization is imaged by X-rays. The entire spin injection structure was lithographically built on a SiN_x coated Si wafer. In the last lithography step,

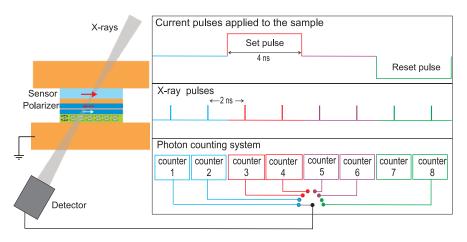


Fig. 15.33. Left: Schematic of the pillar structure, showing the ferromagnetic polarizer (dark blue) and sensor layers (light blue), the antiferromagnetic pinning layer (green) and the Cu leads and spacer layers in orange. The lowest two FM layers are coupled into a fixed antiferromagnetic arrangement by a Ru spacer layer and their magnetization direction is pinned by exchange bias to the green antiferromagnet. The X-ray beam is incident 30° from the surface normal and is focused by a zone plate to a size of about 30 nm. The transmission through the structure as a function of sample position is monitored by a fast X-ray avalanche detector. *Right*: Timing scheme used for the pump-probe spin injection experiments. A positive current pulse, "set pulse," is followed by a negative "reset pulse" and this scheme is repeated. The X-ray probe pulses with a spacing of 2 ns are synchronized to the pump pulses and for each pump-probe cycle the intensities of eight consecutive X-ray pulses are measured by eight separate and fast photon counters. This procedure is repeated for a given sample position in the beam until the signal-to-noise ratio is adequate. The sample is then scanned to a new position and the procedure is repeated

a $100 \,\mu\text{m} \times 100 \,\mu\text{m}$ window was etched from the back through the Si wafer so that the pillar sample was supported only by the remaining SiN_x membrane. Thus X-rays could be sent through the entire pillar structure, as shown in Fig. 15.33.

In an external magnetic field, square GMR magnetization loops are obtained as shown in Fig. 15.34a, indicating that uniform magnetic structures have been reached at the maximum field values. The loop is shifted on the field axis showing that there is residual coupling by the stray field of about -50 Oe from the polarizer at the location of the sensor layer, favoring antiparallel alignment of sensor and polarizer. By injecting positive "set" spin current pulses, corresponding to electron flow from the polarizer to the sensor, and negative "reset" pulses, one expects reproducible jumps of GMR that are of the same magnitude as obtained by switching M in an external field. When such pulses of 4 ns duration are applied, the sample displays an anomaly. As illustrated in Fig. 15.34b the first GMR jump from point A to B is still large and consistent with uniform M reversal, but the reduced GMR jumps under subsequent current injections indicate that a different M state has been created by current injection. This state is stable, as well. The original large GMR jump only appears after the structure has been realigned by an external magnetic field. The nature of the intermediate state, as well as the mechanism leading to it, remains hidden in GMR.

X-ray images of the sample were recorded by means of STXM with a spatial resolution of about 30 nm, limited by the zone plate. The circularly polarized X-rays from the undulator source were incident at an angle of 30° from the

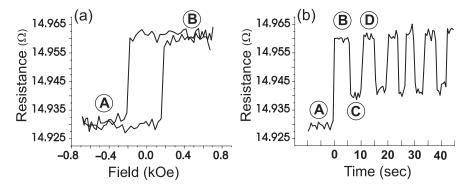


Fig. 15.34. GMR measurements of field and current pulse induced switching for a $100 \text{ nm} \times 150 \text{ m}$ nm sample, also used for Fig. 15.35 below. As shown in (a) the sample shows a square GMR-hysteresis loop in an external field, indicating a uniform saturation magnetization. With current pulses, as applied in the pump-probe X-ray microscopy measurements, the sample exhibits a full change of GMR only on the first current pulse (A to B). Subsequent set and reset pulses (B to C to D etc.) show a smaller GMR effect, indicating the creation of a non-saturated intermediate metastable structure

surface normal of the sample, so that the photon angular momentum had a finite projection along the in-plane magnetization direction of the FM sensor layer. Magnetic contrast was obtained by tuning the X-ray energy to the Co L_3 edge (~780 eV). The rise time of the current pulses was ~200 ps. The current pulse sequence was synchronized with the X-ray pulses which appear every 2 ns. The special photon counting system shown in Fig. 15.33 allowed the measurement of magnetization differences $M_i - M_j$ for each pair of eight consecutive X-ray pulses, suppressing slower drifts and sample vibrations. The delay of the 75 ps wide X-ray pulses to the current pulse sequence could be changed in order to measure the time evolution of the magnetization. Since the GMR data show the formation of a uniform M state after the reset pulse one can use this reference state as input and reconstruct the other Mstates from the appropriate difference measurements. By recording images for two orthogonal azimuthal sample orientations relative to the fixed X-ray direction, arrow plots for the in-plane magnetization directions in the 4-nm thick $Co_{0.86}Fe_{0.14}$ FM sensor layer can then be constructed. The determined magnetization components M_x (horizontal) and M_y (vertical) are shown in Fig. 15.35 as a function of time relative to the onset of the spin injection pulses.

The time evolution of the magnetization near the onset of the current pulses is shown in Fig. 15.35a-i. The changes of the magnetization happen within a few hundred picoseconds after the 200 ps onset of the pulse sequence. The initial magnetization is uniform (Fig. 15.35a). The positive current pulse (electrons flow from the polarizer into the sensor layer) causes the magnetization to bend upward (Fig. 15.35b), forming a vortex. As this vortex moves through the sensor layer, it leaves behind a trail of reversed magnetization. As the vortex center leaves the magnetic structure, a C-state (Fig. 15.35c) is formed. The falling edge of the current pulse has no noticeable effect, showing that the C-state (Fig. 15.35d) is a stable configuration, as well. The negative pulse first leads to an almost uniform magnetization, caused by injection of a new vortex with opposite curl into the sensor layer (Fig. 15.35e). The new vortex moves through the sensor layer and reverses its magnetization (Fig. 15.35f). The new C-state with the component M_x antiparallel to the polarizer is not stable at zero current but relaxes into the original uniform configuration (Fig. 15.35g-i).

In the final uniform state reached after the reset pulse, the magnetization of the sensor M is antiparallel to the magnetization $M_{\rm P}$ in the polarizer. The uniform state is thus stabilized by the stray field of the polarizer. In contrast, the C-state of Fig. 15.35c forms when M is parallel to $M_{\rm P}$ and in his case the stray field opposes and destabilizes a potential uniform state. The possible relaxation of the C-state into the uniform state depends on fine details of the magnetic couplings and other properties of the nanopillar. Metastable C-states are, of course, undesirable in technological applications.

750 15 Ultrafast Magnetization Dynamics

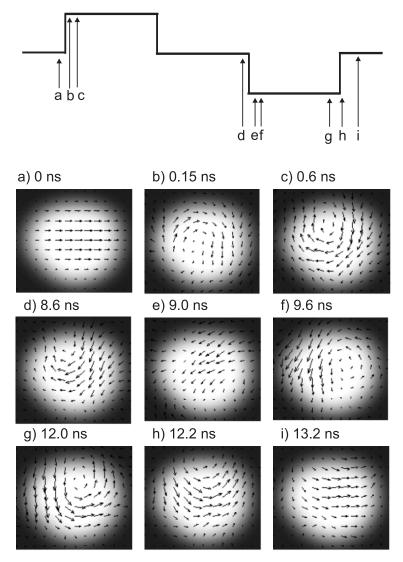


Fig. 15.35. Evolution of the magnetization during the pulse sequence within the 4nm thick $\text{Co}_{0.86}\text{Fe}_{0.14}$ sensor layer inside a $100 \text{ nm} \times 150 \text{ nm}$ nanopillar. The uniform antiparallel configuration (a) is switched into a C-state with parallel M_x (horizontal axis) component (c). The switching process involves motion of a magnetic vortex through the sensor layer, visible in (b). The C-state is stable after the falling edge of the pulse (d) and is reversed by the "reset"-pulse into another C-state (f). The switching of one C-state into another is caused by lateral vortex motion as well, leaving a uniformly magnetized area in the center of the sensor layer (e). The Cstate with its horizontal x-component antiparallel to the polarizer is unstable and relaxes into the uniform state (g-i), but note that this relaxation is comparatively slow

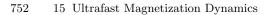
The experiment shows that the motion of vortices inside the sensor layer dominates the switching process. The switching speed of 500 ps leads to a vortex speed of about $150 \,\mathrm{m \, s^{-1}}$. The motion of the vortex across the sensor layer is caused by the spin current and is expected to involve precessional motion of the magnetization that cannot be resolved with the time resolution of our experiment. This finding shows that vortex dynamics, previously observed in small magnetic structures as discussed in Sect. 15.5.2, can dominate the switching mechanism in spin transfer nanopillars. The Oersted field breaks the mirror symmetry along the direction of the injected spin direction (x-axis). This manifests itself in the bending of the magnetization into C-states and vortices. Therefore, no thermal fluctuations are needed to initiate switching. Thus a nonzero torque exists immediately after the rising edge of the current pulse. This explains the short switching time of 100 ps observed previously [855] and the 500 ps switching time observed here. We note that such nonthermal switching is deterministic and therefore desirable in switching applications.

15.6.4 On the Possibility of All-Optical Switching

The principle of all optical switching is based on optical pumping in atoms discovered by Kastler and collaborators and distinguished by the Nobel prize in physics in 1966. Figure 15.36 illustrates how one can induce spin switching with all optical techniques for a Na-atom (the drosophila of atomic physics). With time the Na atoms are converted from the ground state ${}^{2}S_{1/2}, m_{j} = -1/2$ to the excited state ${}^{2}S_{1/2}, m_{j} = +1/2$ with opposite spin polarization relative to the quantization axis of the external magnetic field. The spin reversal is easily detected since the Na-vapor becomes transparent for the incident light when the switching is completed.

At first sight, this seems paradoxical since a change in spin direction would require the presence of a magnetic field \boldsymbol{H} , perpendicular to the external field \boldsymbol{B} and the quantization axis z, about which the spin could precess from the orientation $s_z = -1/2$ to $s_z = +1/2$. The paradox is resolved by the fact that, according to Fig. 15.37, the spin–orbit coupling produces an effective magnetic field $\boldsymbol{H} \propto \boldsymbol{L}$ that is much stronger and not collinear with the applied field \boldsymbol{B} . While there is no spin–orbit coupling in the two lowest l = 0states ${}^2S_{1/2}$ in Fig. 15.36, a spin–orbit field does indeed exist in the excited l = 1 state ${}^2P_{1/2}, m_j = +1/2$ through which the system passes. The vector model of the $P_{1/2}$ atomic state shown in Fig. 15.37 reveals the existence of this perpendicular magnetic field component.

The total angular momentum J = L - S of the state ${}^{2}P_{1/2}$ precesses about the direction of B with a magnetic quantum number $m_{j} = J_{z} = 1/2$ along B. The spin-orbit induced vector addition of the *noncollinear* vectors S and L causes them to precess about J, at a frequency given by the strength ξ of the spin-orbit interaction. In the language of quantum mechanics, the spin is



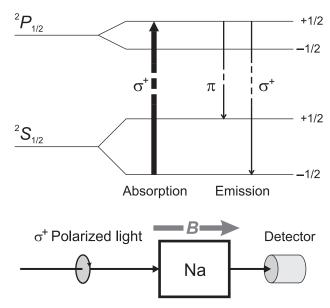


Fig. 15.36. Principle of optical pumping. Na-vapor is enclosed in an inert container like teflon. Circularly polarized light σ^+ , incident parallel to the quantization axis defined by the applied magnetic field B, is tuned to the allowed dipole transition ${}^2S_{1/2}, m_j = -1/2 \rightarrow {}^2P_{1/2}, m_j = +1/2$ (absorption: $\Delta m_j = +1$). The spontaneous radiative decay of the excited state may lead to emission of σ^+ -light (emission: $\Delta m_j = -1$) and linearly polarized light π ($\Delta m_j = 0$), the latter producing the final state ${}^2S_{1/2}, m_j = +1/2$. If spin relaxation on the walls is slow, the Na-atoms in the original state ${}^2S_{1/2}, m_j = -1/2$ will be depleted and with time one will obtain a vapor that is in the state ${}^2S_{1/2}, m_j = +1/2$ with opposite spin polarization. The vapor will then be transparent to the incident light

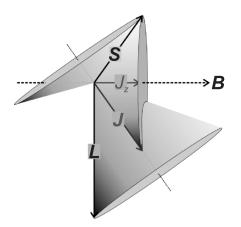


Fig. 15.37. Vector-model for the state $P_{1/2}$. The vectors S and L precess fast with an angular frequency $\omega = \xi/\hbar \approx 10^{14} \text{ rad s}^{-1}$ about J while J precesses slowly with $\omega = (e/m_e)B \approx 10^{11} \text{ rad s}^{-1}$ about the applied field B

in a mixed state as long as the orbital moment is present. From such a mixed spin state, back transitions to either one of the pure ground states can occur.

Angular momentum is conserved in optical pumping since \hbar is deposited in the atom during excitation, but in the transition to the reversed spin state the emitted light is linearly polarized, hence no angular momentum leaves the atom. The angular momentum \hbar left in the atom enables the spin transition. Hence in the end, the angular momentum \hbar necessary to induce the spin transition is supplied by the light. The process is in fact analogous to switching by spin injection, the only difference being that the angular momentum is now imported by the circularly polarized photons instead of the polarized electrons.

15.6.5 The Hübner Model of All-Optical Switching

All-optical switching (AOS) applied to solid magnetic materials represents an intriguing idea that has emerged with the availability of ultrafast, high-intensity (coherent) laser pulses. Hübner and collaborators [784–787] have suggested a scheme that is based on optical transitions driven by a coherent laser field between the ground state and a well-defined excited state of a ferromagnet, and use of the spin–orbit coupling to switch the spin while the system is in the excited state. Indeed, in semiconductors and insulators the creation and coherent manipulation of excited electron spins has been demonstrated [78]. The question arises whether it is also possible to use related techniques to reliably switch the magnetization in ferromagnetic materials.⁸

In order to understand Hübner's model we start with the simplest quantum system consisting of two sharp atomic levels and a laser pulse that connects the two levels as shown in Fig. 15.38. The energy difference between the levels is $\Delta E_{10} \approx 1 \,\text{eV}$ and we assume further that the lifetime of the excited state is infinitely long. The central frequency of the laser pulse is to be in resonance with the transition energy according to $\hbar \omega = \Delta E_{10}$.

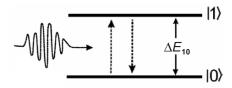


Fig. 15.38. A two level system excited by a laser pulse of central frequency $\omega = \Delta E_{10}/\hbar$, adapted from [785]

With such a laser pulse, transitions from the initial state $|0\rangle$ to the excited state $|1\rangle$ will be induced. A complete occupation of the final state occurs with a certain duration and amplitude of the laser pulse, but as soon as the

⁸The understanding of such optical processes may also shed light on the ultrafast incoherent loss of the magnetization that was discussed in Sect. 15.4.3.

higher lying state is occupied, the laser field stimulates transitions back to the ground state. In this way, the occupation of the excited state oscillates in time as illustrated in Fig. 15.39.

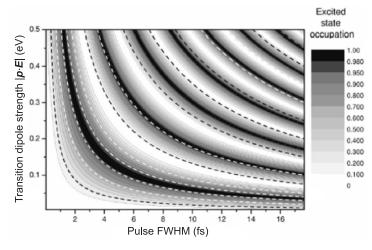


Fig. 15.39. Dependence of the occupation of the excited state on the strength of the dipole operator $|\mathbf{p} \cdot \mathbf{E}|$ of the electronic transition (ordinate) and the duration of the laser pulse of a fixed shape (abscissa) for the main laser frequency resonant with the level splitting ΔE_{10} [785]

The figure illustrates the dependence of the final state population on both the width and the amplitude of the exciting laser pulse. The transition probability is given by the dipole operator $|\mathbf{p}\cdot\mathbf{E}|$ (see Sect. 9.5.2), with the oscillating electric field of the laser $\mathbf{E} = E_0[\exp(-i\omega t) + \exp(i\omega t)]$ driving the absorption $(\exp(-i\omega t))$ and stimulated emission $(\exp(i\omega t))$ of photons. Figure 15.39 shows that the occupation of the excited state $|1\rangle$ oscillates in time between 0 (white) and 1 (black) depending on the combination of the size of $|\mathbf{p}\cdot\mathbf{E}|$ and duration of the laser pulse. Figure 15.39 has been calculated from the time-independent Hamiltonian H(x) of the two-level electronic system and the time-dependent interaction energy V(x,t) of the electromagnetic field, keeping only the dipolar interaction term. The model Hamiltonian is thus H(x,t) = H(x) + V(x,t), and the data of Fig. 15.39 are solutions of the corresponding time-dependent Schrödinger equation [785].

The two-level system is driven back and forth between the two states without change of the spin. The central idea behind AOS is now the manipulation of the electron spins in the *excited state*. This may be accomplished again by a magnetic field that has a component perpendicular to the electron spins. If furthermore the field is strong the spin will rapidly precess by 180° . According to Sect. 3.6, a magnetic field of order 100 T would reverse the spin in about 200 fs. Now, if this magnetic field were to exist solely in the excited state, the spin could change its direction, say from \uparrow to \downarrow during the time it resides in this state. Then, stimulated transitions to the initial state $|0_{\uparrow}\rangle$ would be forbidden. Rather, on continuation of the laser pulse, transitions to the reversed spin state $|0_{\downarrow}\rangle$ would occur. This amounts to AOS.

Figure 15.40 depicts the required three-level system. The process starts in the initial state $|0_{\uparrow}\rangle$ with occupation 1, then the excited state $|1_{\uparrow}\rangle$ is populated to 1 with a suitable strength and duration of the laser pulse. A perpendicular field is then turned on so that all spins precess by 180° and end up in state $|1_{\downarrow}\rangle$. This state is then de-excited by the continuing laser pulse to the final state $|0_{\downarrow}\rangle$.

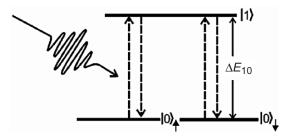


Fig. 15.40. Three-level system, where the initial state $|0_{\uparrow}\rangle$ is a majority spin state and $|0_{\downarrow}\rangle$ is a minority spin state. In the excited state $|1\rangle$ the spins are switched by precession in a perpendicular magnetic field from \uparrow to \downarrow

The calculated dependence of the final state spin orientation for the process in Fig. 15.40 is depicted in Fig. 15.41 [786]. Depending on the length of the laser pulse and the strength of the magnetic field in the excited state, expressed as the energy splitting between opposite spin states $\xi = 2\mu_{\rm B}H$ ($\xi = 0.12 \,{\rm eV}$ correspond to a field $\mu_0 H = 1000 \,{\rm T}$), the spin can end up in the switched state $|0_{\perp}\rangle$ or unswitched in state $|0_{\uparrow}\rangle$.

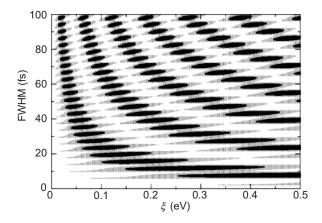


Fig. 15.41. The expectation value of the spin direction (shading) as a function of the laser pulse duration (ordinate) and the magnetic field H in the excited state, expressed as the energy splitting between opposite spin states $\xi = 2\mu_{\rm B}H$ [786]

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The crucial question is how one can produce a suitable strong magnetic field $H \perp M$ in the excited state that leads to spin precession or, in the language of quantum theory, to spin mixing. Hübner et al. suggest to let the spin-orbit coupling do the switching. As shown in Fig. 7.38 one may envision a system with ligand field split 3*d*-states and a typical splitting of about 1 eV as assumed in the model calculation for Fig. 15.41 [786].

We now consider optical transitions between the ligand field split 3d-states. These transitions do occur in transition metal compounds and they are responsible for the beautiful colors of the transition metal oxides (red in Feoxide, blue in Co-oxide, green in Ni-oxide). Since angular momentum has to be conserved in allowed optical transitions, the transitions must deposit the angular momentum \hbar of the photon in the excited state, that is we can populate only one half of the crystal field state in which the angular momentum of the photon is now present as an angular momentum of the electron. This nonequilibrium occupation of the ligand field state now possesses an angular momentum or orbital moment which corresponds to a magnetic field given by $\xi = 2\mu_{\rm B}H$, where ξ is the strength of the atomic spin-orbit coupling.⁹ Since the orbital moment direction is fixed by the ligand field, the magnetic field effective for spin precession is held in place. This field corresponds to the external field B in the optical pumping model with Na shown in Fig. 15.36. The transfer of angular momentum to the crystal lattice now occurs on the femtosecond time scale of the spin precession in the transiently excited state with orbital moment. This time scale should be compared to the picosecond time scale that corresponds to the weak magnetic anisotropy of the order of $\mu \,\mathrm{eV}$ in the electronic ground state of the crystal.

We summarize the situation with AOS as follows:

- 1. Coherent optical manipulation of the spin dynamics requires discrete energy levels such as present in magnetic semiconductors and insulators.
- 2. The exchange field $H_{\rm ex}$ present in the transiently excited state has been neglected. $H_{\rm ex}$ exists unless all or most of the electrons are excited. It adds to the field $H_{\rm ls}$ of the spin–orbit coupling, but it is always parallel to the majority spin direction, hence presents an obstacle to the required spin precession. In fact, AOS is impossible if $H_{\rm ex} \gg H_{\rm ls}$ and incomplete with $H_{\rm ex} \approx H_{\rm ls}$.
- 3. Electron states in solids have a finite lifetime due to nonradiative transitions caused by electron-electron scattering. These lifetimes are very short in transition metals. According to Fig. 15.10, the lifetime of a state 1 eV above $E_{\rm F}$ in Co is only 5 fs, for example. Relaxation of the excited state in electron-electron scattering leads to destruction of spin coherence. Therefore, one cannot expect to induce coherent electron spin dynamics

⁹In the classical relativistic language, we consider the rest system of the electron, in which the charged atom of the crystal rotates around the electron and produces the desired magnetic field in which the spin will precess.

in metals with laser pulses of 30 fs duration. Yet, some optically induced loss of magnetization can be imagined. A loss of spin order through dephasing of spins in the excited state is thus a realistic possibility. It can be of technical interest as it might be useful to facilitate regular magnetic switching with a magnetic field without heating the whole crystal lattice.

4. It is important to remember that the recovery of the magnetization after the application of a laser pulse is still slow as it is governed by the spin–lattice relaxation on the ps-time scale. The slow recovery is a distinguishing characteristic of ultrafast demagnetization induced by laser pulses.

15.6.6 All-Optical Manipulation of the Magnetization

As an example, let us discuss the work of Rasing and collaborators [858] which demonstrates that circularly polarized femtosecond laser pulses can indeed excite coherent spin dynamics in a magnetic material such as ferrimagnetic DyFeO₃. These rare earth orthoferrites crystallize in an orthorhombic perovskite-type structure [859]. The magnetic moments of Dy are not ordered above 4 K, hence Dy is in a paramagnetic state. The Fe³⁺ ions form a spherically symmetric ${}^{6}A_{1g}$ state corresponding to the atomic $3d_{5/2}$ -state of a half full 3d shell in the crystal field. The Fe-moments are coupled antiferromagnetically by isotropic exchange, but the Dzyaloshinskii interaction [860] gives rise to a canting of opposite spins by 0.5° which in turn generates a small magnetization of $M_{\rm s} = 8 \,{\rm G}$. Despite the small $M_{\rm s}$, the Faraday rotation, that is the angle of rotation of the plane of linearly polarized light per unit path length of the light is very large in this material, amounting to $3,000 \deg \mathrm{cm}^{-1}$. This large Faraday rotation indicates a large magneto-optic coupling which can probably be explained with the presence of Dy. Dy doping is known to significantly increase the spin-lattice interaction in other cases as well [782,783]. Figure 15.42 demonstrates that one can excite precession of the Fe-moments with a pump laser in complete analogy to the excitation with a magnetic field pulse.

Two distinct processes can be observed in Fig.15.42. First, a quasiinstantaneous change of the Faraday rotation, and second an oscillation of the Fe moments about the equilibrium position. The change of the magnitude of the Faraday rotation is due to the photoexcitation of the Fe ion in the ${}^{5}S_{5/2}$ state and the relaxation of the excited electron back to the $S_{5/2}$ ground state. When the spin of the electron is inverted during the residence time in the excited state, it can relax back into the ground state only by reducing the magnetic quantum number, that is we have the transition $S_{5/2}, m_j = 5/2 \rightarrow S_{5/2}, m_j = 3/2$ causing precession of $S_{5/2}$ about the equilibrium position, here with a period of about 5 ps. These oscillations are observed with the probe pulse up to long delay times of more than 60 ps, that is the relaxation in the absence of the laser pulse is slow as it is given by the spin–lattice relaxation time.

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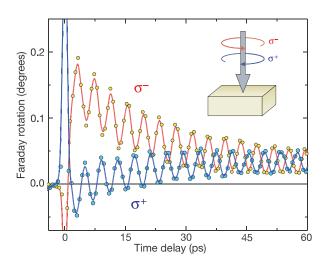


Fig. 15.42. All-optical excitation of the magnetization in DyFeO₃ orthoferrite. During the circularly polarized infrared pump-laser pulse of 200 fs duration, electrons are excited from the $S_{5/2}, m_j = 5/2$ -ground state of Fe to a transient crystal field state with spin-orbit interaction where the spin is reversed and then relaxes back into the ground state $S_{5/2}, m_j = 3/2$. The coherent precession of the $S_{5/2}, m_j = 3/2$ states of the Fe ions about their equilibrium position is revealed by the time-delayed probe pulse. When the helicity of the pump pulse is reversed, the oscillations show opposite phase as expected. Figure courtesy of Theo Rasing [858]

Altogether it follows that stimulation of an optical transition into a virtual state with a strong spin-orbit interaction may lead to the subsequent stimulated relaxation into the ground state, accompanied by spin switching and re-emission of a photon with a fixed phase shift and lower energy relative to that of the incident photon. The exciting photon again has to be circularly polarized while the re-emitted photon must be linearly polarized in order to supply the angular momentum required to switch the spin. The energy difference between exciting and re-emitted photon is given by the energy necessary to invert one spin, hence it is small.

In principle, the process amounts to the excitations of the uniform spinwave mode with light, known from Brillouin light scattering. Hence the experiment [858] demonstrates the excitation of homogeneous magnetization precession by light. It is different and more effective than switching by simply heating the magnetic material with the laser pulse. If excited with sufficient amplitude, the homogeneous mode will lead to deterministic magnetic switching. Yet the switching remains still to be demonstrated, particularly with materials of actual interest in applications.

15.7 Dynamics of Antiferromagnetic Spins

In the context of the previous experiment, we briefly discuss a basic difference in the dynamics of ferromagnets (FM) or ferrimagnets as compared to antiferromagnets (AFM). In AFM, there are two oscillation modes, one with high frequency driven by the exchange interaction where the atomic moments change their relative orientation, and one with lower frequency in which the moments of the AFM oscillate in phase with each other about the direction given by the magnetic anisotropy. In the latter case, one assumes rigid coupling of the two sublattices of the AFM, and the net angular momentum connected to magnetic order is then zero. This means that precession does not occur in this case as there is no angular momentum that has to be conserved.

Upon exciting electrons to a higher lying crystal field state, the magnetic anisotropy can change direction. For example, for NiO a 90° rotation occurs during excitation with a laser pulse that involves only a small change of temperature of 30° C [820]. The change of anisotropy direction can be induced on the femtosecond time scale. In AFM, the magnetizations of the two sublattices M_1 and M_2 can react to the change of the magnetic anisotropy direction by simply rotating into the new direction on a short time scale. In contrast, the magnetization M of a ferromagnet must always precess when the effective magnetic field changes direction because angular momentum has to be conserved. Only through relaxation during precession can the magnetization reach the new equilibrium position. This important difference is depicted in Fig. 15.43.

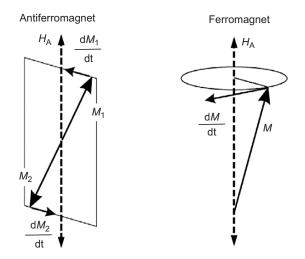


Fig. 15.43. Comparison of spin motion in antiferromagnets and ferromagnets. In contrast to the precessional motion of M in a FM, the sublattice magnetizations M_1 and M_2 of the AFM simply rotate into the new field direction. Consequently, the Landau–Lifshitz equation has serious limitations in understanding the dynamics of AFMs. Figure taken from [817]

Part VI

Appendices

A.1 The International System of Units (SI)

armah al	nhusical quantity	a quina lant	numerical value and units
symbol	physical quantity	equivalent	numerical value and units
\boldsymbol{A}	Vector potential		$\mathrm{Vsm^{-1}}$
${oldsymbol E}$	Electric field		$V m^{-1}$
D	Displacement	$\epsilon\epsilon_0 oldsymbol{E}$	$A \mathrm{s}\mathrm{m}^{-2}$
H	Magnetic field		$\mathrm{A}\mathrm{m}^{-1}$
B	Magnetic Induction	$\mu\mu_0oldsymbol{H}$	$V \mathrm{s} \mathrm{m}^{-2} \ (\equiv T)$
\boldsymbol{p}	Electric dipole moment		Asm
m	Magnetic dipole moment		Vsm
M	Magnetization	$oldsymbol{m}/V$	$V \mathrm{s} \mathrm{m}^{-2} \ (\equiv T)$
c	Speed of light	$1/\sqrt{\epsilon_0\mu_0}$	$2.998 \times 10^8 \mathrm{ms^{-1}}$
ϵ_0	Dielectric constant	$1/\mu_0 c^2$	$8.854 \times 10^{-12} \mathrm{AsV^{-1}m^{-1}}$
μ_0	Permeability	$1/\epsilon_0 c^2$	$4\pi \times 10^{-7} \mathrm{VsA^{-1}m^{-1}}$
$1/4\pi\epsilon_0$	SI units prefactor		$8.99 \times 10^9 \mathrm{VmA^{-1}s^{-1}}$
$\mu_{ m B}$	Bohr magneton	$e\hbar\mu_0/2m_{ m e}$	$1.165 \times 10^{-29} \mathrm{Vms}$
$m_{ m e}$	Electron mass		$9.109 \times 10^{-31} \mathrm{VAs^3m^{-2}}$
h	Planck's constant		$6.626 \times 10^{-34} \mathrm{VAs^2} = 4.136 \mathrm{eVfs}$
$N_{\rm A}$	Avogadro's number		$6.02214 \times 10^{23} \operatorname{atoms/mol}$
q = -e	Electron charge		$-1.602 \times 10^{-19} \mathrm{As}$
$e/m_{ m e}$	Electron charge/mass	ω/B	$1.759 \times 10^{11} \mathrm{rads^{-1}T^{-1}}$
$m_{\rm e}c^2$	Electron rest energy		$0.819 \times 10^{-13} \mathrm{VAs} = 0.511 \mathrm{MeV}$
$E_{\rm R}$	Rydberg energy	$m_{\rm e}e^4/2\hbar^2(4\pi\epsilon_0)^2$	$13.606\mathrm{eV}$
a_0	Bohr radius	$4\pi\epsilon_0\hbar^2/m_{\rm e}e^2$	$0.529 \times 10^{-10} \mathrm{m}$
$r_{\rm e}$	Classical electron radius	$e^2/4\pi\epsilon_0m_{ m e}c^2$	$2.818 \times 10^{-15} \mathrm{m}$
$\sigma_{ m e}$	Thomson cross section	$8\pi r_{ m e}^2/3$	$0.665 \times 10^{-28} \mathrm{m}^2$
$\alpha_{ m f}$	Fine structure constant	$e^2/4\pi\epsilon_0\hbar c$	= 1/137.04

 ${\bf Table \ A.1. \ Physical \ quantities, \ symbols \ and \ their \ SI \ units}$

Conversions of units, see following page

 \mathbf{A}

Conversions of units

1 Oersted (Oe) = $(1,000/4\pi)$ A m⁻¹ = 79.59 A m⁻¹ $1\,{\rm Tesla}~({\rm T}) = 1\,{\rm N}\,{\rm A}^{-1}{\rm m}^{-1} = 1\,{\rm V}\,{\rm s}\,{\rm m}^{-2}$ (i.e., $1\,{\rm T}$ corresponds to $10^4\,{\rm Oe})$ $1 \operatorname{Ohm} (\Omega) = 1 \operatorname{VA}^{-1}$ $1 \operatorname{Coulomb} (C) = 1 \operatorname{As}$ $1 \, \text{Newton} (N) = 1 \, \text{V} \, A \, \text{s} \, m^{-1}$ $1 \,\text{Kilogram (kg)} = 1 \,\text{VA s}^3 \,\text{m}^{-2}$ $1 \, \text{Farad} \, (F) = 1 \, \text{A s V}^{-1}$ 1 Joule (J) = 1 N m = 1 V A s $1 \text{ Watt } (W) = 1 \text{ V A} = 1 \text{ J s}^{-1}$ $1\,{\rm eV} = 1.602\times 10^{-19}\,{\rm V\,A\,s}$ $1 \,\mathrm{eV}/k_{\mathrm{B}} = 1.1605 \times 10^4 \,\mathrm{K}$ (energy to temperature) $1 \,\mathrm{eV}/h = 2.418 \times 10^{14} \,\mathrm{Hz}$ (energy to cycle frequency) $1 \,\mathrm{eV}/hc = 8066 \,\mathrm{cm}^{-1}$ (energy to wavenumber, also $1 \,\mathrm{cm}^{-1} = 1 \,\mathrm{Kayser}$) $h\nu$ [eV] = 1239.852/ λ [nm] (photon energy to wavelength and vice versa) $1\,\mu_{\rm B}/\mu_0 = 0.578\times 10^{-4}\,{\rm eV}\,{\rm T}^{-1}$ 1 barn (b) = $1 \times 10^{-28} \text{ m}^2$ $1 \deg(^{\circ}) = \pi/180 \operatorname{rad} = 17.45 \operatorname{mrad}$ $1\,\mathrm{arcmin}=1/60^\circ=290.9\,\mu\mathrm{rad}$

A.2 The Cross Product

General vector relations:	
$oldsymbol{a} imes oldsymbol{b} = -oldsymbol{b} imes oldsymbol{a}$	(A.1)
$(\boldsymbol{a}+\boldsymbol{b}) imes \boldsymbol{c}=(\boldsymbol{a} imes \boldsymbol{c})+(\boldsymbol{b} imes \boldsymbol{c})$	(A.2)
$(\lambda \boldsymbol{a} imes \boldsymbol{b}) = (\boldsymbol{a} imes \lambda \boldsymbol{b}) = \lambda (\boldsymbol{a} imes \boldsymbol{b})$	(A.3)
$oldsymbol{a} \cdot (oldsymbol{b} imes oldsymbol{c}) = oldsymbol{b} \cdot (oldsymbol{c} imes oldsymbol{a}) = oldsymbol{c} \cdot (oldsymbol{a} imes oldsymbol{b})$	(A.4)
$oldsymbol{a} imes (oldsymbol{b} imes oldsymbol{c}) = oldsymbol{b} \left(oldsymbol{a} \cdot oldsymbol{c} ight) - oldsymbol{c} \left(oldsymbol{a} \cdot oldsymbol{b} ight)$	(A.5)
$(\boldsymbol{a} imes \boldsymbol{b}) \cdot (\boldsymbol{c} imes \boldsymbol{d}) = \boldsymbol{a} \cdot [\boldsymbol{b} imes (\boldsymbol{c} imes \boldsymbol{d})] = (\boldsymbol{a} \cdot \boldsymbol{c})(\boldsymbol{b} \cdot \boldsymbol{d}) - (\boldsymbol{b} \cdot \boldsymbol{c})(\boldsymbol{a} \cdot \boldsymbol{d})$	(A.6)
$(\boldsymbol{a} imes \boldsymbol{b}) imes (\boldsymbol{c} imes \boldsymbol{d}) = \boldsymbol{c} \left[\left(\boldsymbol{a} imes \boldsymbol{b} ight) \cdot \boldsymbol{d} ight] - \boldsymbol{d} \left[\left(\boldsymbol{a} imes \boldsymbol{b} ight) \cdot \boldsymbol{c} ight]$	(A.7)
$oldsymbol{a} imes \left[(oldsymbol{a} imes oldsymbol{b}) imes oldsymbol{a} ight] = oldsymbol{a} imes \left[oldsymbol{a} imes (oldsymbol{b} imes oldsymbol{a}) ight] = oldsymbol{a} imes oldsymbol{b}$	(A.8)
$oldsymbol{e}_x imesoldsymbol{e}_y=oldsymbol{e}_z$	
$e_y imes e_z = e_x$	$(\Lambda, 0)$
$oldsymbol{e}_z imesoldsymbol{e}_x=oldsymbol{e}_y$	(A.9)

The gradient operator:

$$\nabla \times \nabla \psi = 0 \qquad (A.10)$$

$$\nabla \cdot (\nabla \times a) = 0 \qquad (A.11)$$

$$\nabla \cdot (\psi a) = \psi \nabla \cdot a + a \cdot \nabla \psi \qquad (A.12)$$

$$\nabla \times (\psi a) = \psi \nabla \times a + \nabla \psi \times a \qquad (A.13)$$

$$\nabla \cdot (a \times b) = b \cdot (\nabla \times a) - a \cdot (\nabla \times b) \qquad (A.14)$$

$$\nabla \times (a \times b) = (b \cdot \nabla) a - (a \cdot \nabla) b + a (\nabla \cdot b) - b (\nabla \cdot a) \qquad (A.15)$$

$$\nabla (a \cdot b) = (b \cdot \nabla) a + (a \cdot \nabla) b + a \times (\nabla \times b) + b \times (\nabla \times a) \qquad (A.16)$$

$$\nabla \times (\nabla \times a) = \nabla (\nabla \cdot a) - \nabla^{2} a \qquad (A.17)$$

A.3 s, p, and d Orbitals

Table A.2 gives the often used s, p, and d orbitals in terms of linear combinations of the (complex) spherical harmonics. The orbitals are *real* and pictured in Fig. A.1.

Table A.2. Mathematical description of s, p, and d orbitals, pictured in Fig. A.1, in terms of spherical harmonics $Y_{l,m} = |l, m\rangle$. The orbitals o_i are real and normalized according to $\int |o_i|^2 d\Omega = \int_0^{2\pi} \int_0^{\pi} |o_i|^2 \sin \theta \, d\theta \, d\phi = \langle o_i | o_i \rangle = 1$

8	=	$\frac{1}{\sqrt{4\pi}}$	=	$Y_{0,0}$
p_x	=	$\sqrt{\frac{3}{4\pi}}\frac{x}{r}$	=	$\frac{1}{\sqrt{2}}(Y_{1,-1} - Y_{1,+1})$
p_y		$\sqrt{\frac{3}{4\pi}\frac{y}{r}}$	=	$\frac{i}{\sqrt{2}}(Y_{1,-1}+Y_{1,+1})$
p_z	=	$\sqrt{\frac{3}{4\pi}\frac{z}{r}}$	=	$Y_{1,0}$
d_{xy}	=	$\sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$	=	$\frac{i}{\sqrt{2}}(Y_{2,-2} - Y_{2,+2})$
d_{xz}	=	$\sqrt{\frac{15}{4\pi}}\frac{xz}{r^2}$	=	$\frac{1}{\sqrt{2}}(Y_{2,-1} - Y_{2,+1})$
d_{yz}	=	$\sqrt{\frac{15}{4\pi}}\frac{yz}{r^2}$	=	$\frac{i}{\sqrt{2}}(Y_{2,-1}+Y_{2,+1})$
$d_{x^2-y^2}$	=	$\sqrt{\frac{15}{16\pi}} \frac{(x^2 - y^2)}{r^2}$	=	$\frac{1}{\sqrt{2}}(Y_{2,-2}+Y_{2,+2})$
$\underline{d_{3z^2-r^2}}$	=	$\sqrt{\frac{5}{16\pi}} \frac{(3z^2 - r^2)}{r^2}$	=	Y _{2,0}

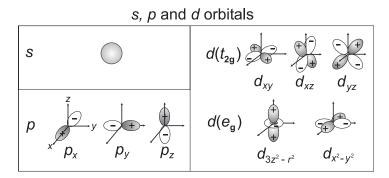


Fig. A.1. Illustration of the s, p, and d orbitals. Plotted is the charge density, given by the square of the angular wavefunctions. The signs of the wavefunctions are also indicated

A.4 Spherical Tensors

Following Racah, we define spherical tensors $C_m^{(l)}$, listed in Table A.3 for $l \leq 4$, in terms of the spherical harmonics as follows,

$$C_m^{(l)} = \sqrt{\frac{4\pi}{2l+1}} Y_{l,m}(\theta,\phi) .$$
 (A.18)

Table A.3. Racah tensor operators $C_m^{(l)}$ for l = 0, 1, 2, 3, 4 defined in (A.18), expressed in Cartesian and spherical coordinates, according to $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$. The operators have the complex conjugate property $(C_m^{(l)})^* = (-1)^m C_{-m}^{(l)}$

$C_0^{(0)}$	=	1		
$C_{0}^{(1)}$	=	$\cos heta$	=	$\frac{z}{r}$
$C_{\pm 1}^{(1)}$	=	$\mp \frac{1}{\sqrt{2}} \sin \theta \mathrm{e}^{\pm \mathrm{i}\phi}$	=	$\mp \frac{1}{\sqrt{2}} \frac{(x \pm iy)}{r}$
		$\frac{1}{2} \left(3\cos^2\theta - 1 \right)$	=	$\frac{\frac{1}{2}}{r^2} \frac{(3z^2 - r^2)}{r^2}$
		$\mp \sqrt{\frac{3}{2}} \cos \theta \sin \theta \mathrm{e}^{\pm \mathrm{i}\phi}$		$\mp \sqrt{rac{3}{2}} rac{(x \pm iy)z}{r^2}$
$C_{\pm 2}^{(2)}$	=	$\sqrt{\frac{3}{8}\sin^2 heta} e^{\pm 2i\phi}$	=	$\sqrt{\frac{3}{8}} \frac{(x \pm iy)^2}{r^2}$
$C_0^{(3)}$	=	$\frac{1}{2} \left(5 \cos^3 \theta - 3 \cos \theta \right)$		$\frac{1}{2} \frac{(5z^2 - 3r^2)z}{r^3}$
$C_{\pm 1}^{(3)}$	=	$\mp \sqrt{\frac{3}{16}} \sin \theta \left(5 \cos^2 \theta - 1 \right) e^{\pm i\phi}$	=	$\mp \sqrt{\frac{3}{16}} \frac{(x \pm iy)(5z^2 - r^2)}{r^3}$
$C^{(3)}_{\pm 2}$	=	$\sqrt{\frac{15}{8}} \cos\theta \sin^2\theta e^{\pm 2i\phi}$	=	$\sqrt{\frac{15}{8}} \frac{z(x\pm iy)^2}{r^3}$
$C_{\pm 3}^{(3)}$	=	$\mp \sqrt{\frac{5}{16} \sin^3 \theta} \mathrm{e}^{\pm 3\mathrm{i}\phi}$	=	$\mp \sqrt{\frac{5}{16}} \frac{(x \pm iy)^3}{r^3}$
$C_0^{(4)}$	=	$\frac{1}{8} \left(35\cos^4\theta - 30\cos^2\theta + 3 \right)$	=	$\frac{1}{8} \frac{(35z^4 - 30z^2r^2 + 3r^4)}{r^4}$
$C_{\pm 1}^{(4)}$	=	$\mp \sqrt{\frac{5}{16}\sin\theta \left(7\cos^3\theta - 3\cos\theta\right)} e^{\pm i\phi}$		$\mp \sqrt{\frac{5}{16}} \frac{(x \pm iy)(7z^3 - 3zr^2)}{r^4}$
$C_{\pm 2}^{(4)}$	=	$\sqrt{\frac{5}{32}}\sin^2\theta (7\cos^2\theta - 1)\mathrm{e}^{\pm 2\mathrm{i}\phi}$		$\sqrt{\frac{5}{32}} \frac{(x \pm iy)^2 (7z^2 - r^2)}{r^4}$
$C_{\pm 3}^{(4)}$	=	$\mp \sqrt{\frac{35}{16}} \cos \theta \sin^3 \theta \mathrm{e}^{\pm 3\mathrm{i}\phi}$	=	$\mp \sqrt{\frac{35}{16}} \frac{z(x\pm iy)^3}{r^4}$
$C_{\pm 4}^{(4)}$	=	$\sqrt{\frac{35}{128}}\sin^4\theta \mathrm{e}^{\pm 4\mathrm{i}\phi}$	=	$\sqrt{\frac{35}{128}} \frac{(x \pm iy)^4}{r^4}$

A.5 Sum Rules for Spherical Tensor Matrix Elements

The matrix elements of the spherical tensors are evaluated by means of the Wigner–Eckart theorem. We can write the matrix element $\langle l, m_l | C_q^{(1)} | c, m_c \rangle$ in Table 9.1 entirely in terms of 3j symbols

$$\langle l, m_l | C_q^{(1)} | c, m_c \rangle$$

$$= (c \, 1 \, m_c \, q \, | c \, 1 \, l \, m_l \,) \, \frac{\langle l | | C^{(1)} | | c \rangle}{\sqrt{2l+1}}$$

$$= (-1)^{l-m_l} \begin{pmatrix} l & 1 & c \\ -m_l \, q \, m_c \end{pmatrix} \langle l | | C^{(1)} | | c \rangle$$

$$= (-1)^{-m_l} \, \sqrt{(2c+1)(2l+1)} \begin{pmatrix} l & 1 & c \\ -m_l \, q \, m_c \end{pmatrix} \begin{pmatrix} l & 1 & c \\ 0 & 0 & 0 \end{pmatrix} . (A.19)$$

For l = c + 1 the reduced matrix element is $\langle l || C^{(1)} || c \rangle = -\langle c || C^{(1)} || l \rangle = \sqrt{l}$ [181].

Later we state some sum rules of matrix elements of the spherical tensor operators $C_q^{(1)}$, associated with electronic dipole transitions. We shall not give the proofs of the sum rules but they are readily derived from the matrix elements in Table 9.1. The first sum rule concerns the angular part of transition matrix elements. When we sum over the complete initial and final manifolds the transition intensity becomes a constant, independent of angles and q

$$\sum_{m} \sum_{M} \left| \langle Y_{L,M} | C_q^{(1)} | Y_{c,m} \rangle \right|^2 = \frac{1}{3} |\langle L| | C^{(1)} | | c \rangle|^2 = \frac{L}{3}.$$
(A.20)

Although the angular momentum q transferred in the transition is not explicitly specified it must satisfy the dipole condition M = q + m. The sums over m and M make the manifolds spherically symmetric and all angular effects average out. We also obtain an angle independent expression of the matrix element if we sum over q, where q = +1, 0, -1 and either the final or initial manifold, i.e.,

$$\sum_{m} \sum_{q} \left| \langle Y_{L,M} | C_q^{(1)} | Y_{c,m} \rangle \right|^2 = \frac{|\langle L||C^{(1)}||c\rangle|^2}{2L+1} = \frac{L}{2L+1}$$
(A.21)

and

$$\sum_{M} \sum_{q} \left| \langle Y_{L,M} | C_q^{(1)} | Y_{c,m} \rangle \right|^2 = \frac{|\langle L||C^{(1)}||c\rangle|^2}{2c+1} = \frac{L}{2c+1}.$$
(A.22)

Finally, summing (A.20) over the three q values q = +1, 0, -1, (A.21) over the index M or A.22 over m we get

$$\sum_{q} \sum_{m} \sum_{M} \sum_{M} \left| \langle Y_{L,M} | C_{q}^{(1)} | Y_{c,m} \rangle \right|^{2} = |\langle L| | C^{(1)} | |c \rangle|^{2} = L.$$
(A.23)

A.6 Polarization Dependent Dipole Operators

Table A.4 lists dipole operators for various polarizations and for three orthogonal photon incidence directions in a Cartesian coordinate system x, y, z. They can be written in the general form,

$$\frac{P_{\alpha}^{q}}{r} = \sum_{p=0,\pm 1} e_{\alpha,p}^{q} C_{p}^{(1)} = e_{\alpha,1}^{q} C_{1}^{(1)} + e_{\alpha,0}^{q} C_{0}^{(1)} + e_{\alpha,-1}^{q} C_{-1}^{(1)} , \qquad (A.24)$$

where the coefficients $a^q_{\alpha,p}$ may be imaginary. We have the following sum rules over q and α ,

$$\sum_{q} |e_{\alpha,p}^{q}|^{2} = 1, \qquad \sum_{q} e_{\alpha,p}^{q} \left(e_{\alpha,p'}^{q}\right)^{*} = 0 \quad (\text{where } p \neq p'), \ (A.25)$$

$$\sum_{\alpha} e_{\alpha,p}^{q} \left(e_{\alpha,p'}^{q} \right)^{*} = 0, \quad \frac{1}{2} \sum_{\alpha} |e_{\alpha,p}^{+1}|^{2} + |e_{\alpha,p}^{-1}|^{2} = 1, \quad (A.26)$$

$$\left|\sum_{\alpha} e_{\alpha,p}^{q}\right|^{2} = 1, \qquad \sum_{\alpha} |e_{\alpha,p}^{0}|^{2} = 1.$$
 (A.27)

These relations can be derived from the listed parameters $e_{\alpha,p}^q$ in Table A.4. They are useful for establishing polarization averages of x-ray absorption intensities which are related to physical observables. Such averages involve sums over angular momenta q = +1, 0, -1 or over directions $\alpha = x, y, z$.

Table A.4. Polarization dependent dipole operators P_{α}^{q} , expressed in terms of Racah tensors $C_{m}^{(l)}$ where α indicates the direction of \boldsymbol{k} or \boldsymbol{E} and q = 0, +1, -1 (abbreviated q = 0, +, -) characterizes the photon angular momentum

linear polarization					
$\boldsymbol{E} \parallel \boldsymbol{x}: P_x^0 =$	= x	$= r \frac{1}{\sqrt{2}} [C_{-1}^{(1)} - C_1^{(1)}]$			
$oldsymbol{E}\parallel y$: P_y^0 =	= y	$= r \frac{i}{\sqrt{2}} [C_{-1}^{(1)} + C_{1}^{(1)}]$			
$\boldsymbol{E} \parallel \boldsymbol{z}: P_{\boldsymbol{z}}^{0} =$	= 2	$= rC_0^{(1)}$			
circular polarization					
$\boldsymbol{k} \parallel x$: P_x^+ =	$= -\frac{1}{\sqrt{2}}(y+iz)$	$= -r\frac{i}{\sqrt{2}}C_0^{(1)} - r\frac{i}{2}[C_{-1}^{(1)} + C_1^{(1)}]$			
$P_x^- =$	$=$ $\frac{1}{\sqrt{2}}(y-iz)$	$= -r\frac{i}{\sqrt{2}}C_0^{(1)} + r\frac{i}{2}[C_{-1}^{(1)} + C_1^{(1)}]$ = $-r\frac{1}{\sqrt{2}}C_0^{(1)} - r\frac{i}{2}[C_{-1}^{(1)} - C_1^{(1)}]$ = $r\frac{1}{\sqrt{2}}C_0^{(1)} - r\frac{i}{2}[C_{-1}^{(1)} - C_1^{(1)}]$			
$oldsymbol{k}\parallel y$: P_y^+ =	$= -\frac{1}{\sqrt{2}}(z+ix)$	$= -r \frac{1}{\sqrt{2}} C_0^{(1)} - r \frac{i}{2} [C_{-1}^{(1)} - C_1^{(1)}]$			
$P_y^- =$	$=$ $\frac{1}{\sqrt{2}}(z-ix)$	$= r \frac{1}{\sqrt{2}} C_0^{(1)} - r \frac{i}{2} [C_{-1}^{(1)} - C_1^{(1)}]$			
$\boldsymbol{k} \parallel \boldsymbol{z}: P_{\boldsymbol{z}}^+$	$= -\frac{1}{\sqrt{2}}(x+iy)$	$= rC_1^{(1)}$			
$P_z^- =$	$= \frac{1}{\sqrt{2}}(x - iy)$	$= rC_{-1}^{(1)}$			

A.7 Spin–Orbit Basis Functions for p and d Orbitals

Table A.5 lists one-electron spin-orbit coupled functions $|l, s, j, m_j\rangle$ for s, p, and d electrons in terms of the uncoupled basis functions $|l, s, m_l, m_s\rangle$. The given transformation is a specific example of the more general transformation between functions in different coupling schemes given by the famous Clebsch-Gordon coefficients (see (9.86)) [181, 224, 225].

Table A.5. One-electron spin–orbit wave functions for s, p, and d electrons. The electron spin wavefunctions are $\chi^+ = |s, 1/2\rangle = \alpha$ (spin-up) and $\chi^- = |s, -1/2\rangle = \beta$ (spin-down). The configuration label is either for one electron or one hole occupation in the particular subshell

one-elec. label	config. label	l,s,j	$j, m_j \rangle$ basis	$ l,m_l,s,m_s\rangle$ basis
l_j	$^{2S+1}L_J$	j	m_{j}	$Y_{l,m_l}\chi^{\pm}$
$s_{\frac{1}{2}}$	${}^{2}S_{\frac{1}{2}}$	$\frac{1}{2}$	$+\frac{1}{2}$	$Y_{0,0} lpha$
_	-		$-\frac{1}{2}$	$Y_{0,0}eta$
$p_{\frac{1}{2}}$	${}^{2}P_{\frac{1}{2}}$	$\frac{1}{2}$	$+\frac{1}{2}$	$\frac{1}{\sqrt{3}}(-Y_{1,0}\alpha + \sqrt{2}Y_{1,+1}\beta)$
2	2		$-\frac{1}{2}$	$\frac{1}{\sqrt{3}}(-\sqrt{2}Y_{1,-1}\alpha + Y_{1,0}\beta)$
$p_{\frac{3}{2}}$	${}^{2}P_{\frac{3}{2}}$	$\frac{3}{2}$	$+\frac{3}{2}$	$Y_{1,+1} \alpha$
2	2		$+\frac{1}{2}$	$\frac{1}{\sqrt{3}}(\sqrt{2}Y_{1,0}\alpha + Y_{1,+1}\beta)$
			$-\frac{1}{2}$	$\frac{1}{\sqrt{3}}(Y_{1,-1}\alpha + \sqrt{2}Y_{1,0}\beta)$
			$-\frac{3}{2}$	$Y_{1,-1}eta$
$d_{\frac{3}{2}}$	${}^{2}D_{\frac{3}{2}}$	$\frac{3}{2}$	$+\frac{3}{2}$	$\frac{1}{\sqrt{5}}(-Y_{2,+1}\alpha + 2Y_{2,+2}\beta)$
-	-		$+\frac{1}{2}$	$\frac{1}{\sqrt{5}} \left(-\sqrt{2} Y_{2,0} \alpha + \sqrt{3} Y_{2,+1} \beta \right)$
			$-\frac{1}{2}$	$\frac{1}{\sqrt{5}} \left(-\sqrt{3} Y_{2,-1} \alpha + \sqrt{2} Y_{2,0} \beta \right)$
			$-\frac{3}{2}$	$\frac{1}{\sqrt{5}} \left(-2 Y_{2,-2} \alpha + Y_{2,-1} \beta \right)$
$d_{\frac{5}{2}}$	${}^{2}D_{\frac{5}{2}}$	$\frac{5}{2}$	$+\frac{5}{2}$	$Y_{2,+2} \alpha$
-	-		$+\frac{3}{2}$	$\frac{1}{\sqrt{5}} (2 Y_{2,+1} \alpha + Y_{2,+2} \beta)$
			$+\frac{1}{2}$	$\frac{1}{\sqrt{5}}(\sqrt{3}Y_{2,0}\alpha + \sqrt{2}Y_{2,+1}\beta)$
			$-\frac{1}{2}$	$\frac{1}{\sqrt{5}}(\sqrt{2}Y_{2,-1}\alpha + \sqrt{3}Y_{2,0}\beta)$
			$-\frac{3}{2}$	$\frac{1}{\sqrt{5}}(Y_{2,-2}\alpha + 2Y_{2,-1}\beta)$
			$-\frac{5}{2}$	$Y_{2,-2}\beta$

A.8 Quadrupole Moment and the X-ray Absorption Intensity

Here we wish to discuss the origin of the link of the XNLD intensity and the quadrupole moment mentioned in Sect. 9.7.4. The formalism is derived by defining a dimensionless *quadrupole tensor*

$$\boldsymbol{Q} = \frac{\left(r^2 \delta_{\alpha\beta} - 3 \, \boldsymbol{r}_{\alpha} \boldsymbol{r}_{\beta}\right)}{r^2} \,, \tag{A.28}$$

which only depends on the angular distribution. The terms r_i denote the three components of the position vector r. In spherical coordinates the quadrupole tensor reads

$$\boldsymbol{Q} = \begin{pmatrix} 1 - 3\sin^2\theta\cos^2\phi & -3\sin^2\theta\sin\phi\cos\phi & -3\cos\theta\sin\theta\cos\phi \\ -3\sin^2\theta\sin\phi\cos\phi & 1 - 3\sin^2\theta\sin^2\phi & -3\cos\theta\sin\theta\sin\phi \\ -3\cos\theta\sin\theta\cos\phi & -3\cos\theta\sin\theta\sin\phi & 1 - 3\cos^2\theta \end{pmatrix}.$$
(A.29)

It is constructed so that the expectation values of all matrix elements $\langle Q_{\alpha\beta}\rangle = \int_0^{2\pi} \int_0^{\pi} Q_{\alpha\beta} \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi = 0$ for a system with spherical symmetry. \boldsymbol{Q} is a symmetric second rank tensor with $Q_{\alpha\beta} = Q_{\beta\alpha}$ and a vanishing trace

$$\sum_{\alpha} Q_{\alpha\alpha} = Q_{xx} + Q_{yy} + Q_{zz} = 0 . \qquad (A.30)$$

For samples with higher than twofold symmetry about Cartesian x, y, and z axes the tensor Q is diagonal and all the information is contained in the diagonal elements that form the trace. For crystalline systems, this holds if the elementary lattice vectors are perpendicular, i.e., for orthorhombic or higher crystal symmetry.

For linearly polarized x-rays with $E \parallel \alpha = x, y, z$, the angle-dependent x-ray absorption intensity I^0_{α} describing transitions from a core state with angular momentum c to a valence orbital $|\phi_L\rangle$ with angular momentum L = c+1 is given by

$$I_{\alpha}^{0} = 2 \mathcal{A} \mathcal{R}^{2} \frac{L}{3(2L+1)} \left(1 - \frac{2L+3}{2L} \langle \phi_{L} | Q_{\alpha \alpha} | \phi_{L} \rangle \right)$$
(A.31)

This equation is identical to (9.117) for $N_{\rm h} = 2$ or two holes per valence orbital $|\phi_L\rangle$. The factor of 2 in (A.31) thus accounts for the spin-degeneracy of each of the 2L + 1 possible empty valence orbitals $|\phi_L\rangle$.

Quantum mechanically, the quadrupole moment for a given direction α is the expectation value of the corresponding diagonal quadrupole tensor matrix element evaluated with the valence band wavefunction $|\phi_L\rangle$. For the tight binding wavefunctions given by (9.108) we have for example

$$\langle Q_{\alpha\alpha} \rangle = Q_{\alpha}^{i} = \langle \phi_{i}(\mathbf{k}) | Q_{\alpha\alpha} | \phi_{i}(\mathbf{k}) \rangle.$$
(A.32)

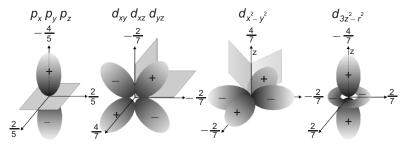
If the matrix elements vanish the x-ray absorption intensity will be angle independent. A simple example are the quadrupole moments of the d orbitals in Table A.2 given by the expectation value of the diagonal matrix elements $\langle Q_{\alpha\alpha} \rangle = \langle d_i | Q_{\alpha\alpha} | d_i \rangle$. The matrix elements are calculated by expressing the quadrupole tensor elements $Q_{\alpha\alpha}$ in terms of Racah's spherical tensors as given in Table A.6. General expressions for the quadrupolar tensor matrix elements are given in Table A.7 and for convenience we have listed the matrix elements $\langle Q_{\alpha\alpha} \rangle$ for representative p_i and d_i orbitals in Fig. A.2.

Table A.6. Left column: Quadrupole operator elements expressed in terms of Racah's spherical tensors of Table A.3. Right column: Relationships of Racah tensor operators $C_m^{(2)}$ and $C_{m'}^{(1)}$. The operators have the complex conjugate property $(C_m^{(l)})^* = (-1)^m C_{-m}^{(l)}$ and $C_q^{(1)} C_{q'}^{(1)} = C_{q'}^{(1)} C_q^{(1)}$

$$\begin{vmatrix} Q_{xx} = C_0^{(2)} - \sqrt{\frac{3}{2}} \left(C_2^{(2)} + C_{-2}^{(2)} \right) \\ Q_{yy} = C_0^{(2)} + \sqrt{\frac{3}{2}} \left(C_2^{(2)} + C_{-2}^{(2)} \right) \\ Q_{zz} = -2 C_0^{(2)} \end{vmatrix} \begin{pmatrix} C_2^{(2)} + C_{-2}^{(2)} \\ C_2^{(2)} + C_{-2}^{(2)} \\ C_{\pm 1}^{(2)} = \sqrt{3} C_0^{(1)} C_{\pm 1}^{(1)} = \sqrt{3} C_{\pm 1}^{(1)} C_0^{(1)} \\ C_{\pm 2}^{(2)} = \sqrt{\frac{3}{2}} C_{\pm 1}^{(1)} C_{\pm 1}^{(1)} \end{aligned}$$

Table A.7. Spherical tensor matrix elements $\langle 2M|C_q^{(2)}|2M'\rangle$

$$\begin{split} E &= -\frac{\sqrt{3} \langle L || C^{(2)} || L \rangle}{\sqrt{2L(2L+1)(2L-1)(L+1)(2L+3)}} > 0 \\ A &= \sqrt{(L-M)(L+M+1)} = \sqrt{L(L+1) - M(M+1)} \\ B &= \sqrt{(L+M)(L-M+1)} = \sqrt{L(L+1) - M(M-1)} \\ V &= \sqrt{(L-M-1)(L+M+2)} = \sqrt{L(L+1) - M(M+3) - 2} \\ W &= \sqrt{(L+M-1)(L-M+2)} = \sqrt{L(L+1) - M(M-3) - 2} \\ \langle LM | C_0^{(2)} |LM \rangle = \sqrt{\frac{2}{3}} E \left[L(L+1) - 3M^2 \right] \\ \langle LM + 2 | C_{+2}^{(2)} |LM \rangle = \langle LM | C_{-2}^{(2)} |LM + 2 \rangle = -E V A \\ \langle LM - 2 | C_{-2}^{(2)} |LM \rangle = \langle LM | C_{+2}^{(2)} |LM - 2 \rangle = -E W B \end{split}$$



Quadrupole matrix elements $\langle \phi_L | Q_{\alpha\alpha} | \phi_L \rangle$

Fig. A.2. Quadrupole matrix elements $\langle p_i | Q_{\alpha\alpha} | p_i \rangle$ (i = x, y, z), $\langle d_{ij} | Q_{\alpha\alpha} | d_{ij} \rangle$ $(i \neq j = x, y, z)$, $\langle d_{x^2-y^2} | Q_{\alpha\alpha} | d_{x^2-y^2} \rangle$ and $\langle d_{3z^2-r^2} | Q_{\alpha\alpha} | d_{3z^2-r^2} \rangle$ for $\alpha \parallel x, y$, or z. Nodal planes are shown shaded

The transition intensities listed in Fig. 9.19, corresponding to the square of the transition matrix elements for \boldsymbol{E} along the principal coordinate axes, agree with those calculated with (A.31) using the quadrupole moments listed in Fig. A.2. Here we have to remember, however, that the intensities in Fig. 9.19 do not allow for two spin orientations per orbital while the intensities given by (A.31) account for both spins. For example, according to Fig. 9.19 the intensity for \boldsymbol{E} along the z axis of the p_z orbital is 1/3 (in units of \mathcal{AR}^2) per spin state. This would give a transition intensity of (2/3) \mathcal{AR}^2 considering the two spin directions per orbital. From (A.31) we obtain for the p_z orbital with L = 1 the intensity

$$I_z^0 = \mathcal{AR}^2 \frac{2}{9} \left(1 - \frac{5}{2} \langle p_z | Q_{zz} | p_z \rangle \right)$$
(A.33)

and with the value $\langle p_z | Q_{zz} | p_z \rangle = -4/5$ from Fig. A.2 we obtain the same intensity $(2/3)\mathcal{AR}^2$.

Starting from the expression (A.31) one may also derive the orientation averaged x-ray absorption intensity given by (9.90).

A.9 Lorentzian Line Shape and Integral

The Lorentzian line shape function is

$$I(E) = H\left[\frac{(\Delta_n/2)^2}{(E - E_n)^2 + (\Delta_n/2)^2}\right],$$
 (A.34)

where H is the peak value and Δ_n is the full width at half maximum (FWHM).

Its integral is a step function given by

$$\int I(E) dE = \frac{H \Delta_n \pi}{2} \left[\frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{E - E_n}{\Delta_n/2}\right) \right], \quad (A.35)$$

where $H^* = H \Delta_n \pi/2$ is the step height.

A.10 Gaussian Line Shape and Its Fourier Transform

The Gaussian line shape function centered at x_0 is given by, $f(x) = A \exp\left(-\frac{c^2(x-x_0)^2}{2\Gamma^2}\right) = A \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right).$ (A.36)

Here A is the peak height and $c = 2\sqrt{\ln 4} = 2.355$. The full width at half maximum (FWHM) Γ is related to the variance σ , corresponding to one standard deviation of the Gaussian distribution width, by $\Gamma = c \sigma$.

Gaussian functions have the interesting property that the Fourier transform of a Gaussian is again a Gaussian. In general, the Fourier transform of a one dimensional function f(x) is defined as

$$F(q) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{i q x} dx \qquad (A.37)$$

and the inverse transform is

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(q) e^{-iq x} dq.$$
 (A.38)

As an example let us take a look at the energy–time Fourier transformation, used in Sect. 4.3.2. Using the standard deviation σ_t for the temporal line width, the temporal Gaussian A.11 Gaussian Pulses, Half-Cycle Pulses and Transforms 775

$$f(t) = A \exp\left(-\frac{t^2}{2\sigma_t^2}\right) , \qquad (A.39)$$

is transformed into a Gaussian in energy or frequency space, given by

$$F(\omega) = A \sigma_t \exp\left(-\frac{\omega^2}{2(1/\sigma_t)^2}\right) . \tag{A.40}$$

It has a peak intensity $A \sigma_t$ and variance width $1/\sigma_t$.

A.11 Gaussian Pulses, Half-Cycle Pulses and Transforms

We have discussed in Sect. 4.3.4 the temporal field pulse associated with a relativistic electron bunch. This Gaussian pulse has a strong resemblance with a half-cycle pulse (HCP). This is illustrated in the left half of Fig. A.3, where a simulated Gaussian pulse of 1 ps FWHM is compared to waves of different frequencies in the THz range. We see that a half cycle of a 0.5 THz wave has a shape that closely resembles its Gaussian envelope. Indeed, such HCP pulses can be created by an electric discharge across an Auston switch that is triggered by a suitably short laser pulse [861], and a typical shape of a half cycle THz pulse is shown on the right side of Fig. A.3. In practice, a positive "half cycle" pulse exhibits a weak negative tail that extends for a long time.

The negative tail has an important effect on the frequency spectrum. A temporal Gaussian pulse or true half cycle pulse without a negative tail has a Fourier transform which is peaked at zero frequency as shown in Fig. 4.6 and

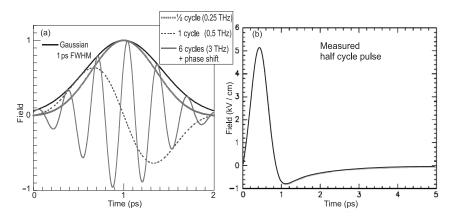


Fig. A.3. *Left*: Illustration of an Gaussian shaped pulse of 1 ps FWHM containing only half or a few cycles of an EM field. The frequencies of the associated fields lie in the THz range. *Right*: Schematic of a typical half-cycle THz pulse [862]. The initial positive pulse is approximately 1 ps in duration. The negative tail of the HCP persists for many picoseconds

the top panel of Fig. A.4, revealing a strong dc-component. In contrast, a full cycle pulse or a "half cycle" pulse with a tail, as observed in practice, have zero amplitude at zero frequency, and the peak is shifted away from zero as illustrated in the bottom panels of Fig. A.4.

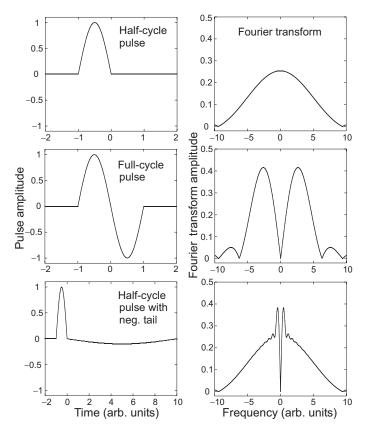


Fig. A.4. Illustration of half and full cycle pulses and their Fourier transforms

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