

Chapter 1

Traditional Magnetism

Abstract A pointed piece of a mineral called magnetite was noticed to turn north–south when supported in air or placed on the surface of water. As such, magnetite was the first magnetic material to be discovered, and people wasted no time exploiting it. From the dawn of the human race, when magnetic phenomena began to fascinate us, we have, thus, learned how to creatively exploit magnetic properties. Since then, magnetism has become a highly diversified discipline that has opened up new possibilities for scientific and technological developments. Novel magnetic applications emerge, roughly every year, in their scientific move toward unexplored natural boundaries that push those of human imagination. Furthermore, new technologies that are currently being developed incorporate more and more magnetic structures, spanning a range of applications, often replacing others in more established fields. Interestingly, a significant number of modern conveniences are based on magnetic phenomena that were already studied half a century ago, but are only now benefiting from increased appreciation. And yet, aside from natural magnets, most magnetic materials are not really known to the public at large, whether they are naturally occurring substances, or artificially created compounds.

Varieties of magnetic properties have atomic origins, and have already become observable on length scales of the order of a few nanometers. For this reason, and given the possibilities these days of advanced fabrication technologies, magnetic structures can be nanoengineered to the extent that entirely new materials are obtained. In this manner, artificial metamaterials can be successfully created, relying on combined magnetic phenomena not observable in the original individual compounds. For instance, when a soft phase is incorporated into an amorphous matrix, a completely different magnetic material can be obtained, such as embedded magnetic nanoclusters, or granular nanosized polymer materials. Similarly, many modern magnetic devices that are presently enjoying widespread use are functional on a nanoscale. The increasingly recognizable structures known as nanodots, where quantum–mechanical effects are no longer negligible, have become a common research topic in laboratories preoccupied with the search for improved magnetic storage. It is therefore no surprise that concepts such as quantum well states and

spin degrees of freedom come into play, expanding nanodot areas of applications to quantum computing and spin electronics.

This introductory chapter is meant to provide the reader with minimal information on some traditional aspects of magnetism. However, the task of revealing a comprehensive view on the historical concepts of magnetism is best left to previously published, classic treatises. Only a few key concepts are mentioned, with the selection of topics left to the discretion of the author. How can we develop advanced nanostructured devices, if we do not even know when we can classify a material as magnetic? Which magnetic properties have served as historical uses of magnetic materials, and what new ideas are actually old concepts presented in a new light? We cannot move forward toward advanced magnetism topics without trying to answer a few critical questions, and in the process of doing so, discover that not all hot subjects in today's magnetism are actually that new. Nevertheless, in order to facilitate a minimal understanding of fundamental ideas on which new technologies are based, we need to first become familiar with basic concepts in magnetism. This way, we can facilitate a transition toward more modern applications discussed in later chapters.

1.1 Magnetic Concepts

1.1.1 Magnetic Dipoles

Bearing on similarities with electrostatics, magnetism has been traditionally viewed as an interaction between magnetic poles of strengths p_1 and p_2 separated by a distance r . This is analogous to the Coulomb interaction between electrically charged particles, and can be written as [1]

$$\mathbf{F} = \frac{p_1 p_2}{4\pi\mu_0 r^2}, \quad (1.1)$$

where \mathbf{F} is the force acting on a magnetic pole and μ_0 is the permeability of vacuum. In a complementary approach, it can also be said that a magnetic field producing electric current or another magnetic pole, will exert a force \mathbf{F} on the initial magnetic pole of strength p

$$\mathbf{F} = p\mathbf{H}_0, \quad (1.2)$$

where H_0 is the applied magnetic field due to the electric current or the other magnetic pole. We know from Maxwell's electromagnetic theory that magnetic poles occur in pairs. As such, when a magnet is cut into pieces, each piece will have a pair of poles. Magnetic poles exert a force on each other such that like poles repel each other with force F described by (1.1), while north and south poles attract. Equation (1.2) implies that if a magnetic material is brought near a magnet,

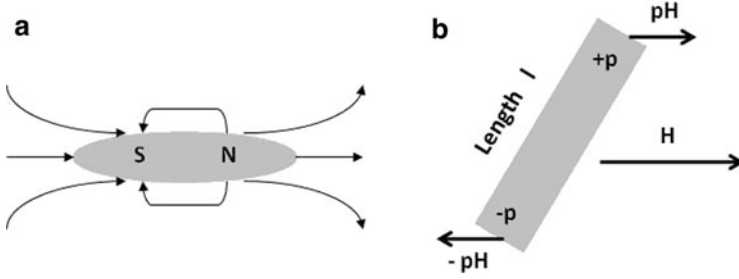


Fig. 1.1 (a) Magnetic field representation outside a magnet or magnetized material, and (b) couple of magnetic force pH acting on a bar of length l placed in a magnetic field H

the magnetic field of the magnet will magnetize the material. Consequently, the magnetic field is sometimes called a *magnetizing force* schematically represented by lines, also called *lines of force* shown in Fig. 1.1a. These lines of force or magnetic field lines are drawn such that lines outside the magnet radiate outward from the north pole, and a compass needle would be tangent to them. Magnetic field lines leave the north pole and enter the magnet again at the south pole, attracting a ferromagnet toward the magnet, even if the two are a certain distance apart.

Consider a bar magnet of length l with magnetic poles p and $-p$ at its ends, placed in a uniform magnetic field (Fig. 1.1b). In this case, the couple of magnetic forces gives rise to a torque L

$$L = -pH \sin \theta, \quad (1.3)$$

where θ is the angle between the direction of the applied magnetic field H and the direction of the magnetization M of the bar magnet. In this case, the product pl is the magnetization M of the bar. The work done by the torque gives rise to a potential energy U in the absence of frictional forces

$$U = -MH \cos \theta. \quad (1.4)$$

This equation is particularly important in the next chapter, when magnetic domains and the realignment of their magnetization toward an externally applied magnetic field are discussed. It can be seen that the potential energy has a minimum value when $\theta = 0$.

When the bar length l tends to zero value, and if the strengths of the magnetic poles p approach infinity simultaneously, the system is called a *magnetic dipole*. Alternatively, a magnetic dipole can also be defined by a circular electric current of infinite intensity spanning an area of zero dimensions. Regardless of how we look at it, the magnetic dipole is only a mathematical concept, merely useful for the definition of some magnetic quantities. For instance, the magnetic moment m of the magnetic dipole is

$$m = MdV, \quad (1.5)$$

where M is magnetization and dV is the unit volume. This equation is considered in earlier books as the definition for M . It is important to emphasize the fact, and hopefully remember later in this book, that if the magnetization is constant throughout the magnetized body, the latter is considered homogeneous from a magnetic point of view.

1.1.2 Magnetic Field Intensity and Magnetic Flux Density

Magnetism has come a long way since these early interpretations mentioned here. And yet, more complex concepts can sometimes be reduced to these basic ideas, so that an easier understanding is facilitated at that moment. As such, the purpose of this section is to name the two most basic quantities of magnetism, *magnetic field intensity* and *magnetic field density* in the way they were historically introduced. However, in order to describe the magnetic properties of materials, and have a quantitative measure of them, we need more than just two quantities. Therefore, for a more rigorous treatment, the reader is directed to the variety of magnetism or electromagnetics related books that deal with these concepts in depth. It suffices to say that the strength of the field of force discussed in the previous section is known as the *magnetic field strength*, *magnetic field intensity*, or *magnetizing force*, and is denoted, very often, by the symbol H . In the cgs system of units, the magnetic field intensity H is measured in *oersteds* (Oe), where 1 Oe is defined as the field strength at 1 cm of the *unit pole*. On the other hand, a magnetic field can also be produced by an electric current, and is therefore defined in terms of current as one *Ampere-turn per meter* (A/m), the measuring unit for magnetic field intensity in the MKS system. Magnetic field intensity is a *vector* denoted in bold letters by \mathbf{H} , and therefore, has both direction and strength. The direction is given by that in which a north magnetic pole starts to move when subjected to a magnetic field, or that indicated by the north end of a compass needle.

The concentration of lines of force at any point is known as *magnetic flux*, whereas the flux per unit area is the *magnetic flux density* represented by the symbol B , or in vector form \mathbf{B} . The units for magnetic flux density are *gauss* (Gs) in the cgs system of units, and *weber/(meter)²* (Wb/m^2) or *tesla* (T) in the MKS system, or the SI system of units developed later. The magnetic flux density is traditionally defined by the relation

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}. \quad (1.6)$$

The quantity $\mathbf{B}-\mathbf{H} = 4\pi\mathbf{M}$ attains a saturation value. The factor 4π is the area of a sphere, and its presence in the equation is attributable to a unit field caused by a unit pole everywhere on the surface of a sphere of unit radius enclosing the pole. Alternative to (1.6), the magnetic flux density can also be defined from the movement of charge or current flow, and the laws of magnetostatics.

1.1.3 Magnetic Susceptibility and Magnetic Permeability

In order to determine whether a material is magnetic or not, we need at least one quantity that can describe the material's magnetic behavior under an applied field. The quantity, termed *magnetic susceptibility* χ , characterizes the magnetic response of a material through the relationship

$$\mathbf{M} = \chi \mathbf{H}_0, \quad (1.6)$$

where \mathbf{M} is the magnetization, also known as magnetic moment per unit volume and \mathbf{H}_0 is the applied magnetic field intensity. The subscript “0” is often added to H to highlight the fact that this field is an applied or external field. Magnetic susceptibility is usually a tensor and a function of both field \mathbf{H}_0 and magnetization \mathbf{M} . For a magnetically isotropic material, \mathbf{M} is parallel to \mathbf{H}_0 , so that χ is reduced to a scalar quantity. The SI units of χ are *henry/meter* (H/m).

A B – H hysteresis loop is obtained by plotting magnetic field density B against magnetic field intensity H . An M – H curve is obtained in a similar way, where magnetization M replaces magnetic flux density B . In both cases, if the field intensity H is increased from zero to a high value and then decreased, the original curve is not retraced (Fig. 1.5). This means that the material acquires a magnetic history where the magnetic flux density B does not follow its original values on the initial curve. If the hysteresis loop is symmetrical about the origin and the material is magnetized to saturation, the value of field intensity H_c for which flux density is zero is known as *coercivity*, often used in magnetic recording to determine the usability of a material. On the other hand, the value of flux density B_r for which intensity H is zero, is called *retentivity*, while that of remanent magnetization is known as *remanence*, although quite often the two are interchanged, and B_r is called “remanence” by some authors. Either way, the remanent magnetic flux density, or remanent magnetization, when the external field has been brought back to zero, are important quantities for determining the quality of a magnetic material.

Another quantity that is determined from the B – H hysteresis loop, and can give us some insight into the magnetic properties of a material, is its *magnetic permeability* μ , obtained through the ratio B/H , although, technically, it is a derivative on the B – H hysteresis loop. The magnetic permeability of a material represents the relative increase in magnetic flux caused by the presence of the material itself, in an external field. The unit for the permeability μ is the same as for χ . Hence, it is possible to measure χ in units of the permeability of vacuum μ_0 which is a constant. In this case, the measured dimensionless quantity is called *relative susceptibility* and is denoted by χ_0 .

$$\chi_0 = \frac{\chi}{\mu_0}. \quad (1.7)$$

The values for relative susceptibilities range from 10^{-5} (very weak)– 10^6 (very strong magnetism) [2]. In some cases, the relative susceptibility is negative. Or, the relationship between M and H is not linear, so that χ_0 depends on H . The behavior of χ_0 leads to various types of magnetism.

1.2 Classification of Magnetic Materials

1.2.1 Diamagnetism

The most common way of classifying magnetic properties of materials is by their response to an applied magnetic field; therefore, both relative permeability and relative susceptibility can be used to differentiate between classes of materials. As such, it is said that materials that can be magnetized to a certain extent by a magnetic field are called *magnetic*. We start with *diamagnetism*, which is a weak form of magnetism, attributed mainly to the orbital motion of electrons that create a magnetic moment when viewed classically as a “current loop.” A magnetic flux is induced in the diamagnetic material when an external magnetic field is applied to it. However, the induced flux counters the change in the external field so that diamagnetic materials show an antiparallel magnetization with respect to the direction of the applied magnetic field, opposing the latter, according to Lenz’s law. Therefore, the magnetization of a diamagnetic material is proportional to the applied magnetic field, as seen in Fig. 1.2a, and they have a negative and very weak relative susceptibility of about 10^{-5} . Their permeabilities are somewhat less than one. Many metals and most nonmetals are diamagnetic. It is interesting to point out that, if only a few magnetic atoms exist in the material, their influence is enough to overshadow the diamagnetism, so that nonmagnetic atoms become spin–polarized by neighboring ferromagnetic atoms. This effect is explored nowadays, in practice, in certain nanoscale spin electronic devices.

1.2.2 Paramagnetism

For a certain class of materials known as *paramagnetic materials*, the relative permeability is only slightly greater than one. It is independent of magnetic field strength, and will decrease with increasing temperature, provided it is not temperature independent. Many metals fall into this class, such as platinum or palladium, and also salts of iron or of the rare earth metals, or elements like sodium, potassium, and oxygen. Ferromagnets become paramagnetic above the *Curie temperature* T_c . When an external magnetic field is applied to a paramagnetic material, a weak induced magnetization is produced parallel to the field. The induced magnetization that is proportional to the external field, nevertheless, stays

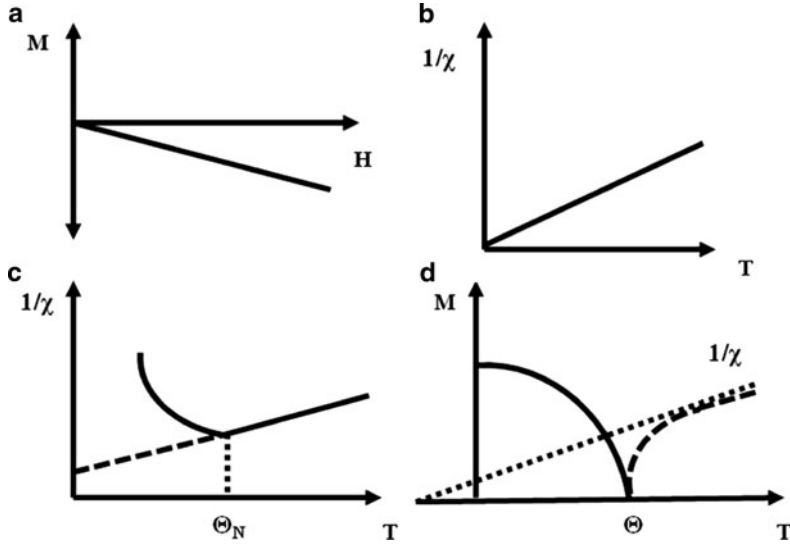


Fig. 1.2 (a) Linear relationship between magnetization and applied magnetic field (intensity) in a diamagnetic material, (b) Curie–Weiss law of paramagnetism, where the susceptibility is inversely proportional to absolute temperature, (c) variation of susceptibility with temperature for an antiferromagnetic material, and (d) Spontaneous magnetization decreases with temperature in ferrimagnetic materials because the arrangement of spins is disturbed with increases in temperature. Upon reaching a critical temperature, the spontaneous magnetization vanishes and the specimen exhibits paramagnetism where the susceptibility decreases with increasing temperature

positive, unlike in diamagnets. On the other hand, the susceptibility as a quantity is inversely proportional to absolute temperature T , and this inverse proportionality is also known as the *Curie–Weiss law* (Fig. 1.2b). For paramagnets, the relative susceptibility is a positive 10^{-3} – 10^{-5} . *Paramagnetism* is in certain ways similar to ferromagnetism (see Sect. 1.2.5 further below), in that it is attributed to unpaired electron spins just as much. Nevertheless, due to a different electronic configuration these spins are free to change their direction, which is unlike the spins in ferromagnets. In paramagnets, spins assume random orientations at certain temperatures as a consequence of thermal agitation.

1.2.3 Antiferromagnetism

Antiferromagnetism is a type of magnetism with an ordered arrangement of antiparallel aligned spins on different sublattices, such that the antiferromagnetic structure has no net spontaneous magnetization. Antiferromagnetic materials have small permeabilities and are, therefore, often classified as paramagnetic. Antiferromagnets exhibit a small positive relative susceptibility that varies with temperature similar to

paramagnetism when higher temperatures are reached; however, this dependence has a unique shape below a critical temperature (Fig. 1.2c). This is because below this temperature, the electron spins are arranged antiparallel so that they cancel each other out. An externally applied magnetic field is faced with a strong opposition due to the interaction between these spins, resulting in a susceptibility decrease with temperature, in contrast to paramagnetic behavior. Therefore, even though antiferromagnetic order may exist at lower temperatures, it vanishes at and above the so-called *Néel temperature*, Θ_N (Fig. 1.2c), when the spins become randomly oriented so that the susceptibility decreases as the temperature is raised. The exchange interaction in antiferromagnets acts to anti-align neighboring spins on different sublattices. For instance, the antiferromagnetism of certain oxides such as MnO was proven to originate in a strong exchange interaction between metal ions on opposite sides of an oxygen ion.

1.2.4 Ferrimagnetism

Ferrites exhibit a kind of magnetism known as *ferrimagnetism* (Fig. 1.2d) that is in some ways similar to both ferromagnetism and antiferromagnetism. In ferrimagnetic materials, since ions are placed on two different types of lattice sites, such that spins on one site type are oppositely oriented to spins on the other lattice site type, they tend to be compared to antiferromagnetic materials. However, one of the resultant magnetizations on the two lattice sites is stronger than the other, so that the result is a total non zero, spontaneous magnetization. Since antiferromagnets are not strongly magnetic, and ferrimagnets have a spontaneous and non-negligible magnetization, ferrimagnetic materials are often compared to ferromagnets. And similar to ferromagnetic materials, an increase in temperature brings about a disturbance in the spin arrangement that culminates in completely random orientation of spins at the Curie temperature. At this temperature, the ferrimagnet loses its spontaneous magnetization and becomes paramagnetic (Fig. 1.2d). Ferromagnetic materials also have a Curie point above which they exhibit paramagnetic behavior [3].

Example 1.1. Comment on the consequences of adding different concentrations of Ge to Fe_3O_4 thin films

Answer: Magnetite, a ferrimagnetic material with extensive history and diverse technical applications, finds use today in advanced areas such as spintronics or spin valves due to its half-metallic character. Nevertheless, the tunnel magnetoresistance behavior on which these modern applications are based (discussed in later chapters) encounters some problems when Fe_3O_4 is used as an electrode grown epitaxially on a MgO single crystal. In this case, the interface between the magnetite electrode and tunnel barrier is complicated and difficult to control. To solve some of these problems, researchers have prepared the magnetite film by sputtering of a composite target with added Ge, in order to suppress the iron deficit which occurs during the

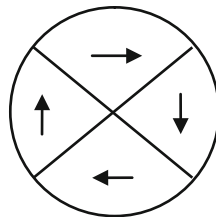
sputtering process [4]. Ge is thermodynamically stable in a magnetite matrix, and it was confirmed that by adding ~ 5 at% Ge, a thin magnetite film is still obtained. Furthermore, these magnetite thin films are ferrimagnetic, even though Ge has been added. Nevertheless, higher concentrations ($\sim 14\%$) of Ge result in the magnetite films becoming paramagnetic. The advantage of adding Ge seems to be that it ensures formation of only the magnetite phase, whereas sputtering the magnetite target without Ge results in two phases, magnetite and hematite. The latter fact is detrimental to the electrode/tunnel barrier interface characteristics of spintronics applications.

1.2.5 Ferromagnetism

We should finally mention *ferromagnetism*; however, given that so many concepts in this book apply directly to ferromagnetic materials, they will be frequently discussed, and, therefore, no section alone can be dedicated to them. In essence, ferromagnetic materials have a permeability that depends on the field strength and on the previous magnetic history (see Hysteresis Loop mentioned above). They approach magnetic saturation as the field strength continues to increase, meaning that the material can only be magnetized to a finite limit. Ferromagnets contain spontaneously magnetized magnetic domains, where a magnetic domain is an entity with a total domain magnetization. This is a small, magnetized region containing many atoms with individual magnetic moments that align parallel to each other, against the forces of thermal agitation. The domain magnetization of one domain is usually oriented differently with respect to the total domain magnetization of neighboring domains. A historically early and rather crude representation of magnetic domains is shown in Fig. 1.3.

We could ask – why would magnetic domains be spontaneously magnetized? The formation of magnetic domains is due to minimization of the total energy, as will be discussed in the next chapter. This implies that, under every condition of the ferromagnet, the domain structure will strive to remain stable, and will, therefore, change until it finds this stability point if conditions change. We know from quantum mechanics [5, 6] that the spontaneous domain magnetization is a result of unpaired electron spins from partially filled electronic shells. These spins align parallel to each other as a result of a strong *exchange interaction*. Since the arrangement

Fig. 1.3 Historical interpretation of domain structure in a ferromagnetic material. Note that magnetostriction is not taken into account



of spins depends on temperature, so does the spontaneous domain magnetization. When the total resultant magnetization for all magnetic domains is zero, the ferromagnetic material is said to be *demagnetized*. However, an applied magnetic field changes the total resultant magnetization from zero to a saturation value. When the magnetic field is decreased and thus, reversed in sign, the magnetization of a ferromagnetic material does not retrace its original path of values, with the material exhibiting so called *hysteresis*. A strong ferromagnet exhibits a relative susceptibility of the order of 10^6 , which is a large value as compared to other types of materials. It explains why ferromagnets can be easily magnetized, while other kinds of magnetic materials fall short on their ability to respond to a magnetic field. The spontaneous magnetization of ferromagnets disappears above a certain temperature called *Curie temperature* T_c , when they become paramagnetic. Technically, ferromagnets are considered a subclass of paramagnetic materials; nevertheless, in time they have been placed in a class of their own. Historically, ferromagnetic materials were the only ones considered “magnetic”; however, this interpretation has changed recently, given that so many other types of materials respond to a certain extent to a magnetic field.

1.3 Origins of Magnetism

1.3.1 Angular Momentum and Its Role in Magnetism

To understand the origins of magnetism, we have to look at the magnetic moment of atoms which originates from electrons in partly filled electron shells. This atomic magnetic moment is determined by a fundamental property known as the *angular momentum* [5,7]. Each individual electron within an atom has an *angular momentum* L , associated with its orbital motion, and an intrinsic or *spin angular momentum* S . Hence, there are two sources of the atomic magnetic moment (a) currents associated with the orbital motion of the electrons and (b) the electron spin. In an n -electron atom, the individual atomic orbital angular momenta couple together to give a total orbital angular momentum \vec{L} , and the individual atomic spin angular momenta couple together to give a total spin angular momentum \vec{S} . As such, the orbital and spin angular momenta each have a magnetic moment expressed as [5–8]

$$\begin{aligned}\vec{\mu}_L &= -\beta\vec{L}, \\ \vec{\mu}_S &= -2\beta\vec{S},\end{aligned}\tag{1.8}$$

where β is the *Bohr magneton*. The total magnetic moment $\vec{\mu}$ is then given by

$$\vec{\mu} = -\beta(\vec{L} + 2\vec{S}).\tag{1.9}$$

For an n -electron atom, the $2n$ angular momenta couple together to give a total angular momentum, \mathbf{J} , whose exact properties depend on the details of the coupling parameters. It should be noted that \mathbf{L} , \mathbf{S} , and $\boldsymbol{\mu}$ precess about the total angular momentum \mathbf{J} .

The magnetic moment of atoms in magnetic materials is largely given by the spin, rather than the orbital motion of electrons. This specifically refers to materials containing iron-series transition metal atoms (e.g., Fe, Co, Ni, and YCo₅), or ferrimagnetic oxides (e.g., Fe₃O₄ and NiO). For these typical magnetic materials, the spin moment $\tilde{\mu}_S$ is equal to the number of unpaired electron spins, while the orbital moment $\tilde{\mu}_L$ is very small. The latter is usually of the order of 0.1β due to the orbital motion of electrons being “quenched” by the *crystal field*, a concept discussed in a subsequent section. The component of $\boldsymbol{\mu}$ perpendicular to \mathbf{J} averages to zero over a time significantly larger than the precession period. As such, when a magnetic field is applied, only the component of $\boldsymbol{\mu}$ parallel to \mathbf{J} is sensed. That parallel component is usually denoted by μ_J [5–8]. We should emphasize that the angular momentum state of an atom is characterized by eigenvalues of J^2 , which is $J(J + 1)$. Thus, using the properties of angular momentum operators and the law of cosines, we have

$$\mu_J^2 = g^2 J(J + 1) \beta^2. \quad (1.10)$$

Choosing the z component of \mathbf{J} , that is J_z with eigenvalues $m_j = J, J - 1, \dots, -J$, the magnetic moment along z is given by

$$\mu_{J_z} = -g\beta J_z, \quad (1.11)$$

where g , the Landé g -factor or spectroscopic splitting factor, is¹

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \quad (1.12)$$

Nevertheless, the Landé g -factor results from the calculation of the first-order perturbation of the energy of an atom, when a weak external magnetic field acts on the sample. Normally, the quantum states of electrons in atomic orbitals are degenerate in energy, and therefore, the degenerate states all share the same angular momentum. However, if the atom is placed in a weak magnetic field, the degeneracy is lifted [8]. Furthermore, this dimensionless g -factor relates the observed magnetic moment μ_{J_z} of an atom to the angular momentum quantum number m_j , and the fundamental quantum unit of magnetism, that is, the Bohr magneton.

1.3.2 Exchange Coupling and Exchange Bias

At this stage, we need to comment on the interaction of spins with each other since this phenomenon was already mentioned a few times. Heisenberg stated, in 1928,

¹For a rigorous derivation of above results, please see any introduction to quantum mechanics [5]–[6], or more specialized books on electric and magnetic susceptibilities [7].

that the force which makes the spins line up is an exchange interaction of quantum mechanical nature, and this view is still being upheld these days. As such, two atoms with spins \mathbf{S}_i and \mathbf{S}_j have a potential energy U_{ij}

$$U_{ij} = -2J\mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.13)$$

where J is the exchange integral. A positive value for J is obtained when the two spins are parallel and the energy is at a minimum. In contrast, an antiparallel alignment of spins gives a negative exchange integral J . The exchange interaction arises due to Pauli's exclusion principle which permits an orbit to be occupied by one "up" and one "down" spin, while two electrons with the same kind of spin cannot approach each other closely. This means that two "up" or two "down" spins cannot belong to the same electron, and therefore, the mean distance between two electrons with parallel spins is different from that between electrons with antiparallel spins. In quantum mechanical terms, the expectation value of the energy of two spins differs for two spins of the same orientation than for those of different orientation when their wave functions overlap.

Example 1.2. Comment on the "flow of spin," also known as *spin current*

Answer: *Spin* has been researched and considered the origin of magnetism for roughly 80 years, in contrast to *charge*, the other degree of freedom of an electron that has been studied for about 200 years. The "flow of charge" has been successfully utilized for a long time; however, many readers may not be that familiar with the "flow of spin" which has attracted much attention and exploitation only in relatively recent years. A charge current contains both "up" spin and "down" spin electrons, where "up" and "down" are with respect to the quantization axis. In contrast to a charge current, a spin current is given by the *difference* in flow between "up" and "down" spin electrons. In ferromagnetic and ferrimagnetic materials, the number of "up" spin and "down" spin electrons differs, making those electrons *spin polarized*. Thus, spin current and charge current flow together in these materials.

A nonconserved quantity, the flow of spin changes through the exchange of angular momentum. It can be generated by electric, magnetic, or optical signals, although its generation is not as straightforward as the one of charge current. On the other hand, spin currents are easily annihilated through spin relaxation when viewed over a length of time, meaning that spins flip in time intervals ranging from picoseconds to nanoseconds. Concurrently, a spin current can be lost through spin diffusion when considering the spatial aspect of the flow. The spatial range in which spin current flows in the material is known as the *spin diffusion length*, and is usually between 100 nm and 1 μm , depending on the material (e.g., metal and semiconductor), structure (e.g., nanostructure), and experimental conditions (e.g. temperature). This type of spin current that diffuses through a material is not accompanied by charge movement. Therefore, it is often referred to as *pure spin current*; nevertheless, electrons still move. Whether pure or carrying electric charge, spin current constitutes the foundation for many devices belonging to a new class of electronics, *spintronics*. More advanced chapters in this book discuss a few aspects

of spin current generation with particular emphasis on the topic of maintaining its flow.

Two separate ferromagnetic layers can become “exchange coupled” when separated by a thin, nonmagnetic spacer layer. However, this process is not straightforward, as one might expect. Most interfaces of bilayers of ferromagnetic or ferrimagnets are either uncoupled or ferromagnetically coupled. Only under special circumstances do the bilayers become exchange coupled. The mechanism of exchange coupling is treated in terms of the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction or the theory of spin dependent quantum well effects [9]. This means that when the two ferromagnetic layers are exchange coupled, an antiparallel alignment of spins occurs, of the type observed in antiferromagnetic materials. In this case, the exchange integral J in relationship (1.13) is negative and fairly large in value. For instance, the strongest interlayer exchange coupling constant of $J \approx -5 \text{ erg/cm}^2$ has been observed in a Co/Ru/Co system with a $\sim 0.5 \text{ nm}$ thick Ru layer [10]. Coupling strength, as well as its sign are both dependent on spacer thickness. Most reported studies have so far been for metallic systems, but this trend is changing. These days, magnetic oxides or combinations of magnetic oxides and metals enjoy a lot of attention. The interlayer exchange coupling constitutes the basis for controlling magnetization alignment in many modern magnetic applications, such as magnetic recording media, magnetic sensors, and magnetic random access memories. An interlayer exchange coupled system is referred to as a *synthetic antiferromagnet*, a topic that will be further discussed in later chapters.

There is a class of magnetic materials known as *half-metallic* compounds, named so because they only have one channel of spin; hence, the flow of spin they generate is either “up” or “down.” Ideally, these materials show 100% *spin polarization* due to one spin channel being present at the Fermi level, with a band gap for the other spin channel. Half-metallic compounds are usually magnetic materials in either their ferromagnetic or ferrimagnetic states. These include CrO_2 , the so-called *half-Heusler* NiMnSb , the *full-Heusler* Co_2MnSi , and the perovskite $\text{Sr}_2\text{FeMoO}_6$. Some of these materials, or the class they belong to, will be discussed further in subsequent chapters. These materials have a total, positive magnetic moment and are good candidates for spintronics applications. Nevertheless, researchers have found another interesting class of materials that displays the half-metallic character but has no net magnetic moment, although they show full spin polarized charge transport. In this case, these antiferromagnetic systems would be relatively insensitive to applied magnetic fields, and, therefore, could possibly lead to a different type of spintronics devices.

For instance, a group [6] in Japan has successfully fabricated the half-metallic antiferromagnet SrLaVMoO_6 by modifying the half-metallic ferrimagnet $\text{Sr}_2\text{FeMoO}_6$. They assumed that Fe^{3+} is antiferromagnetically coupled to Mo^{5+} , and this fact was the starting point for their investigation. Stoichiometric amounts of SrCO_3 , La_2O_3 , V_2O_5 , and MoO_3 were mixed, calcined twice, ground, and sintered, all steps being performed under certain temperature conditions. The SrLaVMoO_6 specimen displayed a majority phase of an ordered perovskite with a small impurity

phase. Nevertheless, the majority phase showed a negative paramagnetic Curie temperature, indicating that the exchange interaction of the magnetic moments is antiferromagnetic. A linearly increasing magnetization with temperature ruled out the existence of ferromagnetic or ferrimagnetic components in the sample. Also, the resistivity shows metallic temperature dependence, attributed to the large Mo $4d$ bandwidth. The V^{3+} ion is assumed to be antiferromagnetically coupled to Mo^{4+} and therefore responsible for the total net zero magnetization. X-ray photoelectron spectroscopy studies support this assumption.

All data thereby suggested that the obtained specimen [6] was a conducting antiferromagnet. However, the observed spin polarization of 50% was well below 100% of the ideal half-metallic compound, which may also be due to the actual measurement method used. Similar spin polarization measurements on Co-based Heusler compounds have previously indicated comparable polarization values. In any case, this study [6] indicates that a high spin polarization may co-exist with a zero net magnetic moment. This is quite unexpected in materials for which identical “up” spin and “down” spin band structures without exchange splitting are assumed, where spin polarization and net magnetization are zero. It shows that progressive knowledge of magnetism has resulted in some compounds being manufactured nowadays with both exchange and crystal field splitting, as well as non-identical, special band structures for “up” and “down” spin channels.

Exchange bias is related to exchange coupling, and occurs at the interface between a ferromagnet and an antiferromagnet. This type of coupling usually happens when the materials are field-cooled through the *Néel temperature* Θ_N of the antiferromagnetic material. The experimental signs are recognized in the $M-H$ hysteresis curves, when magnetizations shift along the field axis. The shift is assumed to be due to the exchange coupling at the interface between “soft” ferromagnet spins and “hard” antiferromagnet spins. Some researchers argue that uncompensated spins at the antiferromagnet surface also play a role in this effect, as these spins are “frozen in” and, therefore, not reversed when the applied magnetic field is acting. Uncompensated spins in antiferromagnets originate in surface imperfections such as intermixing, nonstoichiometry, and structural roughness, where the antiferromagnetic order is disturbed. For instance, reports [11] on NiO/Co, IrMn/Co, and PtMn/Co₉₀Fe₁₀ identified uncompensated Ni or Mn spins located at the antiferromagnetic–ferromagnetic interfaces. As such, it was determined through hysteresis loop measurements that only $\sim 4\%$ of the ferromagnetic monolayer is tightly pinned to the antiferromagnet, therefore not rotating in an external field. Furthermore, a quantitative correlation was found between the size of the pinned interfacial magnetization and the macroscopic magnetic exchange bias field. In these experiments, high sensitivity X-ray magnetic circular dichroism spectroscopy was used in a total electron yield detection because the $1/e$ probing depth makes this method responsive to interfacial surfaces [12]. The exchange bias phenomenon has applications in magnetic recording, as will be seen in later chapters.

1.3.3 Partition Function Z

A few words should also be said about the partition function which is particularly a concept of interest in multi-particle structures, as well as other areas of magnetism. Consider a simple paramagnet where the atoms do not interact with each other. In this case, the only contributions to the Hamiltonian \hat{H} come from their interaction with the applied magnetic field \mathbf{H}_0 . Because the atoms are identical, only the Hamiltonian for a single atom needs to be considered

$$\hat{H} = -\vec{\mu}_J \cdot \vec{H}_0. \quad (1.13)$$

Choosing \mathbf{H}_0 to be along the z -axis, we can write

$$\hat{H} = -\mu_{J_z} H_0. \quad (1.14)$$

The eigenvalues of \hat{H} are then

$$E_m = -g\beta m_J H_0. \quad (1.15)$$

The partition function Z is then defined by

$$Z = \sum_n e^{-E_m/kT} = \text{Tr}(e^{-\hat{H}/kT}) \quad (1.16)$$

or, in our case,

$$Z_J = \sum_{m_J=-J}^J e^{g\beta m_J H_0/kT}. \quad (1.17)$$

As stated, the partition function Z is an important quantity when dealing with multi-particle structures, as it encompasses the statistical properties of the entire system. It depends on a number of factors, such as the system's temperature, the angular momentum quantum number, external magnetic field etc. Furthermore, it is a sum of all states based on their individual energies while determining how the probabilities are divided among the various states that compose the system.

Example 1.3. Give an example of the usefulness of the partition function

Answer: For instance, the magnetic ($g\beta JH_0$) and thermal (kT) energies can be expressed in terms of the partition function. As such, denoting by x , the ratio of magnetic and thermal energies

$$x = \frac{g\beta JH_0}{kT}, \quad (\text{E1.1})$$

the partition function becomes

$$Z_J(x) = \sum_{m_j=-J}^J e^{m_j x/J} = \frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{1}{2J}x\right)}. \quad (\text{E1.2})$$

This expression of the partition function allows calculation of the expectation value of the magnetic moment μ_{J_z} , a quantity observed experimentally.

Consider a sample of N atoms, where the magnetization is given by

$$M = N \langle \mu_{J_z} \rangle = Ng\beta \langle J_z \rangle \quad (\text{E1.3})$$

and

$$\langle J_z \rangle = \frac{\text{Tr}(J_z e^{-\hat{H}/kT})}{\text{Tr}(e^{-\hat{H}/kT})}. \quad (\text{E1.4})$$

In this case,

$$M = Ng\beta \frac{\text{Tr}[J_z e^{\hat{H}/kT}]}{Z_J(x)}. \quad (\text{E1.5})$$

This expression can be reduced to the useful form

$$M = Ng\beta JB_J(x), \quad (\text{E1.6})$$

where, B_J is called the *Brillouin function* [5–8]. This function describes the dependency of the magnetization on the applied magnetic field, temperature, and the total angular momentum quantum number, and hence it is a useful concept. It is used to derive important laws of magnetism, such as the Curie–Weiss law mentioned earlier.

1.3.4 Intrinsic and Induced Anisotropy

A magnetically anisotropic material is one whose magnetic properties depend on the direction in which they are measured. It is an interesting fact that a magnetic material can display various types of anisotropy, but nevertheless the anisotropy of most magnetic materials is of magnetocrystalline origin. This anisotropy is a magnetic property determined by crystal structure and is the only *intrinsic* anisotropy, while other types of magnetic anisotropy are *induced*. Magnetocrystalline anisotropy arises in a magnetic material because each atomic moment is acted on by a *crystal field*, proportional to the local magnetization of its environment. This means that if an atomic moment were to be removed from its environment, it would leave behind a magnetic field. This field is produced by the surrounding spins, and is a manifestation of the local symmetry of the crystal, and hence the name “crystal field.” When an external field tries to reorient the spin of an electron, the orbit of that

electron also tends to reorient, as spin and orbit are coupled. Nevertheless, the orbit of the electron is also strongly coupled to the crystal lattice, and, therefore, resists reorientation. The competition between the spin–orbit coupling and the crystal field gives rise to magnetocrystalline anisotropy, which manifests itself in the energy required to overcome the spin–orbit coupling.

Magnetocrystalline anisotropy is one of those material properties that affects the shape of the hysteresis curve, allowing us to make a general distinction between permanent magnets and magnetically softer materials. This is because in essence, magnetocrystalline anisotropy manifests itself as a variation of the magnetic properties of the material with a specific, crystallographic orientation, being largest along preferred crystallographic directions. For instance, an iron crystal has directions of the form $\langle 100 \rangle$ as preferred crystallographic directions, along which magnetic moments from magnetic domains tend to align. Magnetic saturation can be achieved in iron, in these easy directions of magnetization with fields of only a few tens of Oe. In contrast, nickel crystals display easy directions of magnetizations along $\langle 111 \rangle$ directions of form, and so do all the cubic ferrites with the exception of cobalt ferrites and their derivatives which exhibit $\langle 100 \rangle$ easy axes. Magnetocrystalline anisotropy is, thus, a valuable characteristic of a magnetic material in as much as it allows a materials engineer to design a device who exploits this fact in a commercial application.

Permanent magnets, such as SmCo_5 or $\text{Nd}_2\text{Fe}_{14}\text{B}$, require a high magnetic anisotropy in order to maintain the domain magnetization in a chosen direction. This preferred magnetization orientation through anisotropy is permitted in permanent magnets by the electronic configuration that gives rise to a particular interaction between the crystal field and the spin–orbit coupling. Specifically, the magnitude of the magnetocrystalline anisotropy depends on the ratio of crystal field energy and spin–orbit coupling [13]. As such, the crystal field acts on the orbits of the inner shell d and f electrons, and given that spin–orbit coupling is a relativistic phenomenon, it is most pronounced for inner-shell electrons in heavy elements, such as rare-earth $4f$ electrons. This fact results in a rigid coupling between spin and orbital moment in heavy elements [14]. On the other hand, in magnetic materials such as Fe, Ni, and Co, the magnetocrystalline anisotropy is due to $3d$ electron spins, in contrast to the magnetocrystalline anisotropy for rare earth elements that originates in the $4f$ shells. In fact, the strong magnetocrystalline anisotropy in permanent magnets is given by the comparatively small electrostatic interaction of the unquenched $4f$ charge clouds with the crystal field. The absence of quenching means that typical single ion anisotropies (rare earth ions) are much larger than $3d$ anisotropies. This strong magnetocrystalline anisotropy is exploited in advanced permanent magnets, where it leads to very high coercivities, for instance, 4.4 T in $\text{Sm}_3\text{Fe}_{17}\text{N}_3$ -based magnets. Therefore, a large number of magnetic applications are based on rare earth metal alloys.

Unlike magnetocrystalline anisotropy, induced anisotropies are due to some external material treatment which has more or less directional properties. For instance, most ferromagnetic materials are known to exhibit a uniaxial anisotropy

after heat treatment in a magnetic field. This is quite often known as the *magnetic annealing effect*. It was discovered in the first half of the twentieth century, and has since then been used in many laboratory studies or engineering applications. Similarly, mechanical processing such cold rolling or cold working can also induce anisotropy, termed in the former case as *roll magnetic anisotropy*. This type of anisotropy is also purposely exploited in industrial products. For instance, 3.25% silicon steel employed as a core material for power transformers, had started to be investigated and used decades ago, for the crystal orientation and the silicon content of the steel. A (110) [001] texture can be obtained by a sequence of cold rolling and annealing operations so that the [001] easy direction is parallel to the rolling direction, while a magnetically harder direction [110] is present in the transverse direction. As such, electrical equipment is designed so that the magnetic flux is carried mostly in the rolling direction. Further research has been performed in an attempt to increase the Si content beyond the 3.25%; however, many barriers had to be surmounted (see problem question P1.10 at the end of the chapter). Nevertheless, it was observed that for obtaining optimum results for the improved silicon steels with higher Si content, the magnetic annealing field has to be strong enough to saturate the sample in the desired direction, while the temperature and time conditions must be sufficient to accomplish short range Si diffusion. Within these limits, most combinations of annealing field and temperature will yield the desired results [15]. It was apparent from these studies that magnetic properties perpendicular to the rolling direction are more sensitive to magnetic annealing than those parallel to the rolling direction, irrespective of Si content.

Example 1.4. What are the effects of a transverse annealing field on an amorphous, Co-rich magnetic alloy?

Answer: Magnetic properties of amorphous, Co-rich magnetic alloys depend strongly on the induced transverse magnetic anisotropy which is obtained after magnetic annealing in a transverse field. A group of researchers [16] investigated a few magnetic properties such as magnetic remanence, coercivity, and domain structure of the magnetostrictive compound $\text{Co}_{71.5}\text{Fe}_{2.5}\text{Mn}_2\text{MoSi}_9\text{B}_{14}$ after a two-step annealing process. This process involved first annealing the samples at 570 K without a magnetic field, and then cooling them to room temperature in a range of transverse fields spanning 8–160 kA/m. The higher annealing fields resulted in a lower magnetic remanence, as well as lower coercivity values, in comparison to smaller annealing fields. At the same time, in those specimens with an existing longitudinal magnetic anisotropy, a reorientation of this anisotropy axis was noticed toward the transverse direction after annealing in higher magnetic fields, a fact which was expected. High annealing magnetic fields also cause a strong magnetic ordering in the domain structure, thus explaining the lower remanence and coercivity values. It was noted that the cooling rate contributed to the magnetic annealing process, altering magnetic properties. The higher the cooling rate, the longer the time required for magnetic ordering.

1.3.5 Magnetostriction

Aside from exchange coupling, spontaneous magnetization, or magnetocrystalline anisotropy, other intrinsic magnetic properties such as magnetostriction also have origins in atomic scale magnetism [17]. Although they manifest themselves on length scales of a few angstroms, their consequences already reach bulk values at ~ 1 nm and are, therefore, exploited in today's nanotechnology applications. Magnetostriction was first discovered in 1842, by Joule who noticed a change in the length of an iron rod that was magnetized in a weak field. As such, under the influence of the magnetic field, the shape of the iron rod changed due to a magnetic property that was coined *magnetostriction*, and is, nowadays, often denoted by λ . This change in shape is schematically shown in Fig. 1.4; however the change is exaggerated, as this type of deformation is very small, only of the order of 10^{-5} – 10^{-6} , or even smaller in weakly magnetic materials. It was observed that when the specimen elongates under an applied magnetic field, its volume remains constant, implying that a *transverse* magnetostriction exists. Indeed, the transverse magnetostriction is about half the value of the longitudinal magnetostriction, and of opposite sign.

The existence of magnetostriction is attributed to the spin–orbit coupling of valence electrons in ferromagnets, and as such, when spins change direction to align with domain magnetization, the orbits change shape to conserve angular momentum, because electron orbits are coupled to spins. Since electron orbits are also coupled to the crystal lattice, the lattice inside a magnetic domain deforms spontaneously in the direction of domain magnetization. For instance, a single iron crystal that is magnetized to saturation in the [100] direction will increase in that direction due to magnetostriction. In this case, the strain due to magnetostriction will continue to increase with the applied magnetic field until it reaches a saturation value. This value of saturation magnetostriction can be positive, negative, or in some alloys, zero. Additionally, magnetostriction will saturate along a specific crystallographic axis. For example, we have $\lambda_{100} = 19.5 \times 10^{-6}$, and $\lambda_{111} = -18.8 \times 10^{-6}$ in a single cubic crystal, where λ_{100} and λ_{111} are the saturation values of the longitudinal magnetostriction in the directions [100] and [111], respectively [18]. Quite often, an “isotropic saturation magnetostriction” denoted

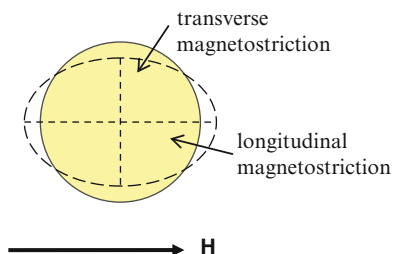


Fig. 1.4 Elongation of a ferromagnetic object in the direction of an applied magnetic field

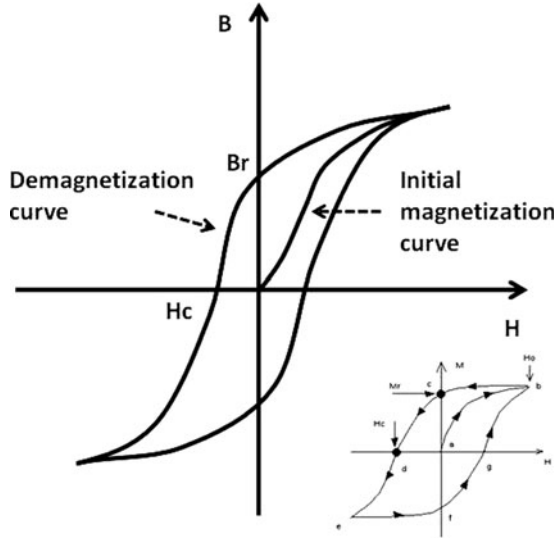


Fig. 1.5 Hysteresis loop that includes the initial magnetization curve. Also shown are coercivity H_c and remanent magnetic flux density B_r . A hysteresis loop can be obtained by plotting magnetic field density B vs. applied magnetic field intensity H , or as shown in the inset, by plotting magnetization M vs. applied magnetic field intensity H

λ_s and equal to $\lambda_s = \lambda_{100} = \lambda_{111} = -7 \times 10^{-6}$ is assumed, although it was not found to be representative of experimental results [19].

Many magnetic materials of practical importance undergo additional magnetic treatment, such as magnetic annealing, in order to enhance their magnetic properties. Silicon steels are a group of such materials that have traditionally been improved through further processing, and their magnetostriction has also been altered through mechanical and magnetic treatments. It was, thus, observed that the magnetostriction of these materials is positive but rather small in the rolling direction without magnetic annealing, and that upon magnetic annealing, the magnetostriction became even smaller and negative. Alloys with reduced Si content had lower magnetostriction values without magnetic annealing but their magnetostriction was closer to zero upon annealing [15].

1.4 Historical Uses of Magnetic Materials

1.4.1 Permanent Magnets

There are materials that can be magnetized which remain magnetized after the magnetizing field has been removed. These materials store magnetic energy permanently

without getting drained through repeated use, thus being employable in a variety of instruments. Humanity has long been fascinated with this interesting class of materials known as *permanent magnets*, as they are able to produce constant external magnetic fields available at any time. Nevertheless, any discussion about permanent magnets has to first answer the question as to what distinguishes this class of materials from other magnetic compounds. The clue lies in the second quadrant, between remanence and coercivity, in the so-called *demagnetization curve*. The demagnetization curve is part of the *hysteresis loop* (Fig. 1.5), which is obtained by plotting magnetic field density B , or magnetization M of the material being magnetized versus the applied magnetic field H . The hysteresis loop reveals the magnetic history of a ferromagnetic material, and is, therefore, very useful in assessing a magnetic material. From the hysteresis loop, we can determine the two quantities, retentivity B_r (or remanent magnetization M_r) and coercivity H_c , as well as the product $B_{\max}H_{\max}$ of the maximum field values. These characteristics are commonly used by engineers in evaluating the quality of permanent magnetic materials [20].

For instance, the product $B_{\max}H_{\max}$ is related to the minimum volume of a magnet that is required to produce a given field in a given gap in the magnetic circuit. Similarly, engineers are interested in the magnetic flux density B_r , because it indicates how much magnetic flux or magnetization has been retained after the externally applied field is brought to zero on the demagnetization curve of the hysteresis loop, after magnetic saturation has been attained. The capability of the material of retaining a magnetization is an indication of the ability of the material to be permanently magnetized, useful for magnetic memory applications. On the other hand, the value of the magnetic field intensity H_c , necessary to bring the magnetization of the material to zero, is an indication of how magnetically *hard* or magnetically *soft* the material is. It measures the resistance of the ferromagnetic material to becoming demagnetized. Soft magnetic materials are usually employed as transformer cores, or used in motors and generators, with some example materials discussed in the next section. Magnetically soft materials need to have a high permeability, low coercivity, and a small hysteresis loss. Conversely, permanent magnets have to be magnetically hard in order to display a high coercivity and a high remanence. Nevertheless, as it may already be known to the reader, certain magnetic properties are not sufficient on their own for a material to be considered a permanent magnet. Geometry counts as well, because a permanent magnet needs “free” magnetic poles in order to provide an external field. The magnetic flux circuit cannot close within the material; it has to be able to leak outside the material by offering a gap in the circuit. Furthermore, the energy stored in the field in the air gap is directly proportional to BH , which is also called the *energy product*. As such, permanent magnets always have open circuit geometry in order to be operational.

Historically, the most familiar magnetic material may have been the lodestone, followed by high carbon steel magnets of the type used in compass needles. Nevertheless, one of the best magnetic steels employed for a while in magnetic applications was a type of steel made with 30–40% Co, as well as W and Cr. When magnetic recording started to flourish, it required its own magnetic materials

with particular magnetic characteristics. Consequently, Co–Pt–Fe alloys gained ground, given their excellent remanence value and low coercivity, in spite of being very expensive. New developments in rare earth metal alloys such as SmCo_5 and others followed soon, giving better magnets at lower costs, with rare-earth magnets still enjoying many uses in today's modern magnetic applications. Nevertheless, aside from magnetic recording, permanent magnets have traditionally enjoyed employment in loudspeakers, electric meters, magnetic particle separation, microwave devices, nuclear magnetic resonance, linear accelerators, and a variety of lifting or holding devices, to name just a few. The group of materials that were most used as permanent magnets were the Al–Ni–Co–Fe alloys (i.e., alnicos) with additions of Ti. Adding Ti gave these materials an exceptionally high coercivity, a very desirable quality in many applications. On the other hand, there were other permanent magnets that may have competed with the alnicos because of their magnetic properties. In spite of displaying lower flux densities and higher coercivities than the alnicos, they had their own share of the market because some applications could function solely on this class of materials. These permanent magnets that were considerably used in the past were the Ba or Sr hexaferrites, also known as “ceramic magnets” [1].

Many times in history when a magnetic field was required in a particular environment or space, permanent magnets were employed due to their convenience as energy storage devices and quite often, due to lack of a better alternative. These days, many industrial applications requiring permanent magnets such as ion pumps or focusing devices no longer rely on a particular magnetic material or magnetic compound, but rather make use of electromagnets or a superconducting magnetic circuit. Unfortunately, these constructions necessitate a large expenditure of electric power and also generate a considerable amount of heat. Although these latter human inventions are still related to magnetism in some way, they are not part of the class of magnetic materials that are based on the magnetic phenomena and principles we are discussing in this book. As such, superconducting magnets are not a topic we intend to cover here, due to the highly specialized branch of engineering that they represent. Separate treatments of this subject and its underlying physics are required, and the reader is thus encouraged to seek further information elsewhere. Nevertheless, a few words can be said about the significance of superconducting magnets, and why it is worth for the readers to pursue further investigation on their own.

A group of researchers [21] have recently demonstrated a cryogen-free 23 T superconducting magnet where the insert coil was a 7.5 T $\text{YBa}_2\text{Cu}_3\text{O}_7$ conductor. This achievement is particularly timely due to troublesome experimental barriers encountered in today's magnetics experiments, where really high magnetic fields are required for very precise measurements. High magnetic field experimental research contributes significantly to the development of fundamental research in many areas of magnetics. Yet, it is difficult to maintain a high static field over a long period of time, especially while performing high precision measurements. Many problems arise when trying to generate high static fields of 20 T or more, especially since huge electrical powers in the range of 20–30 MW are necessary to power a water-cooled

resistive magnet of a hybrid magnet system. Many institutions cannot afford such costs. Hence, superconducting magnets can help with these applications, and, nowadays, their magnetic field capabilities have reached impressive high values. The mentioned researchers [22], managed to demonstrate functionality of a unique cryogen-free superconducting magnet that can be maintained in a room temperature bore without using liquid helium or nitrogen. By incorporating an $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123) coated conductor tape, they were able to improve on an earlier version of their design and obtain the generation of a 23 T magnetic field. The coil has a total inductance of 244 H, and is capable of storing a magnetic energy of 8.7 MJ, thus showing quite remarkable characteristics. There is also a low Curie temperature background magnet composed of four Nb_3Sn coils and one NbTi coil. The magnetic field generated by either coil is directly related to the coil current density. The whole assembly has demonstrated superior use in as far as it generates a maximum 23.4 T field and, thus exceeds magnetic field generation of similar, but liquid helium cooled, superconducting magnets.

1.4.2 Silicon–Iron Alloys. Wound Cores

The electrical industry has benefited significantly from alloys of silicon and iron, with specific applications depending on the silicon content. As such, low percentage alloys (1.5–3.5% Si) have enjoyed employment in motors, generators, and relays, while higher percentage alloys (3–5% Si) have been used for high-efficiency motors and power transformers [23]. Therefore, we need to say a few words about the magnetic properties of this important group of materials. Silicon–iron alloys, also known as silicon steels, are usually melted in an open hearth, an electric arc, or an induction furnace. A rigid control of furnace conditions is performed, especially during refining when oxygen is introduced. Because magnetic properties of silicon steel are so important in a variety of industrial products, it is necessary to produce a low loss material. A large number of researchers have thoroughly studied these alloys over many years. It was discovered as early as the beginning of the twentieth century that, adding more silicon to the already known silicon–iron alloys made them magnetically softer, inasmuch as their coercivity was only half of that of iron, a standard material used till then in transformer cores. Surprisingly, it was soon observed that their permeability was also increased, while hysteresis losses and eddy currents were diminished.

Today we know that silicon–iron alloys possess a high magnetic permeability, and display low hysteresis losses in the cold rolling direction. This fact can be attributed to the directionality of the domain structure which shows antiparallel domains along the rolling direction, rendering particular magnetic properties of these type of steels along this direction. Therefore, any factor that destroys or improves this antiparallel domain structure directly affects magnetic properties in this direction. As a matter of fact, only grain-oriented silicon steels particularly of (110) [001] orientation are of interest for many applications; therefore, many

studies and production procedures (e.g., specially designed annealing furnaces) refer exclusively to these type of textured materials. Furthermore, domain refining methods and the mechanisms associated with them have been at the forefront of many improvement techniques. As such, it has been found [24] that there is an interaction between the tensile stresses created during rolling and the newly formed sub domains, the latter consisting of transverse domains resulted from magnetic “free” poles and internal stresses.

A large number of electrical steels that are being produced are used for wound cores. Core losses in silicon steels depend on saturation values of magnetic flux density B achievable in these materials. It has been assumed for a while that larger 180° domain wall spacing due to larger grains leads to increase in anomalous eddy currents and, hence, higher losses. Thus, by refining magnetic domain structure, the domain wall spacing is reduced by counteracting the increase in magnetostatic energy. That, in turn, reduces anomalous eddy currents, allowing a larger saturation flux density, which will then decrease losses. Nevertheless, domain refining needs to be heat resistant, as wound cores are subjected to stress relief annealing. Furthermore, a secondary recrystallization technique is required during material fabrication to ensure a highly oriented crystallographic structure, so that a large number of magnetic domains have the same magnetization orientation.

Another way of reducing eddy current and hysteresis losses is by reducing the thickness of the silicon steel sheet down to a minimum value. Some studies report a $40\text{ }\mu\text{m}$ optimum thickness for use of the silicon steel at 50 Hz frequency, whereas higher frequencies require even smaller thicknesses of $\sim 10\text{ }\mu\text{m}$ ([25] and references therein). To further investigate sheets of the thinner kind, two types of silicon steel sheets were compared, where the starting material had been fabricated in two different ways [24]. The first sheet was obtained by cold rolling a $300\text{ }\mu\text{m}$ thick conventionally fabricated silicon steel sheet down to a $5\text{ }\mu\text{m}$ thickness. During this process, the sheet was annealed at $1,100^\circ\text{C}$ for 1 h in vacuum while at a thickness of $10\text{ }\mu\text{m}$ to decrease work hardening. The second type of sheet was also obtained by cold rolling, this time down to $8\text{ }\mu\text{m}$, however, a hot rolled 2 mm thick silicon steel sheet was chosen as a starting material. Similarly, the second sheet was annealed at $1,250^\circ\text{C}$ for 10 h in vacuum at a thickness of $300\text{ }\mu\text{m}$ to restore a highly necessary crystallographic texture. Results indicated that the conventionally fabricated silicon steel sheet of $5\text{ }\mu\text{m}$ thickness had a saturation magnetic flux density of 1.96 T and a coercivity of 6.6 A/m, both illustrating good magnetic properties. Surprisingly, the initially hot rolled steel sheet that was further processed by cold rolling and annealing also showed a similar saturation magnetic flux density of 1.95 T, indicating that the final thickness of the silicon steel sheet plays a more important role than the fabrication details of obtaining it.

Conventional transformers have historically used grain oriented silicon steel sheets. However, some fabrication studies have demonstrated the process of obtaining silicon steel wires instead of sheets, with the lowest possible magnetic losses [26]. A silicon–iron wire of 7.2 mm diameter was drawn down to 0.4 mm in several stages. A few heat treatment steps were necessary in order to relieve stress and recrystallize the deformed material. A magnetic anisotropy direction along the

wire is highly desired, as well as a large saturation magnetization. However, a coldly deformed wire acquires a strong $\langle 110 \rangle$ texture parallel to the wire axis, obviously not a direction of easy magnetization. It was noticed that in silicon steel sheets, a small grain size leads to the disappearance of the dominant (001) $\langle 110 \rangle$ component during processing, a reduction in the (111) $\langle 110 \rangle$ component, and the appearance of a strong (111) $\langle 112 \rangle$ texture component. On the other hand, a large grain size $>100 \mu\text{m}$ in the original material, leads to a strong (011) $\langle 100 \rangle$ crystallographic component, suitable for magnetic applications. This latter result obtainable in silicon steel sheets was desired for drawn silicon steel wires. As such, through a sequence of deformation and annealing processes, decarburization and recrystallization, it was possible for researchers [25] to induce a grain growth at crucial stages of fabrication. Unfortunately, the crystallographic texture of the silicon steel wires did not quite have the desired (011) $\langle 100 \rangle$ crystallographic component, but showed an intermediate magnetization axis with a somewhat better permeability compared to that of small grain sized traditional silicon steel sheets. Hence, they felt encouraged to continue their experiments, this time by applying magnetic annealing treatments. It is hoped that magnetic annealing will lead to an improvement in magnetic properties by increasing the grain size, and maximizing $\langle 100 \rangle$ crystallographic directions along the wire axis. An improvement in magnetic losses is also highly desired.

1.4.3 *Nickel-Iron Alloys. Permalloys*

Magnetic recording and, in particular, recording heads are topics that have fascinated several generations. A magnetic recording head should preferably have a high magnetic moment, low coercivity, zero magnetostriction, a large electrical resistance, no internal stresses, and a high corrosion resistance. However, none of these properties are achievable in one single material, and manufacturers have to make compromises. Ni-Fe alloys have enjoyed long time use in magnetic recording, in spite of new materials having entered the recording market since. It was noticed early on that, unfortunately, Ni-Fe alloys have limited applicability in their “as is” state. This is because they are weakly magnetoresistive at room temperature, requiring low temperatures and fields in excess of 20 kOe. Magnetoresistance and its applications are subjects discussed in detail in a more advanced chapter in this book but nevertheless, it suffices to say that room temperature functionality and sensitivity to low magnetic fields are highly desirable attributes. As such, Ni-Fe alloys display a weak magnetoresistance at ambient temperatures. This fact is detrimental to magnetic recording applications that have to function at room temperature while responding to small fields.

Fortunately, the invention of electroplating baths, as well as improved fabrication processes for magnetic recording heads brought progress to IBM in the earlier days of magnetic recording. As such, magnetic heads used a plated inductive permalloy head [23] which was the only selected material for this purpose. “Traditional”

permalloy has 20% Fe and 80% Ni, being a material with a high magnetic permeability, low coercivity, and an almost zero magnetostriction. Permalloy has been historically used in transformer laminations, where it is wrapped around the insulated copper conductors of telecommunication cables, reducing signal distortion by improving inductive compensation of cable capacitive reactance. But the low magnetostriction of permalloy is particularly significant for the earlier magnetic recording heads, where variable stresses in thin films would have otherwise caused a large variation in magnetic properties. The permalloy head had the advantage that, it was able to meet the strict requirements for both reading and writing processes, especially given its soft magnetic properties [20]. Permalloy heads became quickly established as they were easily plated into films, had negligible magnetostriction, and good corrosion resistance, displaying a saturation flux density [27] of 1 T.

A certain nickel–iron alloy with a specific elemental content also gained ground in magnetic recording in the previous century, particularly as areal densities of disk drives increased. $\text{Ni}_{45}\text{Fe}_{55}$ also known as 45 Permalloy is a magnetically soft alloy, not as good as “traditional” permalloy, but with an increased magnetic moment. This larger magnetic moment attributed to the higher Fe content allowed writing in higher coercivity media, which was a significant improvement at that time. Ni–Fe alloys became heavily researched and improved upon, encouraged by the fact that the magnetic moment for binary NiFe alloys was found [28] to increase monotonically with Fe content up to about 65% Fe composition. The better corrosion properties of this alloy were an added bonus when compared to Co-based high moment alloys. A disadvantage was, however, that efforts to optimize the material in order to improve the writeability process were noticed to deteriorate readability. Inductive writing was used, and such a process necessitates specific magnetic properties which differ from those of reading. The inductive writing with these heads required a larger magnetic anisotropy, a smaller coercivity as well as negligibly low magnetostriction. After some serious improvements, $\text{Ni}_{45}\text{Fe}_{55}$ or 45 Permalloy became the new standard in the thin film head industry [29]. In fact, the read/write challenge of NiFe heads was overcome when the newly emerged magnetoresistive heads made their appearance. These heads were both read and write heads, as a read sensor [30] was used in conjunction with an inductive write head [31], leaving a small physical separation between the two. Such separation of processes allowed tremendous optimization of writing and reading in an individual manner. Consequently, the soft magnetic property requirements of the inductive writer material became less stringent. However, in order to achieve even higher recording densities, larger magnetic moments were needed.

The magnetic recording industry turned for a while to soft magnetic ternary alloys, such as CoFeCu with high Co content in excess of 75%. They displayed a low magnetostriction, reduced internal stresses, and saturation flux densities as high as 2 T. IBM developed these materials for write heads [32], in an effort to replace “traditional” permalloy and $\text{Ni}_{45}\text{Fe}_{55}$. It was noticed that the addition of Cu reduced Barkhausen noise while it also refined grain sizes, and, as such, improved domain configuration. These latter topics will be discussed in subsequent

chapters, and, therefore, we will not go into further detail here. Unfortunately, the fabrication process of these CoFeCu ternary alloys was not straightforward, as it was challenging to deposit the alloy and obtain a uniform composition. This was because a bath was used which contained a reduced concentration of a diffusion-controlled element such as Cu. Also, the weak corrosion resistance made CoFeCu ternary alloys impractical in magnetic recording. Because these alloys did not display a visible advantage over $\text{Ni}_{45}\text{Fe}_{55}$ in terms of head performance, they were not implemented in magnetic recording. Partly because of these reasons, IBM decided to consider other soft magnetic ternary alloys such as CoNiFe instead of CoFeCu [33]. It was noticed that CoNiFe films displayed a magnetic flux density higher than 2 T when electrodeposited galvanostatically from a sulfate/chloride bath similar to the plating bath used for the fabrication of $\text{Ni}_{45}\text{Fe}_{55}$. Consequently, more than 250 alloy compositions were obtained by changing the Ni^{2+} , Fe^{2+} , and Co^{2+} concentrations and varying the current density for a given bath composition. However, this CoNiFe plating system was not consistently reproducible in the high moment region of the ternary diagram. More reliable data was obtained for samples with compositions around $\text{Co}_{44}\text{Ni}_{27}\text{Fe}_{29}$ displaying a slightly lower magnetic flux density (~ 2 T), a coercivity of 1.2 Oe, and a low internal stress (115 MPa). It was important that most samples underwent thermal annealing treatments without damage to their structure [34].

In the end, IBM managed to bring significant improvements to magnetic recording heads from permalloy to CoFe alloys, by developing innovative methods of electrodepositing soft magnetic alloys that displayed magnetic flux densities between 1 and 2.4 T. This re-evaluation process began at some point, when it was decided to have another look at NiFe binary alloys with higher iron content [28], in spite of challenges encountered earlier. It had been noticed that magnetic properties of bulk alloys differ from those that have been electrodeposited, especially if these materials have been annealed at high temperatures. Therefore, electrodeposition of NiFe with compositions ranging from $\text{Ni}_{35}\text{Fe}_{65}$ to $\text{Ni}_{15}\text{Fe}_{85}$ was performed according to patented recipes. These processes included using sulfate/chloride baths containing boric acid, saccharin, and a surfactant, while electrodeposition occurred in magnetic fields of ~ 800 Oe, at temperatures varying between 15°C and 30°C [35]. A thermal annealing process was also performed at 225°C for 8 h [36]. Following this fabrication process, the films were noticed to display higher values of internal stress and a larger magnetostriction than CoFeNi. However, in spite of these shortcomings, the films were more corrosion resistant and easier to manufacture. In time and with further investigation, IBM obtained $\text{Ni}_{32}\text{Fe}_{68}$ and $\text{Ni}_{20}\text{Fe}_{80}$ alloys with saturation flux densities of 2 T and 2.2 T, respectively [37]. Furthermore, they noticed that plating a nickel–iron alloy with 50–70 wt% Fe in a galvanostatic bath with a proprietary additive leads to magnetic flux densities of 2.4 T [38]. These significantly improved plated alloys exhibited a large positive magnetostriction ($+45$ ppm), and high internal stresses of up to [22] 850 MPa.

1.4.4 Compounds with Rare Earth Elements

Of historically great interest, and even more so these days, compounds of a rare-earth metal and a transition metal such as Mn, Fe, Co, or Ni have been extensively studied all over the world and employed as practical magnets. These materials display large anisotropy constants, by far larger than other magnetic materials, and are of great interest in magnetic recording as well as in our modern conveniences such as cell phones. Nevertheless, rare earth magnets may have also been known to the reader from other applications requiring strong magnets, such as nondestructive testing or audio speakers. As such, the neodymium alloy $\text{Nd}_2\text{Fe}_{14}\text{B}$ may be the most familiar permanent magnet used extensively in audio devices, and, for a while, in most computer hard drives. The strong magnetic brushes used in magnetic flux leakage techniques are also made of neodymium alloys. Although these compounds have the highest magnetic field strength B , another rare earth compound, SmCo_5 , has outperformed them in some applications, due to better resistance to oxidation and higher Curie temperature. Thus, SmCo_5 has created a niche in applications where high field strength is needed at high operating temperatures. Unfortunately, SmCo_5 magnets are brittle and prone to cracking and fracture, limiting their use.

Rare earth elements are not particularly scarce, but the terminology refers to the difficulty and high cost of separating them from each other. Ores usually contain more than one element, and these elements are chemically very similar. Demand fixes the price, as well as world economic interests; thus, any new technological development requiring magnetic materials can lead to these materials making news headlines. It should also be noted that several alloys in this rare earth compound category are not usually thought of as permanent magnets, because they are often not single magnets but rather conglomerate structures of a large number of micro or nanoscale magnets. Magnetic recording is a good example of an area of application that rests on these materials, and where individual entities have complex magnetic structures that fall into more than one classification group.

Rare earth compounds contain lanthanide elements which are ferromagnetic metals, but with an individual Curie temperature per element that is below room temperature. Fortunately, as stated earlier, these elements form alloys with transition metals such as Fe, Ni, and Co, and the resulting alloy can reach Curie temperatures well above room temperature. A significant advantage of rare earth compounds is that their crystalline structures have a very high magnetic anisotropy and, therefore, easy to magnetize in a particular direction, at the expense of being magnetized in any other direction. The atoms of rare earth elements have high magnetic moments due to the incomplete filling of the $4f$ -shell, which can contain as many as seven unpaired electrons with aligned spins. $4f$ -Electrons in these orbitals are strongly localized and can thereby, easily retain their magnetic moments. This fact stands in contrast to magnetic moments in other orbitals which are often lost because of a strong overlap with their neighbors, thus leading to zero net spin. The combination of high atomic magnetic moments with a high magnetic anisotropy results in high

magnetic strength, leading to a variety of applications, some discussed later in this book.

To appreciate the vast world of magnetic materials, one has to look at the many subfields of magnetism and the multitude of phenomena that govern them. Audio, video, digital applications, transformers, brakes, cordless devices, and even toys, all benefit from the fascinating materials that respond to an external magnetic field, with some materials able to retain a magnetic flux density of their own. From disks, drums, and recording tapes not usually thought of as permanent magnets, to powerful brushes or magnetoresistive heads, each category involves its own type of magnetic materials, thus bringing its own contribution to the diversity of magnetic effects exploited for the use of humankind. The purpose of this book is therefore, to offer the reader a glimpse into this world, and, in the process, facilitate gaining some knowledge of magnetism and how this scientific/engineering branch evolved over the years. Some questions are ultimately answered: Why do regions within materials become magnetized in one direction while the others can barely be magnetized, or how can magnetism benefit recording and playback of digital information, to how can we ignore the charge of an electron and use its spin instead, in order to develop new types of electronic devices? In the end, it may thus seem less curious that of all the magnetic materials available to humans, only particular ones were essentially chosen, the reasons for these choices becoming hopefully clearer.

Tests, Exercises, and Further Study

- P1.1 Identify the different kinds of magnetism from the schematic representations in Fig. P1.1.
- P1.2 From a historical perspective, why was the concept of spin introduced, and how was it experimentally verified?
- P1.3 A large number of materials are considered magnetic and are commercially employed in devices. However, only three pure metals exhibit ferromagnetism at room temperature. Many magnetic alloys contain at least one of these ferromagnetic metals. What are these three metals, and where does their ferromagnetism originate?
- P1.4 In Fig. 1.2c, the magnetic field is applied parallel to the spin axis. Explain what happens to the spins when the magnetic field is applied perpendicular to the spin axis.

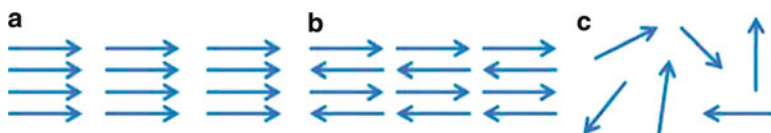


Fig. P1.1 Different kinds of magnetism

- P1.5 What are ferrites? Give a few examples.
- P1.6 What are perovskite-type oxides and what kind of magnetism, if any, do they display?
- P1.7 How are spontaneous magnetizations distributed in a ferromagnet?
- P1.8 What constituted the first direct observation of ferromagnetic domain structure and what interpretation was it given?
- P1.9 Can magnetostriction influence domain structure?
- P1.10 Comment on the influence of the Si content on the magnetic properties of silicon steel. What are the barriers encountered in obtaining higher Si content in commercial silicon steels? *See for instance* [15].
- P1.11 What is the observed domain structure in a silicon steel with a (110) [001] crystallographic texture obtained by a sequence of cold rolling and annealing operations?
- P1.12 Nanocrystalline ribbon alloys with thickness below $10\text{ }\mu\text{m}$ are sought after in electronic devices due to their soft magnetic properties displayed at high frequencies. Particularly, these materials have a high effective permeability and a high magnetic saturation around 1 MHz. They need to have flat $B-H$ curves but also minimum core losses. Because magnetic annealing can change their magnetic properties, this effect on these types of alloys warrants further study. What is the effect of annealing in a magnetic field on the magnetic properties of ultrathin Fe-based nanocrystalline alloys? *See for instance* [39].
- P1.13 Hot rolling of rare earth permanent magnets is a type of mechanical processing that has the advantage of not having to handle magnetic powders. In addition to fabrication steps that involve hot rolling, rare earth permanent magnets also undergo magnetic annealing in order to alter their magnetic properties. What are the effects of magnetic annealing on hot rolled rare earth permanent magnets? *See for instance* [40].
- P1.14 Amorphous Co-based thin films are known for their good high frequency characteristics when integrated in miniaturized devices, such as transformers or inductors. Their soft magnetic properties can be controlled with high precision, particularly when used in a high frequency magnetic field. As such, Co-Nb-Zr thin films display an in-plane magnetic anisotropy. The in-plane magnetic anisotropy is an important attribute of these films because they are used at high magnetic fields where the dominant magnetization reversal process occurs through magnetization rotation. The high frequency magnetic field is applied parallel to the hard axis. The permeability along the hard axis depends strongly on the in-plane anisotropy. Controlling this anisotropy and decreasing coercivity are necessary for minimizing hysteresis losses. Studies show that the in-plane magnetic anisotropy can be controlled by magnetic annealing. Comment on how the annealing field angle influences the in plane magnetic anisotropy. *See for instance* [34].
- P1.15 $\text{Nd}_2\text{Fe}_{14}\text{Si}_3$ is a permanent magnet compound, a Si solid solution in the binary intermetallic $\text{Nd}_2\text{Fe}_{17}$. Specifically, $\text{Nd}_2\text{Fe}_{17}$ crystals have a spontaneous magnetic moment of $39\mu_{\text{B}}$ per formula unit and a Curie temperature

of 348 K. The c -axis is the hard magnetization axis, while [120] is an easy magnetization axis, estimated to exceed 20 T. These materials belong to a wide class of rare earth compounds with a high content of 3d transition metal which combines the localized magnetism of the rare earth sublattice with itinerant magnetism of the transition metal sublattice. Comment on the magnetic properties of this compound. *See for instance* [41].

- P1.16 Ferrimagnetic oxides are important magnetic materials due to their use in transformer cores, microwave antennas, and some magnetic recording devices. Their magnetic properties can be modified nowadays in nanosized structures of the same material as the bulk compound. Nanotechnology is known for the ability to obtain properties in the nanomaterials not seen in their bulk counterpart. Comment on the *reasons* behind the tailored structural, magnetic, and electrical properties of nanosized $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ used in high frequency applications. *See for instance* [42].
- P1.17 Comment on the thickness dependence of the Curie temperature of ferromagnetic thin films. *See for instance* [43].
- P1.18 Magnetostrictive materials that contain transition metals, such as iron, are known for their large magnetostriction values observable at low saturation fields. Furthermore, these materials have high mechanical strength, a good ductility, and are cost effective. Comment on the magnetocrystalline anisotropy of Fe–Ga alloys, which is responsible for the large magnetostriction. *See for instance* [44].
- P1.19 Carbon nanotubes can be filled with Fe and ferrite nanoparticles. Comment on the properties of these novel compounds and their applications. *See for instance* [45].
- P1.20 Ferromagnetic shape memory alloys enjoy widespread use as magnetic actuators due to the strain that can be induced in these materials by a magnetic field. Ni–Mn– X ($X = \text{In}, \text{Sn}, \text{Sb}$) Heusler alloy systems are particularly interesting as ferromagnetic shape memory alloys because of the transformation they undergo when a magnetic field is applied, from a ferromagnetic to a nonmagnetic martensitic phase. A very good shape memory effect is observed in the martensitic phase, once the transformation has occurred. Comment on the magnetic properties of this martensitic phase. *See for instance* [46].

Hints and Partial Answers to Problems in Chap. 1

The answers to these problems are, in many instances, just a hint as to where further information is to be found. They contain the main idea, but the reader needs to find the references that are sometimes recommended for each exercise and complete the answer through further bibliographic reading and study. Reference numbering follows the one used in that particular chapter.

- P1.1 From Fig. P1.1: (a) Ferromagnetism; (b) Antiferromagnetism; (c) Paramagnetism.
- P1.2 The concept of spin was introduced to explain the multiplet structure of atomic spectra. It was initially seen as a spinning motion of the electron around its own axis with angular momentum $\pm\hbar/2$. The magnetic moment due to spin was experimentally verified by the Zeeman effect, which revealed a spectral line split into two or three lines when atoms were placed in a magnetic field. The spin angular momentum changes by the unit $\hbar/2$, and the unit of spin magnetic moment is a Bohr magneton.
- P1.3 These metals are iron, cobalt, and nickel. Each of these elements has an unfilled $3d$ electronic shell which constitutes the origin of their ferromagnetism. *See [1–3] for further details.*
- P1.4 When the magnetic field is applied perpendicular to the spin axis, magnetization of the antiferromagnet takes place by the rotation of each spin from the direction of the spin axis. As a consequence, the susceptibility becomes independent of temperature. This is valid in case of a single antiferromagnetic crystal, since in a polycrystal, the susceptibility is the average between the two cases (i.e., variation of susceptibility with parallel and perpendicularly applied field). Nevertheless, above the transition temperature, the susceptibility decreases with an increase in temperature, independently of the direction of the applied magnetic field.
- P1.5 Ferrites are a group of iron oxides with the general formula $\text{MO} \cdot \text{Fe}_2\text{O}_3$, where M is a divalent metal ion such as Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+} , or Cd^{2+} . The best known ferrite is magnetite Fe_3O_4 , also known as $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. The type of divalent ion M, determines how strong the spontaneous magnetization of the ferrite is. Mixed ferrites are also possible, obtained by mixing two or more kinds of M^{2+} ions. Ferrites have the so-called “spinel” structure.
- P1.6 The type of mineral known as perovskite has usually the composition CaTiO_3 and is non-magnetic. However by replacing Ti with Fe, a ferrimagnetic perovskite-type oxide is obtained of the general formula MFeO_3 where M is a large metal ion such as La^{3+} , Ca^{2+} , Ba^{2+} , or Sr^{2+} . These oxides have a cubic crystal structure and are a type of magnetic material used in many modern devices, as will be discussed in later chapters. *See published articles on magnetic perovskites for further details.*
- P1.7 Atomic magnetic moments in ferromagnetic materials order in such a way as to give rise to magnetic domains. Within a domain, atomic magnetic moments are aligned, resulting in a spontaneous magnetic domain magnetization. The spontaneous domain magnetization of one domain is usually oriented differently with respect to the spontaneous domain magnetization of neighboring domains. The spontaneous domain magnetization of all domains gives rise to a total magnetization of the ferromagnet, which depends on the temperature. When the total resultant magnetization for all magnetic domains is zero, the ferromagnetic material is said to be demagnetized.

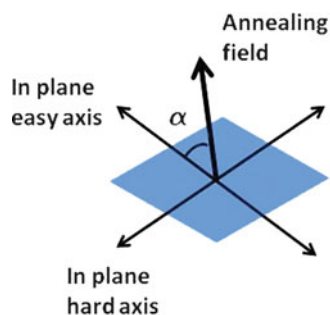
However, an applied magnetic field changes the total resultant magnetization. *See [1–3] for further details.*

- P1.8 Ferromagnetic domain structure was observed directly in 1931 by Bitter who applied a drop of a ferromagnetic colloidal suspension to the polished surface of a ferromagnetic specimen. The suspensions contained numerous fine ferromagnetic particles that rearranged so that they formed domains on the surface of the specimen. The micrographs were interpreted by Bitter to reveal inhomogeneities in ferromagnetic substances, and were, unfortunately not seen as images of domain structure, as the latter were thought to be of smaller size than the observed structures. It was not until 1949 that Williams, Bozorth, and Shockley finally observed well defined domain structures on Si–Fe crystals. *See [2] for further details.*
- P1.9 Magnetostriction can influence domain structure. As such, in a ferromagnetic material with a positive magnetostriction, a magnetic domain will have a tendency to expand parallel and contract perpendicular to the direction of domain magnetization. Given that the magnetostrictive strain has a low value of about 10^{-5} it is not strong enough to break the crystal at the domain boundaries. However, magnetoelastic energy is stored in a crystal, in part, due to magnetostriction.
- P1.10 Si–Fe alloys exhibit decreasing magnetization saturation, magnetic anisotropy, and magnetostriction with increasing Si content. At 3.25% Si, an optimum electrical resistivity is obtained that limits eddy current losses. Nevertheless, at higher Si concentrations, further reduction in eddy current losses is obtained, concurrent with a lower anisotropy and magnetostriction that help in reducing noise problems when magnetic flux deviations take place, such as at transformer core corners or induced by strains due to core assemblies. Unfortunately, silicon steels with Si content higher than 3.25% are very brittle and, therefore, almost impossible to cold roll. Researchers have tried to develop methods of introducing higher Si concentrations in these steels, but with a lower impact on their brittleness. Methods such as adding Si by diffusion in a gaseous atmosphere have shown some success and an improved performance over the starting material, especially after further annealing the sample in a magnetic field.
- P1.11 By using magneto-optical Kerr observations, it was determined that a predominantly antiparallel domain structure is formed, aligned with the rolling direction which is also the magnetic easy axis. When these domains were exposed to a cyclic and longitudinal magnetic field, magnetization reversals took place by motion of antiparallel domain walls which have a higher mobility. It was concluded that the directionality of the domain structure remains basically unchanged by the magnetization process. *See indicated reference and P1.10 for further details.*
- P1.12 The magnetic properties of ultrathin $\text{Fe}_{78}\text{Al}_4\text{B}_{12}\text{Nb}_5\text{Cu}$ and $\text{Fe}_{83}\text{B}_9\text{Nb}_7\text{Cu}$ ribbons were investigated after annealing in a transverse magnetic field of 1.5 kOe. The magnetic field was continuously applied during all heating and

cooling stages. Effective permeability and core loss were measured with an impedance analyzer, and a $B-H$ analyzer, respectively. It was noticed that the alloy with added Al is more sensitive to magnetic annealing, displaying improved properties, such as lower core losses and higher effective permeability. This is indicative of significantly different domain structures between the two types of alloys. *See indicated reference for further details.*

- P1.13 Rare earth permanent magnets of the type $\text{Pr}_{15}\text{Fe}_{78}\text{B}_{5.5}\text{Cu}_{1.5}$ (at%), and the related compound $\text{Pr}_{15}\text{Fe}_{79}\text{B}_{5.5}\text{Ga}_{0.5}$ (at%) were annealed in a two step process. In the second compound, Cu was replaced with Ga. Prior to annealing; the compounds were fabricated from ingots by hot rolling at 950°C until a reduction ratio of 76% was obtained. Note that no magnetic field was applied during annealing; however, a magnetic field was used to magnetize and demagnetize the magnets after the two step annealing process. Magnetic properties of the two-step annealed magnets were compared to those of samples that only underwent a conventional single-step annealing process. The two step annealing process involved annealing at an elevated temperature of $1,000^\circ\text{C}$, prior to the next annealing process carried out at 475°C , a temperature which is near the eutectic temperature of the rare earth rich phase. It was determined that the two step annealing process resulted in improved magnetic properties of the permanent magnets, such as coercivity, remanence, and squareness of $B-H$ curve. This stands in contrast to the conventional single step annealing process that results only in an improved coercivity, but does little for other magnetic properties. Microstructural investigations revealed that a two step annealing process leads to a better definition of the network structure of the two phases, the matrix phase and the rare earth phase surrounding the former. Thus, the disorder in the matrix phase brought about by hot rolling is responsible for the reduced crystal alignment, and, therefore, the poor magnetic properties observed prior to annealing. *See indicated reference for further details.*
- P1.14 Sputtered, amorphous Co-Nb-Zr thin films were investigated for their in-plane magnetic anisotropy. Researchers observed that local anisotropy dispersions form in the plane of these films that degrade their magnetic properties, especially at high frequencies where the material is functional. It was found that the in-plane magnetic anisotropy can be changed by magnetic annealing, and that the change depends on the angle of the applied magnetic field with respect to the surface of the film. As such, the magnetic field is applied obliquely, at an angle α with the plane of the film (Fig. P1.14). After magnetic annealing at this angle, the magnetic easy axis of the film is no longer in plane, but along the direction of the annealing field. By suppressing local anisotropy dispersions that occur in the plane of the film, a degradation of the frequency characteristics of magnetic permeability are avoided, thus rendering the material highly functional at MHz frequencies. *See indicated reference for further details.*

Fig. P1.14 Annealing in an oblique magnetic field



- P1.15 The $\text{Nd}_2\text{Fe}_{17}$ compound is one of the widest groups of rare earth inter-metallic base units used for permanent magnets and magnetostrictors, given its magnetic properties. For instance, $\text{Nd}_2\text{Fe}_{14}\text{Si}_3$ has a large magnetic anisotropy and magnetostriction originating from the rare earth sublattice. On the other hand, the transition metal sublattice renders the compound a high spontaneous magnetic moment and a low Curie temperature. These particular magnetic properties can be traced back to the atomic structure of the compound, specifically distances between Fe atoms in the sublattice, which are shorter than those in typical bcc Fe crystals. The short distances between Fe atoms give rise to negative exchange interactions which lower the Curie temperature. However, any Fe atom substitution with magnetic or nonmagnetic atoms of a different kind (e.g., Si) destroys the negative exchange interaction balance, resulting in an increase in Curie temperature. This is the principle behind obtaining permanent magnet materials, by manipulating the Fe, rare earth, and nonmagnetic atom content, and their arrangement on sublattices. *See indicated reference for further details.*
- P1.16 From the study in the indicated reference, it seems that Zn substitution for Mn has a major impact on the dielectric properties of the mixed ferrite. In particular, the size of the samples and method of preparation influence the properties obtained. As such, Zn is found to occupy the octahedral sites of nanosized manganese zinc ferrites prepared by co-precipitation methods, pulsed laser deposition, or high energy ball milling. This alters cation distributions, reduces lattice parameters, modifying exchange interactions, and thereby the magnetization values, while increasing Curie temperature. None of these effects seem to be observed in the bulk counterpart of these materials, not even in micron-sized compounds.
- P1.17 Ferromagnetic materials are described by the Heisenberg model (see (1.13)), which predicts the basic characteristics of a ferromagnetic phase transition. Ferromagnetic thin films can, thus, be analyzed using this model. In the indicated reference, a study was undertaken to predict the Curie temperature of such ferromagnetic thin films. A few differences can be noted between thin films and bulk materials. A thin film is anisotropic by nature, and hence, its magnetic properties are expected to be different from the bulk.

Furthermore, since interaction partners can be from the same atomic layer or from a neighboring layer, this gives different results for thin films than for bulk materials, as thin films create a “surplus” monolayer. Calculations show that the Curie temperature is lower for a reduced number of monolayers, but increases as the number of monolayers increases. The Curie temperature for thin films approaches that of bulk materials when the number of monolayers approaches infinity. This explains why so many experiments performed nowadays on nanoscale ferromagnetic materials occur at low temperatures.

- P1.18 The magnetocrystalline anisotropy of Fe–Ga alloys is believed to be due to their electronic structure, in particular, the $3d$ electrons of Fe. The indicated reference shows that the electron cloud is not isotropic, leading to anisotropy due to the exchange interaction between different atoms. The authors calculated an orbit projected density of states for Fe atoms which led to the conclusion that the B2-like structure had the highest magnetic anisotropy. Results are in good agreement with previous theoretical studies and experimental values of the magnetic anisotropy constant, which assumed that the anisotropy of Fe–Ga is due to the electron cloud of the Fe atoms.
- P1.19 Fe and ferrite filled carbon nanotubes form magnetic composites that are used as microwave absorbers tuned by matching the dielectric loss and the magnetic loss by changing the ratio of ferrite. It is known that hexagonal ferrites have a high saturation magnetization and high complex permeability values in a wide frequency range. Furthermore, carbon nanotubes enjoy an increased popularity because of their low density and high complex permittivity values for microwave absorption and electromagnetic interference shielding. Fe has a higher coercivity than ferrite, and adding Fe to these composites seems to make a difference in the microwave absorption quality. The microwave absorbing properties of these compounds have been found to be superior to those absorbers containing only carbon nanotubes or ferrite. This is due to a better electromagnetic matching of the dielectric loss of the carbon nanotubes with the magnetic loss of the ferrite and additional Fe filling. *See indicated reference for further details.*
- P1.20 High magnetic field measurements were carried out in $\text{Ni}_{50}\text{Mn}_{50-x}\text{In}_x$ alloys for different x concentrations in order to study the shape memory effect. The strong spontaneous magnetization was found to decrease with In concentration, suggesting that Mn atoms substitute at In sites, coupling ferromagnetically to the magnetic moments at existing Mn sites. This determines the observed magnetic properties which differ for different In concentrations, with no ferromagnetic phase observed for $x = 14$ and below. *See indicated reference for further details.*

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