Lectures in Paleomagnetism, 2005
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Citation:
http://earthref.org/MAGIC/books/Tauxe/2005/

May 30, 2005

Chapter 3

Induced and Remanent Magnetism

Suggested Reading

For background:
pages 21-26 of Butler (1992)
For a review of basic quantum mechanics, see:
http://www.chemistry.ohio-state.edu/betha/qm/index.html, or
http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/quantum.html
For some nice visualizations, see http://web.mit.edu/3.091/www/orbs/
General background in Statistical Mechanics (see, e.g.,
http://en.wikipedia.org/wiki/Statistical_mechanics)
To learn more:
Chapter 3.1 of O'Reilly (1984)
Chapter 2.1 to 2.7 in Dunlop and Özdemir (1997)

3.1 Introduction

In the last lecture we learned something of the present geomagnetic field. In order to study its past behavior, we are forced to use accidental records such as those left in rocks, sediments or archeological materials. But how are these materials magnetized and how are the magnetizations related to the magnetic field? This topic is the subject of the next few lectures.

Scientists in the late 19th century considered that it might be possible to exploit the magnetic record retained in rocks in order to study the geomagnetic field in the past. Early work in rock magnetism provided the theoretical and experimental basis for presuming that rocks might retain a record of past geomagnetic fields. There are several books and articles that describe the subject in detail (see e.g., the suggested readings). We present here a brief overview of theories on how rocks become and stay magnetized. We will begin with magnetism at the atomic level caused by electronic orbits and spins. Then we will see how electronic spins working in concert give rise to permanently magnetized substances (like magnetic minerals).

3.2 Magnetism at the atomic level

Substances generally respond to external magnetic fields by generating magnetic fields of their own; a few generate them spontaneously, in the absence of an external field. Therefore it is convenient to separate the magnetization of a material **M** into two contributions: that which exists only in the presence of an external magnetic field (induced magnetization) and that which exists in zero external magnetic field (remanent magnetization).

As we learned in the first lecture, magnetic fields are generated by electric currents. At the atomic level, the electric currents are the motions of the electrons about the nucleus: the electronic orbit and the electronic spin. Let us first consider the role of the electronic orbit (see Figure 3.1).

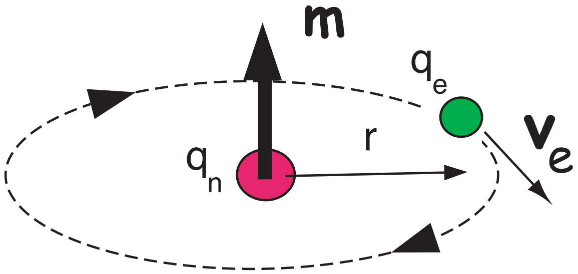

Figure 3.1: Orbital motion of electron with charge q_e and velocity v_e around the nucleus with charge q_n at a radius of r is like a current loop and generates moment **m**.

Classical physics (see Lecture 1) suggests that the magnitude of the moment generated by an orbiting electron is the current i times the area of the current loop πr^2 or $m = i\pi r^2$. The current is the charge per second:

$$i = \frac{q_e v_e}{2\pi r}$$

where v_e is the electronic velocity, so moment is:

$$m = i\pi r^2 = \pi r^2 \frac{q_e v_e}{2\pi r} = \frac{q_e v_e r}{2}. \tag{3.1}$$

The direction of **m** is given by the right hand rule (see Lecture 1 and remember that the charge of an electron is negative).

Quantum physics tells us the basic model just described cannot be. An electron zipping around a nucleus would be generating radio waves hence losing energy. It would eventually have to crash into the nucleus, which it appears not to do. In quantum mechanics, this is prevented by the fact that the angular momentum of the electron must be quantized and is an integer multiple of $h/2\pi$, where h is Planck's constant (6.63 x 10^{34} Js). In this view we have:

$$\mu_e v_e r = n \cdot \frac{h}{2\pi}$$

where μ_e is the mass of an electron (9.11 x 10^{-31} kg) and n is the energy level of the orbit. Solving for $v_e r$ and substituting into Equation 3.1, we find that the fundamental unit of magnetic moment of electrons ($n = 1$), termed the *Bohr magneton* (m_b), is given by:

$$m_b = \frac{h}{2\pi} \cdot \frac{q_e}{2\mu_e} = 9.27 \times 10^{-24} \frac{\text{kg m}^2}{\text{s}} \cdot \frac{\text{C}}{\text{kg}} = 9.27 \times 10^{-24} \text{A m}^2.$$

The balance of the attractive force of the nucleus drawing the electron towards it and the centripetal "force" pushing the electon away is what keeps the charge in orbit. The attracive force between the nucleus (q_n) and the electron (q_e) is given by Coulomb's law:

$$F = \frac{kq_nq_e}{r^2},$$

where k is Boltzmann's constant, 1.381 x 10^{-23} JK^{-1}, and the centripetal "force" is given by:

$$F = \frac{\mu_e v_e^2}{r} = 2\pi\mu_e\omega^2 r,$$

where ω is the orbital frequency and remembering that $v = 2\pi\omega r^2$. Balancing these two competing forces and solving for ω gives a fundamental orbital frequency ω_o.

Recalling from Lecture 1 there is a torque $\mathbf{m} \times \mu_o\mathbf{H}$ on the electron in the presence of an external field $\mathbf{H}$, This torque changes the electronic orbit which creates a new balance of forces. The changed balance changes the orbital frequency, which in turn results in a changed magnetic moment. The sense of the change in moment is always to oppose the applied field. Therefore, the response of the magnetic moments of electrons creates an induced magnetization $\mathbf{M}_I$ that is observable outside the substance. As stated in Lecture 1, $\mathbf{M}_I$ is a function of the applied field $\mathbf{H}$, *i.e.*,

$$\mathbf{M}_I = \chi\mathbf{H}.$$

We also learned in Lecture 1 that the parameter χ is known as the *magnetic susceptibility.* The ratio $\mathbf{M}_I/\mathbf{H}$ for the response of the electronic orbitals is termed the *diamagnetic susceptibility* χ_d; it is negative, essentially temperature independent, and quite small (see Figure 3.2).

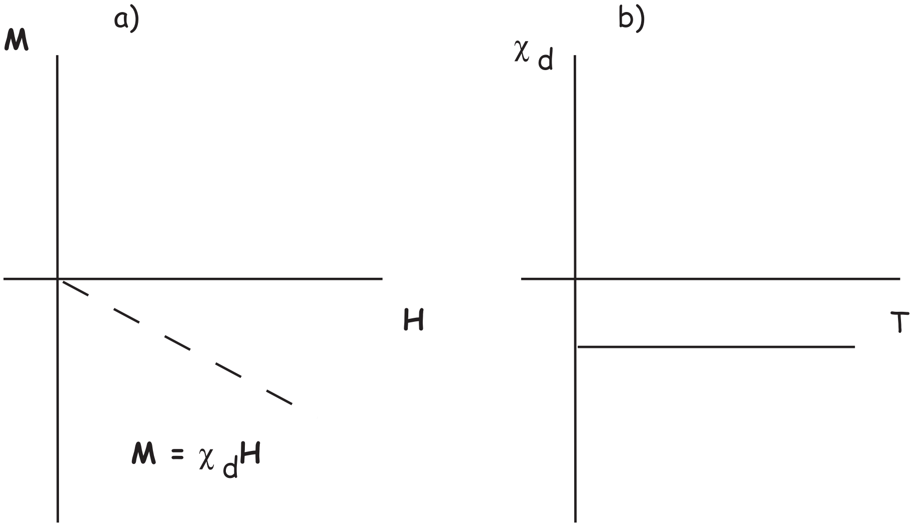

Figure 3.2: The diamagnetic response to externally applied magnetic fields. a) The magnetization $\mathbf{M}_I$ induced by a field $\mathbf{H}$ is inversely proportional to the field. b) The diamagnetic susceptibility is independent of temperature.

Diamagnetism is exhibited by all matter, arising as it does from the response of electronic orbitals to externally applied magnetic fields. In the absence of unpaired electronic spins, diamagnetic susceptibility dominates the magnetic response. Common diamagnetic substances include quartz (SiO_2), calcite ($CaCO_3$) and water (H_2O). The mass susceptibility of quartz is -0.62 x 10^{-9} m^3kg^{-1} to give you an idea of the magnitudes of these things.

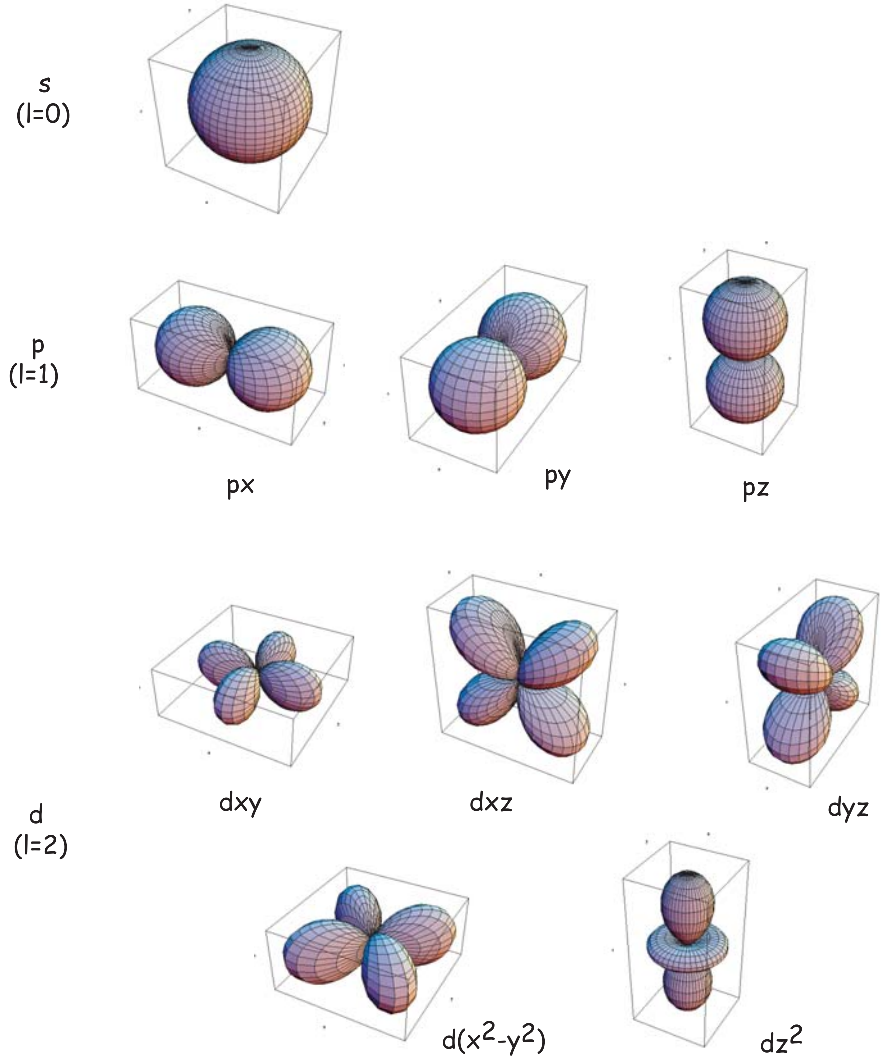

Figure 3.3: Schematic of surfaces of equal energy of the first three shells ($l = 1, 2, 3$). Modified from Alan Crosby's web site at http://solution.bu.edu/acrosby/orbitals/dxy.html.

3.2.1 Role of electronic spins

In most geological materials, the orbital contributions cancel out (they are "quenched") and the magnetization arises from the electronic spins. Electronic spins are a concept in quantum mechanics and have no easy to understand classical analogue. To understand spins, then, we have to review a few quantum mechanical principles.

Quantum mechanics describes the electronic structure of atoms in terms of the four quantum numbers n, l, m, s. The energy (size?) of a shell is given by n. The shape and orientation of the shell is given by l and m respectively and the so-called "spin" is given by s which can be $\pm\frac{1}{2}$. Figure 3.3 shows surfaces of equal probability of finding electrons in several possible shapes and orientations of the first three shells (s, p, d).

Each level of increasing n has an increasing number of possible orbitals. For $n = 1$, we have only the $1s$ shell. For $n = 2$ we have the $2s$ orbital and three p orbitals. For now we don't really have to have a deep understanding of quantum mechanics, we may simply regard the quantum numbers as book keeping devices that specify how electronic orbitals are filled and the consequences for the magnetic properties of the material.

Electronic orbitals are filled according to three rules:

1) No two electrons may have the same set of quantum numbers. This is Pauli's exclusion principle. Because spin (s) can be $\pm\frac{1}{2}$, two electrons fit in one orbital. When a single electron occupies a given orbital, it is called "unpaired" and has a magnetic moment of 1 m_b.

2) Orbitals are filled in order of increasing energy. The energy state of a given orbital is dependent on the context (whether the atom is bound to other atoms or not), but in general they will be filled according to the scheme shown in Figure 3.4.

3) Electrons are added so that the atom has the spins as parallel as possible (Hund's rule). The scheme followed is shown in Figure 3.4. Notice that when filling the third energy level $(n = 3)$, all five d shells are filled up with one kind of spin (say, up, or $+\frac{1}{2}$), before the electrons begin to pair up. Also, because the energies of the shells change somewhat according to the context they are in, the $4s$ shell will actually give up an electron to a d shell, before the d shells begin to pair up. Hund's rule gives the atoms with some d shell electrons (the so-called "transition elements") the possibility of large magnetic moments.

Unpaired electronic spins behave as magnetic dipoles with a moment of one Bohr magneton. In the absence of an applied field, or in the absence of the ordering influence of neighboring spins which are known as *exchange interactions*, the spins are essentially randomly oriented. An applied field acts to align the spins which creates a net magnetization equal to $\chi_p \mathbf{H}$. χ_p is the *paramagnetic susceptibility.*

Each unpaired spin has a moment of one Bohr magneton $\mathbf{m}_b$. The elements with the most unpaired spins are the transition elements which are responsible for most of the paramagnetic behavior observed in rocks. For example, in Figure 3.4 we see that Mn^{25} has a structure of: $(1s^2 2s^2 2p^6 3s^2 3p^6)3d^5 4s^2$, hence has 5 unpaired spins and a net moment of 5 m_b. Fe^{26} has a structure of $(1s^2 2s^2 2p^6 3s^2 3p^6)3d^6 4s^2$ with a net moment of 4 m_b, In minerals, the transition elements are in a variety of oxidation states. Fe commonly occurs as Fe^{2+} and Fe^{3+}. When losing electrons to form ions, transition metals lose the 4s electrons first, so we have for example, Fe^{3+} with a structure of $(1s^2 2s^2 2p^6 3s^2 3p^6)3d^5$, or 5 m_b. Similarly Fe^{2+} has 4 m_b and Ti^{4+} has no unpaired spins. Iron is the main magnetic species in geological materials, but Mn^{2+} (5 m_b) and Cr^{3+} (3 m_b) occur in trace amounts.

A useful model for paramagnetism was worked out by P. Langevin in 1905. Langevin theory is based on a few simple premises:

1) Each unpaired spin contributes a dipole moment.

2) In the absence of an applied field, the moments are essentially randomly oriented, *i.e.*, all directions are equally likely to occur.

3) An applied field acts to align the spins which creates a net moment.

4) There is competition between thermal energy kT (k is Boltzmann's constant and T is temperature in kelvin) and the magnetic energy E_m. Recalling Lecture 1 we know that E_m of a magnetic

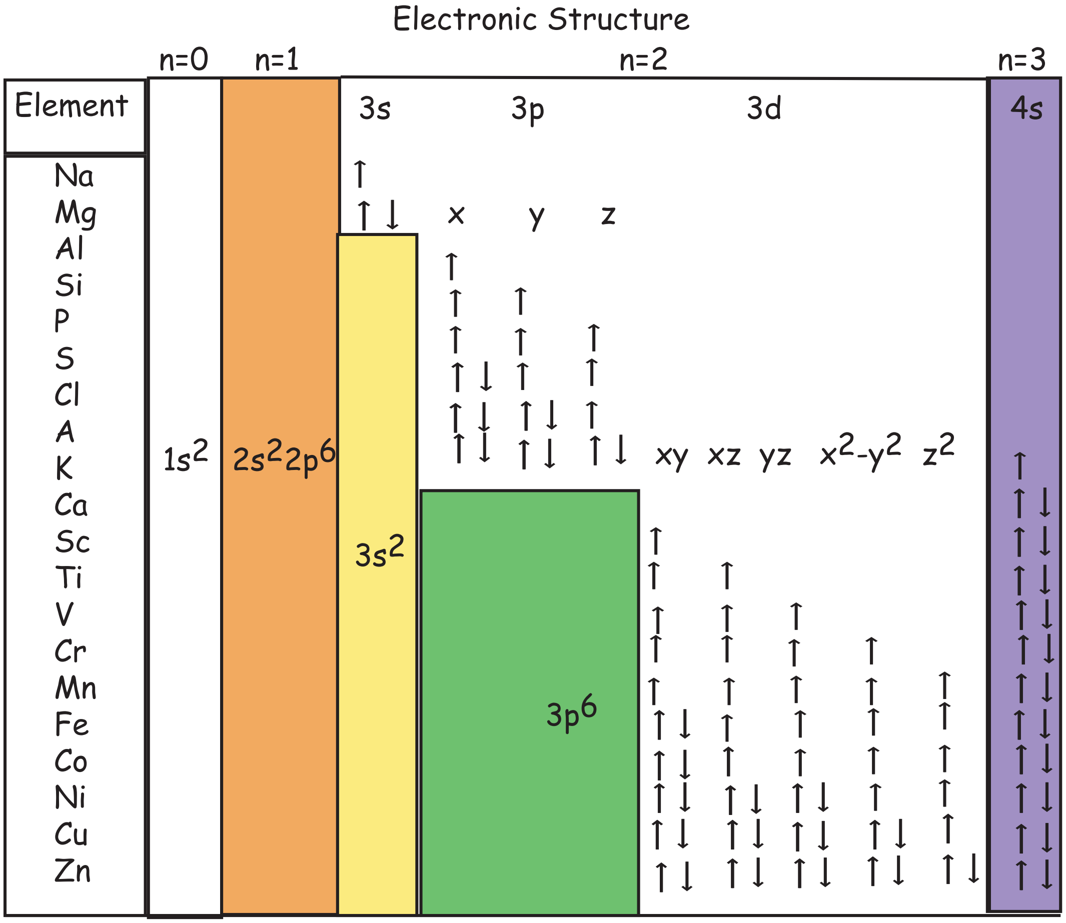

Figure 3.4: The electronic structure of the elements from Na to Zn.

moment **m** at an angle θ with an external magnetic field **H** is given by:

$$E_m = -\mathbf{m} \cdot \mu_o \mathbf{H} = -m\mu_o H \cos\theta. \tag{3.2}$$

Magnetic energy is at a minimum when the magnetic moment is parallel to the magnetic field. Using the principles of statistical mechanics, we find that the probability density of a given moment having energy E_m is:

$$P(E) \propto \exp{(-E_m/kT)}. \tag{3.3}$$

This probability leads directly to the relationship:

$$\frac{M}{M_s} = [\coth a - \frac{1}{a}] = L(a). \tag{3.4}$$

The function enclosed in square brackets is known as the *Langevin function* which is derived in the Appendix. The magnetization, shown in Figure 3.5a, approaches saturation (in this case, M_s) when $m\mu_oH$ is some 10-20 times kT. When $kT >> m\mu_oH$, $L(a)$ is approximately linear

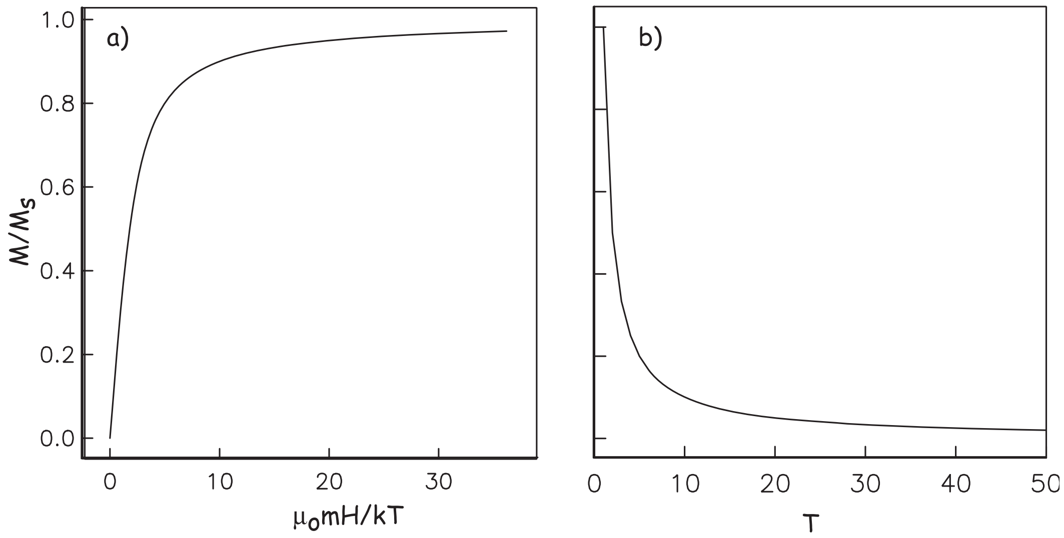

Figure 3.5: a) Paramagnetic magnetization (obtained from the Langevin function $L(a)$ versus $a = \mu_o mH/kT$. b) Paramagnetic magnetization as a function of temperature (Curie Law).

with a slope of ∼ 1/3. At room temperature and fields up to many tesla, L(a) is approximately $\mu_o mH/3kT$. If the moments m are unpaired spins ($m = m_b$), then $M_s = Nm_b/v$, and:

$$\frac{M}{M_s} \simeq \frac{m_b\mu_o}{3kT}H.$$

Please note that we have neglected all deviations from isotropy including quantum mechanical effects as well as crystal shape, lattice defects, and state of stress. These complicate things a little, but to first order the treatment followed here a good assumption. We can rewrite the above equation as:

$$\frac{M}{H} = \frac{m_b\mu_o}{3kT} \cdot M_s = \frac{Nm_b^2\mu_o}{3kv} \cdot \frac{1}{T} = \chi_p. \tag{3.5}$$

To first order, paramagnetic susceptibility χ_p is positive, larger than diamagnetism and inversely proportional to temperature. This inverse T dependence (see Figure 3.5b) is known as Curie's law of paramagnetism. The paramagnetic susceptibility of, for example, biotite is 790 x 10^{-9} m^3 kg^{-1}, or about three orders of magnitude larger than quartz (and of the opposite sign!).

We have considered the simplest case here in which χ can be treated as a scalar and is referred to as the *bulk magnetic susceptibility* χ_b. In detail, magnetic susceptibility can be quite complicated. The relationship between induced magnetization and applied field can be affected by crystal shape, lattice structure, dislocation density, state of stress, etc., which give rise to possible anisotropy of the susceptibility. Furthermore, there are only a finite number of electronic moments within a given volume. When these are fully aligned, the magnetization reaches saturation. Thus, magnetic susceptibility is both anisotropic and non-linear with applied field.

3.3 Remanent magnetization

Some substances give rise to a magnetic field in the absence of an applied field. This magnetization is called *remanent* or *spontaneous* magnetization, and constitutes the phenomenon which is loosely known as *ferromagnetism (sensu lato).* Magnetic remanence is caused by strong interactions between neighboring spins that occur in certain crystals.

The so-called *exchange energy* is minimized when the spins are aligned parallel or anti-parallel depending on the details of the crystal structure. Exchange energy is a consequence of the Pauli exclusion principle (no two electrons can have the same set of quantum numbers). In the transition elements, the **3d** orbital is particularly susceptible to exchange interactions because of its shape and the prevalence of unpaired spins, so remanence is characteristic of certain crystals containing transition elements with unfilled $3d$ orbitals.

In oxides, oxygen can form a bridge between neighboring cations which are otherwise too far apart for direct overlap of the $3d$ orbitals in a phenomenon known as superexchange. In Figure 3.6 the $2p$ electrons of the oxygen are shared with the neighboring $3d$ shells of the iron ions. Pauli's principle means that the shared electrons must be antiparallel to each of the electrons in the $3d$ shells. The result is that the two cations are coupled. In the case shown in Figure 3.6 there is an Fe^{2+} ion coupled antiparallel to an Fe^{3+} ion. For two ions with the same charge, the coupling will be parallel. Exchange energies are huge, equivalent to applying a field of the order of 1000 T. [The largest field available in the Scrips paleomagnetic laboratory is about 2.5 T, and that only fleetingly.]

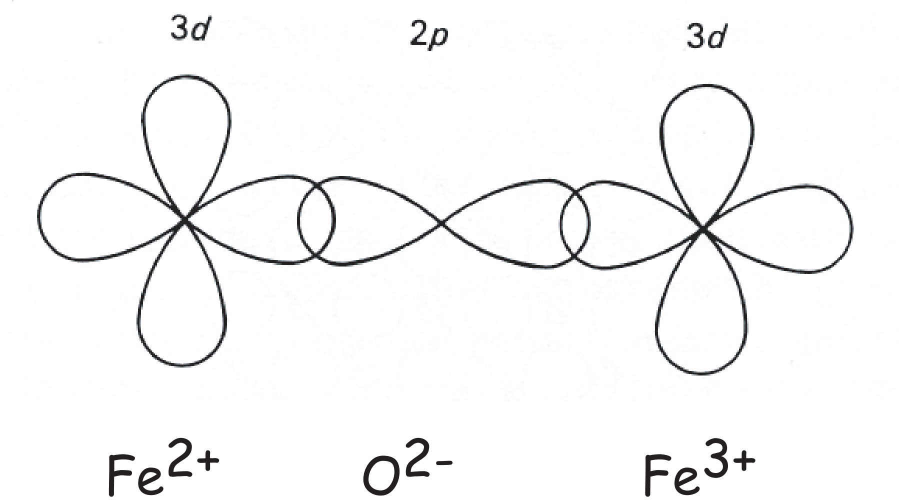

Figure 3.6: Exchange energy associated with overlapping orbitals. Example of super-exchange between the $3d$ orbitals of two iron cations through the $2p$ orbitals of the intervening oxygen anion. The two electrons in the $2p$ shells are, by necessity antiparallel. These are shared by the $3d$ shells, hence to two cations have anti-parallel spins. Modified from O'Reilly (1984).

As temperature increases, crystals expand and exchange becomes weaker. Above a temperature characteristic of each crystal type (known as the *Curie temperature* T_c), cooperative spin behavior disappears entirely and the material becomes paramagnetic.

While the phenomenon of ferromagnetism results from complicated interactions of neighboring spins, it is useful to think of the ferromagnetic moment as resulting from a quasi-paramagnetic response to a huge internal field. This imaginary field is termed here the *Weiss molecular field* H_w. In Weiss theory, H_w is proportional to the magnetization of the substance, *i.e.*,

$$H_w = \beta M,$$

where β is the constant of proportionality. The total magnetic field that the substance experiences is:

$$H_{tot} = H + H_w = H + \beta M,$$

where H is the external field. By analogy to paramagnetism, we can substitute $a = \mu_o m_b (H_{tot})/kT)$ for H in Langevin equation:

$$\frac{M}{M_s} = L\left(\frac{\mu_o m_b (H + \beta M)}{kT}\right). \tag{3.6}$$

For temperatures above the Curie temperature T_c (i.e. $T - T_c > 0$) there is by definition no internal field, hence βM is zero. Substituting $N m_b / v$ for M_s, and using the low-field approximation for $L(a)$, Equation 3.6 can be rearranged to get:

$$\frac{M}{H} = \frac{\mu_o N m_b^2}{v 3k (T - T_c)} \equiv \chi_f. \tag{3.7}$$

Equation 3.7 is known as the Curie-Weiss law and governs ferromagnetic susceptibility above the Curie temperature.

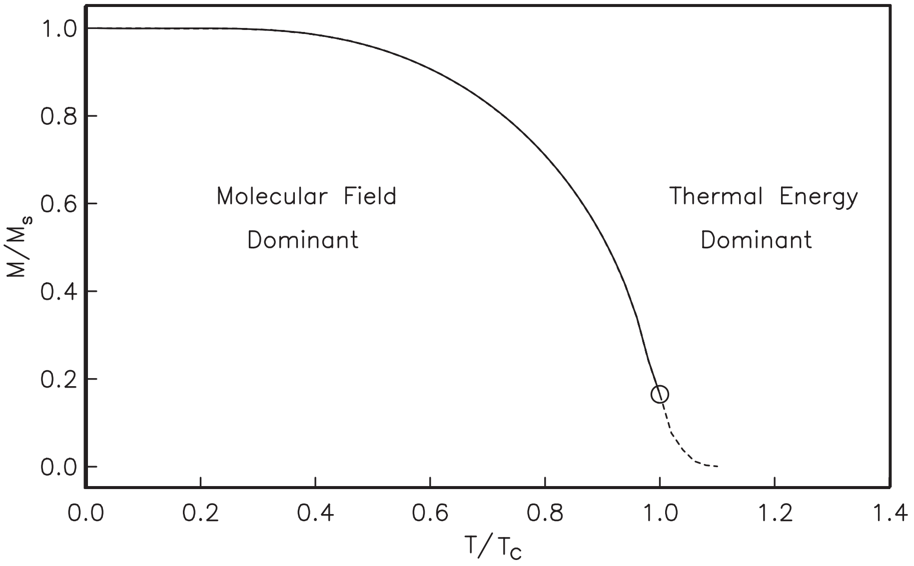

Figure 3.7: Behavior of magnetization versus temperature of a ferromagnetic substance.

Below the Curie temperature, we can neglect the external field H and get:

$$\frac{M}{M_s} = L(\frac{\mu_o m_b \beta M}{kT}).$$

Substituting again for M_s and rearranging, we get:

$$\frac{M}{M_s} = L(\frac{Nm_b^2\beta}{vkT} \cdot \frac{M}{M_s}) = L(\frac{T_c}{T} \cdot \frac{M}{M_s}), \tag{3.8}$$

where T_c is the Curie temperature and is given by:

$$T_c = \frac{Nm_b^2\beta}{vk}.$$

Equation 3.8 can be solved graphically or numerically and is sketched in Figure 3.7. Below the Curie temperature, exhange interactions are strong relative to the external field and the magnetization is governed by Equation 3.8. Above the Curie temperature, it follows the Curie-Weiss law (Equation 3.7).

We have treated ferromagnetism from a classical point of view and this is strictly incorrect as it results primarily from quantum mechanical phenomena. The primary difference between the classical derivation and the quantum mechanical one lies in the fact that in quantum mechanics, only certain angles of the magnetic moments are allowed, not all as in Langevin theory. In the end, the predictions of magnetization as a function of temperature are different in detail. However, the classical approach is sufficient for the purpose of understanding the rudiments of rock magnetism.

3.3.1 Types of ferromagnetism

As we have seen, below the Curie temperature, certain crystals have a permanent (remanent) magnetization resulting from the alignment of unpaired electronic spins over a large area within the crystal. Spins may be either parallel or anti-parallel; the sense of spin alignment is controlled entirely by crystal structure. The energy term associated with this phenomenon is the exchange energy. There are three categories of spin alignment: ferromagnetism (*sensu stricto*), ferrimagnetism and antiferromagnetism (see Figure 3.8).

In *ferromagnetism* (*sensu stricto*, Figure 3.8a), the exchange energy is minimized when all the spins are parallel, as occurs in pure iron. When spins are perfectly antiparallel (*antiferromagnetism*, Figure 3.8b), there is no net magnetic moment, as occurs in ilmenite. Occasionally, the antiferromagnetic spins are not perfectly aligned in an antiparallel orientation, but are canted by a few degrees. This *spin-canting* (Figure 3.8c) gives rise to a weak net moment, as occurs in hematite. Also, antiferromagnetic materials can have a net moment if spins are not perfectly compensated owing to defects in the crystal structure, as occurs in fine-grained hematite. The uncompensated spins result in a so-called *defect* moment (Figure 3.8d). We note in passing that the temperature at which spins become disordered in antiferromagnetic substances is termed the *Néel temperature*. In *ferrimagnetism*, spins are also aligned antiparallel, but the magnitudes of the moments in each direction are unequal, resulting in a net moment (Figure 3.8e).

Appendix

A Derivation of the Langevin function

Because we have made the assumption that there is no preferred alignment within the substance, we can assume that the number of moments ($n(\theta)$) between angles θ and $\theta + d\theta$ with respect to $\mathbf{H}$ is proportional to the solid angle $\sin\theta d\theta$ and the probability density function, *i.e.*,

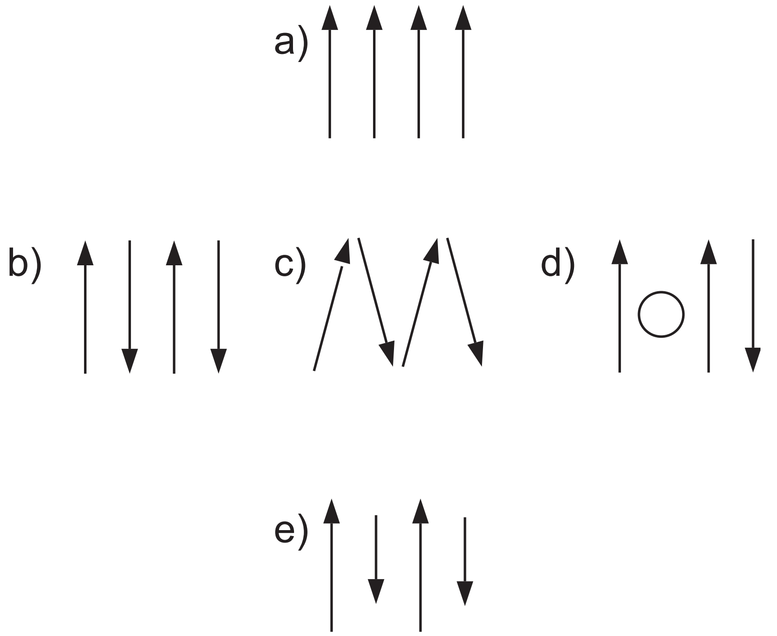

Figure 3.8: Types of spin alignment in ferromagnetism *(sensu lato)*: a) ferromagnetism (*sensu stricto*), b) antiferromagnetism, c) spin-canted antiferromagnetism, d) defect anti-ferromagnetism, e) ferrimagnetism.

$$n(\theta)d\theta \propto \exp\left(\frac{-E_m}{kT}\right)\sin\theta d\theta. \tag{A1}$$

When we measure the induced magnetization, we really measure only the component of the moment parallel to the applied field, or $n(\theta)m\cos\theta$. The net magnetization of a population of particles with volume v is therefore:

$$M_I = \frac{m_b}{v}\int_0^\pi n(\theta)\cos\theta d\theta. \tag{A2}$$

By definition, $n(\theta)$ integrates to N, the total number of moments, or

$$N = \int_0^\pi n(\theta)d\theta. \tag{A3}$$

The total saturation moment of a given population of N individual magnetic moments m is Nm. The saturation value of magnetization M_s is thus Nm normalized by the volume v. Therefore, the magnetization expressed as the fraction of saturation is:

$$\frac{M}{M_s} = \frac{\int_0^\pi n(\theta)\cos\theta d\theta}{\int_0^\pi n(\theta)d\theta}$$

$$= \frac{\int_o^\pi e^{(m\mu_o H\cos\theta)/kT}\cos\theta\sin\theta d\theta}{\int_o^\pi e^{(m\mu_o H\cos\theta)/kT}\sin\theta d\theta}.$$

By substituting $a = m\mu_o H/kT$ and $\cos\theta = x$, we write

$$\frac{M}{M_s} = N\frac{\int_{-1}^{1} e^{ax}xdx}{\int_{-1}^{1} e^{ax}dx} = (\frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a}), \tag{A4}$$

and finally

$$\frac{M}{M_s} = [\coth\, a - \frac{1}{a}] = L(a). \tag{A5}$$

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