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: //winter.group.shef.ac.uk/orbitron/AOs/1s/index.html
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

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. From here on we quickly get deep in the weeds of quantum mechanics. In this lecture we will cover the bare minimum necessary to grasp the essentials of rock magnetism.

In Lecture 1 we took the classical approach and suggested that the orbit of an electron about the nucleus could be considered a tiny electric current with a correspondingly tiny magnetic moment. But quantum physics tells us that this planetary view of the atom cannot be. An electron zipping around a nucleus would generate radio waves hence lose energy. It would eventually have to crash into the nucleus, which apparently doesn't happen.



Figure 3.1: Stationary waves that "fit" between 0 and 360°.

In quantum mechanics, the electronic motion is stabilized by the fact that electrons can only have certain energy states; they are quantized. The energy of a given electron is described by something called Schrödinger's wave equation. The function $\Psi(r, \theta, \phi)^2$ gives the probability of finding and electron at some point. [Remember from Lecture 2 that r, θ, ϕ are the three spherical coordinates.] Wave equations tend to evolve through time, but there are special functions that are "stationary"; think of standing waves. For example, in Figure 3.1 there are certain functions that "fit" between 0 and 360°, so as you go around the circle in θ , the function is always the same, no matter how many times around you go. There might be one or more waves (labelled n = 1, n = 2, n = 3), but they are stationary. In quantum mechanics, electronic wave functions depend on three special "quantum" numbers (n, l, m):

$$\Psi_{r,\theta,\phi} = R_{n,l}(r)Y_{l,m}(\phi,\theta) \tag{3.1}$$

where and R and Y are increasingly wavy functions, r is the effective radius in atomic units and n is the so-called "principal" quantum number. The number $l, (0 \rightarrow n-1)$ relates to orbital angular

momentum L:

$$L = \sqrt{l(l+1)}\hbar,$$

where \hbar is the "reduced" Planck's constant (or $\frac{h}{2\pi}$ where $h = 6.63 \times 10^{-34}$ Js). The number m is the magnetic quantum number which runs from l backwards to -l. The lowest energy of these wave equations is with n = 1 (l and m are both 0) and the two functions are:

$$R_{1,0} = 2Z^{\frac{3}{2}}e^{-\rho/2},$$

$$Y_{0,0} = (\frac{1}{4\pi})^{\frac{1}{2}}$$
(3.2)

where Z is the atomic number and ρ is 2Zr/n. The probability density for an electron at a radius of r is sketched in Figure 3.2. This wave equation has no dependency on θ or ϕ and is a spherical shell. All the l, m = 0 shells are spherical and are often referred to as the 1s, 2s, 3s shells, where the numbers are the energy levels n. Shells with l = 1 are referred to as "p" shells and l = 2 are the "d" shells examples of which are shown in Figure 3.3.



Figure 3.2: Plot of radial distribution and "dot-density" for the 1s electron shell.



Figure 3.3: Examples of surfaces of equal energy of the first three shells (l = 1, 2, 3). Modified from figures of Alan Crosby.

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Returning to the tiny circuit idea, we create a magnetic moment m through the electronic orbit. 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 $m = i\pi r^2$. In quantum mechanics, the angular momentum of the electron must be quantized. It is an integer multiple of \hbar and the moment is given by:

$$m = \frac{-q_e}{2\mu_e}L$$

where μ_e is the mass of an electron (9.11 x 10^{-31} kg), $q_e = -1.6x \ 10^{-19}$ C, and L is the angular moment $(\sqrt{l(l+1)}\hbar^2)$. Setting l = 0, we find that the fundamental unit of magnetic moment of electrons, termed the *Bohr magneton* (m_b) , is given by:

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

So far we haven't mentioned we have not mentioned the last quantum number, s. This is the "spin" of the electon and has a value of $\pm \frac{1}{2}$. The spin also produces a magnetic moment which is giving by $2sm_b$, hence is numerically identical to that produced by the orbit.

Atoms have the same number of electrons as protons in order to preserve charge balance. Hydrogen has but one lonely electron which in its lowest energy state sits in the 1s electronic shell. Helium has a happy pair, so where does the second electron go? To fill in their electronic shells, atoms follow 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 spins remain 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, all 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", e.g., Cr, Mn, Fe, Co and Ni) the possibility of large magnetic moments.

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: $(1s^22s^22p^63s^23p^6)3d^54s^2$, hence has 5 unpaired spins and a net moment of 5 m_b . Fe²⁶ has a structure of $(1s^22s^22p^63s^23p^6)3d^64s^2$ with a net moment of 4 m_b , In minerals, the transition elements are in a variety of oxidation states. Fe commonly occurs as Fe²⁺ and Fe³⁺. When losing electrons to form ions, transition metals lose the 4s electrons first, so we have for example, Fe³⁺ with a structure of $(1s^22s^22p^63s^23p^6)3d^5$, or 5 m_b . Similarly Fe²⁺ has 4 m_b and Ti⁴⁺ 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.

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

3.3 Induced magnetization

We have learned that there are two sources of magnetic moments in electronic motions: the orbits and the (unpaired) spins. These moments respond to external magnetic fields giving rise to an induced magnetization, which was mentioned briefly in Lecture 1. We will consider first the contribution of the electronic orbits.

3.3.1 Orbital contribution

An electron orbiting about the nucleus has an angular momentum of L (Figure 3.5). The angular momentum has an associated magnetic moment which, in the presence of a magnetic field **H** experiences a torque which nudges the angular moment to the side (ΔL). This causes the angular momentum vector to precess around the magnetic field direction, much like a spinning top precesses around the direction of gravity. This is called Larmor precession. The changed angular moment in turn results in a changed magnetic moment Δm . The sense of the change in moment is always to oppose the applied field. Therefore, the response of the magnetic moments of electronic orbitals creates an induced magnetization \mathbf{M}_I that is observable outside the substance and is related to the



Figure 3.5: Larmor precession. The orbit of the electron has an angular momentum L which creates a magnetic moment. In the presence of a magnetic field **H**, the moment experiences a torque which causes a change in angular momentum ΔL . The precession of the electronic orbit about **H** creates an induced magnetic moment Δm in a sense opposite to the applied field.

applied field by

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

We learned in Lecture 1 that the proportionality between induced magnetization and the applied field 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. In the absence of unpaired electronic spins, diamagnetic susceptibility dominates the magnetic response. Common diamagnetic substances include quartz (SiO₂), calcite (CaCO₃) and water (H₂O). The mass normalized susceptibility of quartz is -0.62 x 10⁻⁹ m³kg⁻¹ to give you an idea of the magnitudes of these things.

3.3.2 Role of electronic spins

In most geological materials, the orbital contributions cancel out (they are "quenched") and the magnetization arises from the electronic spins. We mentioned that 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 electronic 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*.

A useful first order model for paramagnetism was worked out by P. Langevin in 1905. (Of course

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in messy reality things are a bit more complicated, but Langevin theory will work well enough for us at this stage.) 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 moment **m** at an angle θ with an external magnetic field **H** is given by:

$$E_m = -\mathbf{m} \cdot \mu_o \mathbf{H} = -m\mu_o H \cos \theta. \tag{3.3}$$

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:

$$P(E) \propto \exp\left(-E_m/kT\right). \tag{3.4}$$

This probability leads directly to the relationship:

$$\frac{M}{M_s} = \left[\coth a - \frac{1}{a} \right] = \mathcal{L}(a). \tag{3.5}$$



Figure 3.6: a) Paramagnetic magnetization (obtained from the Langevin function $\mathcal{L}(a)$ versus $a = \mu_o m H/kT$. b) Paramagnetic magnetization as a function of temperature (Curie Law).

The function enclosed in square brackets is known as the Langevin function (\mathcal{L}) which is derived in the appendix. The magnetization, shown in Figure 3.6a, approaches saturation (in this case,

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 M_s) when $m\mu_o H$ is some 10-20 times kT. When $kT >> m\mu_o H, \mathcal{L}(a)$ is approximately linear with a slope of ~ 1/3. At room temperature and fields up to many tesla, $\mathcal{L}(a)$ is approximately $\mu_o mH/3kT$. If the moments m are unpaired spins $(m = m_b)$, then the maximum magnetization possible (the saturation magnetization M_s is given by the number or moments N, their magnetude (m_b) normalized by the volume v or $M_s = Nm_b/v$, so

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

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:

$$\frac{M}{H} = \frac{m_b \mu_o}{3kT} \cdot M_s = \frac{N m_b^2 \mu_o}{3kv} \cdot \frac{1}{T} = \chi_p.$$
(3.6)

To first order, paramagnetic susceptibility χ_p is positive, larger than diamagnetism and inversely proportional to temperature. This inverse T dependence (see Figure 3.6b) is known as Curie's law of paramagnetism. The paramagnetic susceptibility of, for example, biotite is 790 x 10⁻⁹ m³ 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.

3.4 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 3.7 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 3dshells. The result is that the two cations are coupled. In the case shown in Figure 3.7 there is an Fe²⁺ ion coupled antiparallel to an Fe³⁺ ion. For two ions with the same charge, the coupling

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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 3.7: 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.

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:

$$\frac{M}{M_s} = \mathcal{L}\left(\frac{\mu_o m_b (H + \beta M)}{kT}\right). \tag{3.7}$$

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 Nm_b/v for M_s , and using the low-field approximation for $\mathcal{L}(a)$, Equation 3.7 can be rearranged to get:

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$$\frac{M}{H} = \frac{\mu_o N m_b^2}{v 3k(T - T_c)} \equiv \chi_f. \tag{3.8}$$

Equation 3.8 is known as the Curie-Weiss law and governs ferromagnetic susceptibility above the Curie temperature.



Figure 3.8: Behavior of magnetization versus temperature of a ferromagnetic substance. Below the Curie temperature, we can neglect the external field H and get:

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

Substituting again for M_s and rearranging, we get:

$$\frac{M}{M_s} = \mathcal{L}(\frac{Nm_b^2\beta}{vkT} \cdot \frac{M}{M_s}) = \mathcal{L}(\frac{T_c}{T} \cdot \frac{M}{M_s}), \qquad (3.9)$$

where T_c is the Curie temperature and is given by:

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

Equation 3.9 can be solved graphically or numerically and is sketched in Figure 3.8. Below the Curie temperature, exhange interactions are strong relative to the external field and the magnetization is governed by Equation 3.9. Above the Curie temperature, it follows the Curie-Weiss law (Equation 3.8).

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. The end

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product of the quantum mechanical treatment (see Dunlop and Özdemir, 1997) is that the variation of saturation magnetization as a function of temperature can be reasonably well approximated (near the Curie Temperature, T_c) by:

$$\frac{M_s(T)}{M_s(T_o)} = (\frac{T_c - T}{T_c})^{\gamma}$$
(3.10)

where γ is 0.5 from simple molecular field theory. Dunlop and Özdemir (1997) quote a value of around 0.43 for γ , but the data from commercial magnetite (Ward's standard) give the results shown in Figure 3.9 which are best fit with a value of γ of 0.3.



Figure 3.9: Solid red line, data of J.S. Gee from Ward's standard magnetite. Dashed blue line, curve from Equation 3.8 with $\gamma = 0.3$.

3.4.1 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 3.10).

In ferromagnetism (sensu stricto, Figure 3.10a), the exchange energy is minimized when all the spins are parallel, as occurs in pure iron. When spins are perfectly antiparallel (antiferromagnetism, Figure 3.10b), 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 3.10c) 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 3.10d). We note in passing that the temperature at which spins become disordered in antiferromagnetic substances is termed the Néel temperature.



Figure 3.10: Types of spin alignment in ferromagnetism *(sensu lato)*: a) ferromagnetism *(sensu stricto)*, b) antiferromagnetism, c) spin-canted antiferromagnetism, d) defect anti-ferromagnetism, e) ferrimagnetism.

In *ferrimagnetism*, spins are also aligned antiparallel, but the magnitudes of the moments in each direction are unequal, resulting in a net moment (Figure 3.10e).

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 **H** is proportional to the solid angle $\sin \theta d\theta$ and the probability density function, *i.e.*,

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

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

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

and finally

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