

Magnetic materials

Summary of electromagnetism

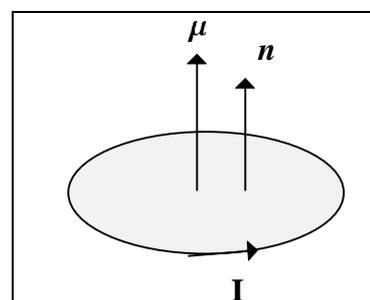
All materials acquire a magnetisation \mathbf{M} in a magnetic field. \mathbf{M} is the magnetic dipole moment per unit volume and is a vector.

The magnetic field \mathbf{B} in a material with a magnetisation \mathbf{M} is given by

$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ which defines the magnetic field strength \mathbf{H} . In practical situations

(for example a solenoid), the \mathbf{H} field can be calculated from external currents and can be considered to be the driving force. The magnetisation and the overall \mathbf{B} field are the material response to this force. For a linear, isotropic, homogeneous material the magnetisation is proportional to \mathbf{H} , and we define the magnetic susceptibility, χ by the identity $\mathbf{M} = \chi\mathbf{H}$. Therefore, $\mathbf{B} = \mu_0\mu\mathbf{H}$ and we have the relative permeability $\mu = 1 + \chi$. As in the electric case, it is the *susceptibility* that is the material property.

Unfortunately, magnetic dipole moments are denoted by μ (but that is convention for you). Classically, a magnetic dipole moment is associated with a current loop; the magnitude of the dipole is the area (shaded in the diagram) multiplied by the current. $\mu = IAn$ where \mathbf{n} is the unit normal defining the plane of the loop



Materials contain elementary magnetic dipoles in the form of electrons. They have intrinsic angular momentum (spin) as well as the potential for orbital angular momentum (when bound to a specific nucleus) and since they are charged they can be thought of as a flow of current in a loop. The problem for the rest of this section is to relate the magnetic properties of materials to the properties of electrons.

Diamagnetism (cf the 2B23 course)

When a charged particle is accelerated by a changing magnetic field, momentum is apparently created from nowhere. This paradox is resolved by writing the momentum of a charged particle as $\mathbf{p} = M\mathbf{v} + q\mathbf{A}$ where \mathbf{A} is the magnetic vector potential (recall that $\mathbf{B} = \text{curl } \mathbf{A}$). The momentum possessed by a charged particle at rest is the *electromagnetic momentum*. When a particle is accelerated by a changing magnetic field, the total momentum is conserved, but there is an exchange between the kinetic momentum $M\mathbf{v}$ and the electromagnetic momentum $q\mathbf{A}$. These ideas can be transferred to quantum mechanics by replacing the momentum \mathbf{p} by the quantum mechanical analogue $-i\hbar\nabla$. In an atom, there are only discrete electronic states with different wavefunctions. These states are separated by large energies and so are perturbed only weakly by a normal magnetic field. The wavefunction of the system does not change significantly; when a magnetic field is applied to an atom \mathbf{p} cannot alter greatly (since it is controlled by the geometry of the wavefunction of the atom); thus any change must be in \mathbf{v} . Hence from the definition above, the induced velocity $\mathbf{v} = -q\mathbf{A}/M = e\mathbf{A}/m$, and the induced current density is $\mathbf{j} = n(-e)\mathbf{v} = -ne^2\mathbf{A}/m$. This current sets up an opposing magnetic dipole to the applied field. The effect is usually slight and the susceptibility is small and negative; $\chi \approx -10^{-6}$. However, all materials are diamagnetic and so all bodies can be affected in this way. This mechanism is the way that superconductors levitate materials. These are the only strong diamagnets; in this case $\chi \approx -1$

Paramagnetism

The energy of a magnetic dipole in a magnetic field with a component \mathbf{B}_z along a specified z axis is

$$E = -\mu_z \mathbf{B}_z \quad (1)$$

where μ_z is the z component of the dipole moment. (From now on, we will denote \mathbf{B}_z simply by B). If reorientation is possible, the dipoles align with the field and an overall magnetisation results. Reorientation is often not possible; many materials are not paramagnetic. Susceptibilities are small and positive. The paramagnetic response of electrons depends on their state in the material.

Delocalised electrons

Free electrons have a magnetic moment $\boldsymbol{\mu} = -g\mu_B \mathbf{s}$ where \mathbf{s} is the electron spin (with components $\pm \frac{1}{2}$ along the z axis); $\mu_B = e\hbar / 2m$ the Bohr magneton and g the gyromagnetic ratio (which is approximately equal to 2). This was all discovered in the spirit of enlightened empiricism; the justification is to be found in the Dirac equation where the relativistic origin of all this is revealed. The components of $\boldsymbol{\mu}$ along the z axis are (from the above) $\pm \mu_B$.

Consider the free-electron density of states, but split into densities of states for electrons with spin up and spin down with respect to the z axis. In the absence of a magnetic field, there are equal numbers of spin-up and spin-down electrons and there is no resultant magnetisation. When a field is applied, the spin-up states are raised in energy by $\mu_B B$ and the spin-down states are lowered by $\mu_B B$. Since $\mu_B \approx 9.4 \times 10^{-24} \text{ JT}^{-1}$, this change is much less than the Fermi energy.

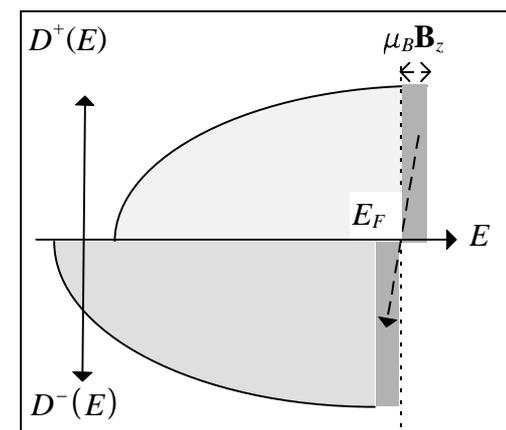
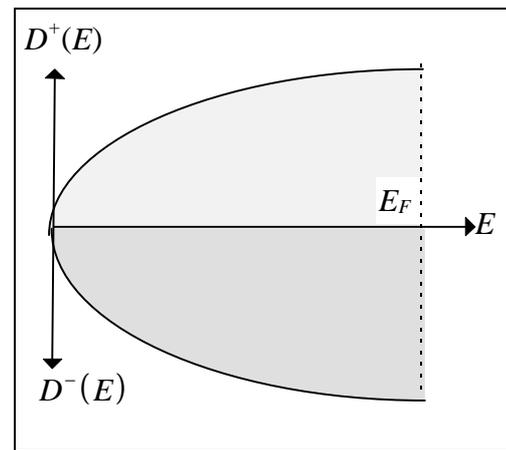
Thus, at zero temperature, a total of $\frac{1}{2} D_{FE}(E_F) \mu_B B$ electrons flip their spins to minimise the energy (where $D_{FE}(E)$ is the free-electron density of states and E_F is the Fermi energy) - the deeply shaded areas in the diagram. The magnetisation is the difference between down spins and up spins (down - up) per unit volume, multiplied by the Bohr magneton and so

$$\begin{aligned} M_z &= (D_{FE}(E_F) \mu_B B) (\mu_B / V) \\ &= 3\mu_B^2 n B / 2E_F \end{aligned} \quad (2)$$

where we have used the result (derived when we were considering the free-electron model) that $E_F D_{FE}(E_F) = 3N_e/2$ where N_e is the number of electrons and $n = N_e/V$ is the electron density. Assuming that the susceptibility (χ) is small, $B \approx \mu_0 H$ and so

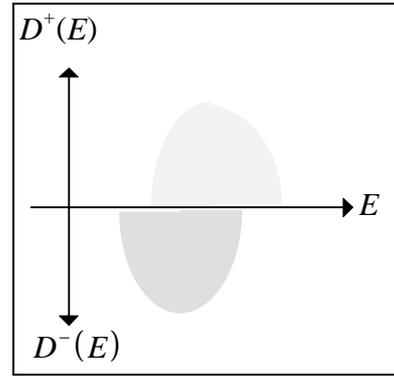
$$M_z = 3\mu_B^2 n \mu_0 H / 2E_F \quad (3)$$

which gives



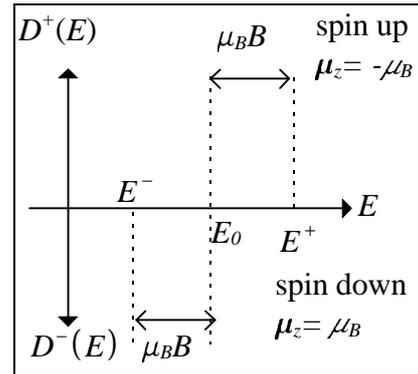
$$\chi = 3\mu_B^2 n \mu_0 / 2E_F \approx 10^{-6} \quad (4)$$

That is, the paramagnetic susceptibility is small, positive and (in this approximation) temperature independent. This line of argument also shows that materials with filled bands are not paramagnetic since the electrons cannot re-orientate - there are no available states for them to move into to reduce their energy.



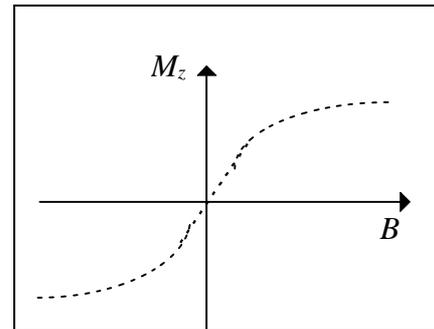
Core electrons

Matters are quite different for electrons which are localised on atoms and unable to move about the lattice. First let us consider a single electron in an atomic orbit with $\mathbf{L} = 0$. When we apply the B field, the energies of the up and down spin states are altered by $\pm\mu_B B$. Let us consider the statistical mechanics of such a system. The probability of occupying each state is $P^\pm \propto \exp(-E^\pm / k_B T)$, so the mean value of μ_z (the z component of the magnetic dipole) per atom is given by



$$\begin{aligned} \langle \mu_z \rangle &= \frac{\mu_B P^- - \mu_B P^+}{P^- + P^+} = \mu_B \frac{\exp(-[E_0 - \mu_B B] / k_B T) - \exp(-[E_0 + \mu_B B] / k_B T)}{\exp(-[E_0 - \mu_B B] / k_B T) + \exp(-[E_0 + \mu_B B] / k_B T)} \quad (5) \\ &= \mu_B \tanh(\mu_B B / k_B T) \end{aligned}$$

Hence, the magnetisation is $M_z = N_a \mu_B \tanh(\mu_B B / k_B T)$ where N_a is the atomic number density. If both spin states had been occupied, no reorientation would have been possible; the paramagnetism of core electrons relies on the existence of *partially filled shells*. The magnetisation as a function of B is shown on the right. Since $\mu_B B \ll k_B T$ usually we need only consider the linear part of the curve and write



$$M_z \approx N_a \mu_B^2 B / k_B T. \quad (6)$$

Again, if the susceptibility is small, we can write $B \approx \mu_0 H$, $M_z = \chi H$ where

$$\chi = N_a \mu_B^2 \mu_0 / k_B T = C / T \quad (7)$$

which defines the *Curie constant* (his not hers).

Putting in typical numbers at room temperature we get $\chi \approx 10^{-3}$. This is much more than for the free electrons - the effect of different degrees of constraint on electron re-orientation.

Finally, let us consider the general case of a set of core electrons in an atomic shell with angular momentum \mathbf{J} , comprising a total spin \mathbf{S} and a total orbital angular momentum \mathbf{L} . The same kind of argument leads to a paramagnetic susceptibility

$$\chi = N_a g^2 \mu_B^2 J(J+1) \mu_0 / 3k_B T \quad (8)$$

where the *Landé g-factor* is

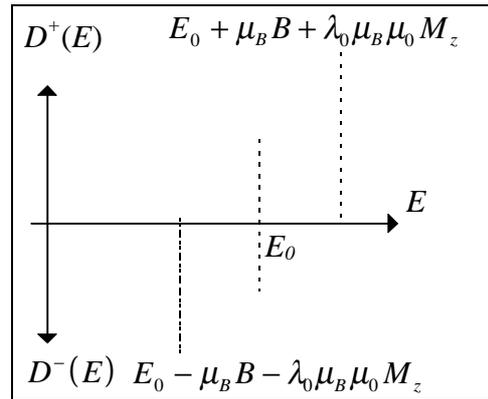
$$g = \frac{3J(J+1) - L(L+1) - S(S+1)}{2J(J+1)} \quad (9)$$

as in atomic physics. Thus the paramagnetic response enables us to determine the angular momentum state of the electrons attached to each atom.

Magnetic order

This includes the most obviously ‘magnetic’ materials - ferromagnets. In some materials, the magnetic dipoles of core electrons align spontaneously. No external field is needed for a permanent magnetisation to exist. The current understanding of magnetic ordering is that it is a collective electronic effect induced by the Pauli principle. We leave this until later; let us first imagine that the single electron in the

$L=0$ state we considered earlier feels a force which tends to align its spin with the spins of electrons on neighbouring atoms. Magnetic dipole - magnetic dipole interactions are far too weak to do this, so we cannot construct a magnetic analogue to the electric polarisation theory we considered earlier. Let us then simply imagine that the spin-up state is raised in energy by an amount $\lambda_0 \mu_0 \mu_B M_z$ and the down-spin reduced by the same amount, when a magnetisation M_z is induced in the material. λ_0 is



a dimensionless number that characterises this energy change. These shifts are in addition to the usual $\pm \mu_B B$ (and much bigger). The new terms promote an alignment of spins; the up-spin will be less favoured if M_z and λ_0 are both positive, this effect then increases M_z and so on.

If we use the same analysis as for the paramagnetic response, we find that the magnetisation of the material is given by

$$M_z = N_a \mu_B \tanh(\mu_B (B + \lambda_0 \mu_0 M_z) / k_B T) \quad (10)$$

where N_a is the number density of the atoms. Insert $B = \mu_0 (H + M_z)$ into this and absorb $\mu_0 M_z$ into the second term. (There are some slight complications involving the exact coefficient of M_z introduced by the replacement of B by H but these are not important). Then we have

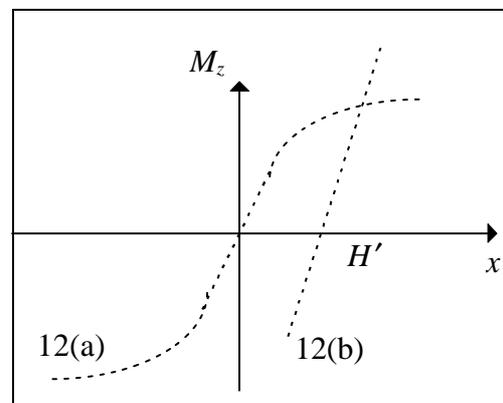
$$M_z = N_a \mu_B \tanh(\mu_B \mu_0 (H + \lambda M_z) / k_B T) \quad (11)$$

where λ differs from λ_0 by about unity. This equation can be written in the dimensionless parametric form

$$M'_z = \tanh x \quad (12a)$$

$$M'_z = T'(x - H') \quad (12b)$$

where $M'_z = M_z / N_a \mu_B$; $H' = \mu_0 \mu_B H / k_B T$ and $T' = T / T_C$ where T_C is the Curie-Weiss critical temperature given by $T_C = \lambda \mu_0 \mu_B^2 N_a / k_B$



The two parametric equations (12a, b) can be solved graphically as shown. There are two different cases of interest

Paramagnetic response

If the situation is as shown on the right above (i.e. the gradient of (12b) at the origin is greater than equation (12a), then the magnetisation M'_z is single-valued for a given field H' . This corresponds to the situation when $T > T_C$. For small x , $\tanh(x) \sim x$ and so we must solve the parametric equations

$$M'_z = x \quad (13a) \quad M'_z = T'(x - H') \quad (13b)$$

This is trivial; the solution is

$$M'_z = T'(M'_z - H') \quad (14)$$

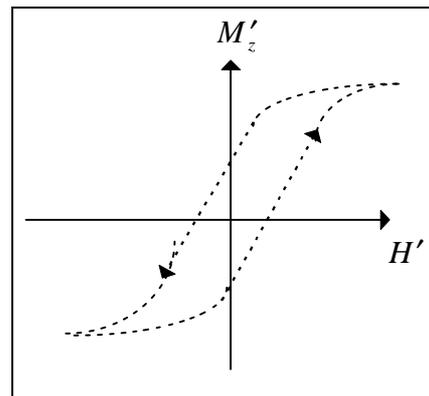
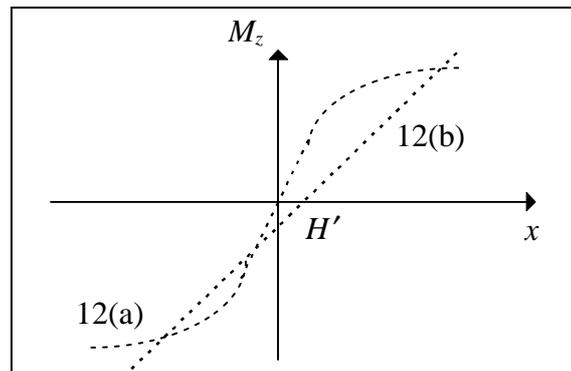
and, if we substitute back for all the various relations, we get

$$M_z = \frac{(\mu_0 \mu_B^2 / k_B) H}{T - T_C}$$

i.e. the magnetic response is paramagnetic with Curie law behaviour except that the temperature is shifted by the constant T_C . This is known as the *Curie-Weiss Law*. Iron, for example, is paramagnetic above 1043K.

Permanent magnetic ordering

If $T < T_C$, then the graphical construction shows that there are multi-valued solutions and permanent magnetisation, as shown on the right. Moreover, if we sketch a graph of M'_z against H' (shown on the right below), it is clear that the magnetisation does not vanish after the driving field, H , is removed. Equally, the permanent magnetisation can be shifted to other directions by using a suitable external field. This is magnetic ordering emerging in a simple model, but so far it is empirical. We have said nothing about the origin of the ordering force or the constant λ .



The exchange field

In we use the expression for the critical temperature and insert values for iron, we can deduce that

$\lambda \approx 10^4$, in other words, the alignment energies are far greater than can be ascribed to magnetic dipole interactions (which would give a value of $\lambda \approx 1$). It

is believed that the Pauli principle is ultimately responsible for this high value of λ .

This alignment effect is known in atomic physics. The antisymmetry of the wavefunction (i.e. the Pauli principle) ensures that electrons with the same spin cannot be found in the same place. Thus, the electrostatic repulsion between electrons of the same spin will be less than the repulsion between electrons of opposite spin. This is the *exchange interaction* and is responsible for Hund's first rule in atomic spectroscopy (that states with maximum \mathbf{S} value are the lowest in energy). A similar argument applies here. Although we have ignored it, the electron-electron repulsion is important in materials. A good approximation is to consider each electron as interacting with the

smear-out density of all the others. However, we must take account of the effect discussed above. If, for example, our electron is spin-up; its interaction with the density of the spin-up electrons will be less than the interaction with the spin-down density. There must be a 'hole' in the 'spin-up' density close to our electron because of the Pauli principle and so the interaction is less

(Note: this argument looks as though we are able to 'pick out' and distinguish one electron which is not possible. In fact, it can be shown that we are not doing this, and the idea of solving the electronic structure of materials by looking at a one-electron model but incorporating the effects of the others in terms of a density is the basis of most modern calculations in this area.)

This argument leads to the conclusion that electron spins in materials will tend to order *if they can* to minimise the total energy. Because the exchange interaction is responsible for the ordering, the term $\lambda\mu_0 M_z$ is called the *exchange field*. This field is a combination of electrostatics and quantum mechanics; the calculation of the exchange field and therefore of λ is distinctly messy. Free electrons can order their spins, but the effect is small. The greater effect comes from ordering the spins of the core electrons. This leads to the various forms of permanent magnetism

Types of magnetic ordering

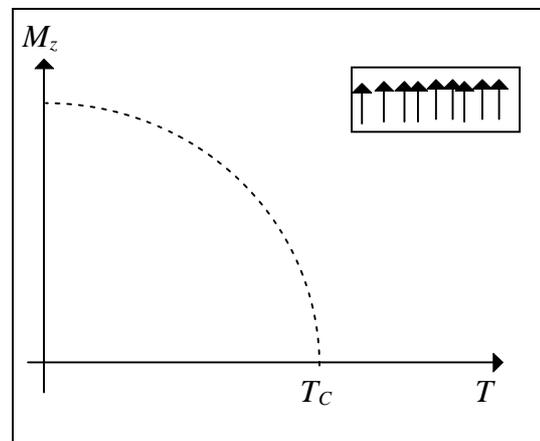
Ferromagnetism

The exchange field aligns the magnetic dipole moments of the core electrons. Hence $\lambda > 0$ and the permanent magnetisation which appears below the critical temperature T_C is given by the solution to our simple model equation

$$M'_z = \tanh(M'_z / T')$$

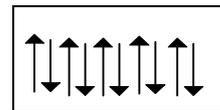
This gives the behaviour of M_z as a function of temperature shown on the right. Below

T_C the spins tend to be aligned even in the absence of an external field. The classic material exhibiting this behaviour is iron (hence *ferromagnetism*).



Antiferromagnetism

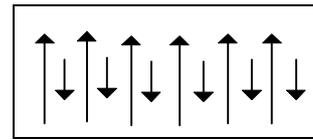
Despite the above argument, it is possible for λ to be negative, at least between nearest neighbours. We can then get two sub-lattices of aligned spins; one up and one down such that the



nearest neighbour spins are anti-parallel. There is now no magnetisation in the absence of an external field. The effect can, however be detected in two ways. First, there is a characteristic kink in the susceptibility curve at the Néel temperature (analogous to the Curie temperature in ferromagnetism). The susceptibility is a maximum at this point. Second, the unit cell is different if it is determined by a probe (like neutrons) that can interact with the magnetic moments of the atoms. Recall that the definition of a lattice point is that the environment must look the same for all points. Thus, if one 'lattice point' is an up-spin surrounded by down-spins and another is a down-spin surrounded by up-spins, although in terms of atomic arrangement they can still seem to be the same (and therefore can both be lattice points), in terms of magnetic structure they are not (and so only one of them can be). We have a *magnetic lattice* with a different structure to the lattice that can be detected by X-rays. The commonest antiferromagnetic element is chromium. Many oxides are also antiferromagnetic; one of the most studied in MnO

Ferrimagnetism

This occurs when there is an antiferromagnetically ordered lattice, but the two sub-lattices (up and down) contain atoms with different intrinsic magnetic dipole moments. In this case, the material does have a resultant magnetisation when there is no applied field. The commonest example is magnetite,



Fe_3O_4 . This can be considered to be a mixture of FeO and Fe_2O_3 and the two magnetic ions are Fe^{2+} and Fe^{3+} . The mineral occurs naturally, it is *lodestone* and its magnetic properties have been known for millenia; it is the material traditionally used in compasses (*lode* = a course or way (Old Norse)).

Spin waves (magnons)

An ordered system of spins (or magnetic dipoles) can be excited such that wave-like disturbances pass through the material. These are *spin waves*. At low temperatures, these excitations are quantised in the same way as the vibrational excitations we studied earlier. The excitations are called *magnons* by analogy with *phonons*.