12

Magnetic solids

- What atomic feature renders a material paramagnetic?
- Why do ferromagnetic solids show a domain structure?
- What is a ferrimagnetic material?

Magnets pervade everyday life. In reality, these magnets are examples of a group of materials called ferromagnetic compounds. If a small rod magnet is freely suspended, it will align (approximately) north–south. The end pointing north is called the north pole of the magnet and the end pointing south, the south pole of the magnet. This fact proves that the Earth also acts as a magnet. It is found that opposite magnetic poles attract each other and similar magnetic poles repel each other. [Because of this, the end of a freely suspended magnet that points towards the north should be labelled as a south pole, but it is too late to change things now!] A ferromagnetic solid behaves as if surrounded by a magnetic field, and will attract or repel other ferromagnets via the interactions of the magnetic fields.

Not only solids but also wires carrying an electric current give rise to magnetic fields, the strength of which is proportional to the current flowing. Most solids, however, including wires not carrying a current, and ferromagnetic materials above a certain temperature, are loosely termed 'nonmagnetic'. Strictly speaking, this is inaccurate, as these materials simply exhibit extremely weak magnetic effects.

12.1 Magnetic materials

12.1.1 Characterisation of magnetic materials

The weak magnetic properties of most solids can be measured using a Gouy balance (Figure 12.1a). In this equipment, the sample is suspended between the poles of an electromagnet from a sensitive balance. The vast majority of solids show only miniscule magnetic effects. Of these, most weigh slightly less when the electromagnet is on than when the electromagnet is turned off (Figure 12.1b). The materials, which are weakly repelled by the magnetic field, are the diamagnetic materials. The rest of the 'nonmagnetic' group weigh slightly more when the electromagnet is on than when it is off (Figure 12.1c). These substances are drawn weakly into a magnetic field and are called paramagnetic materials. Ferromagnetic materials are strongly attracted to one or other of the pole pieces of the magnet and the technique does not give a result.

Diamagnetic and paramagnetic substances are characterised by their 'susceptibility' to the magnetic

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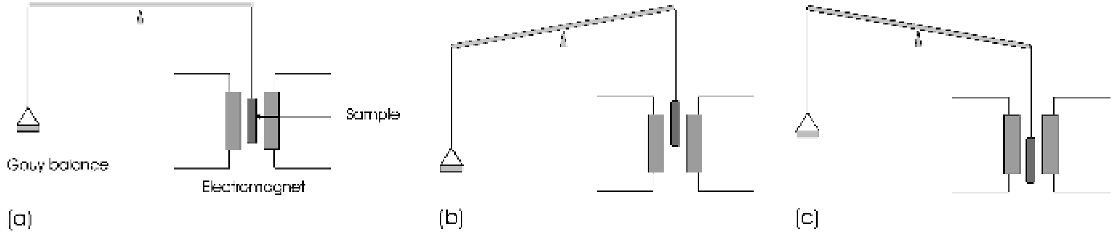

Figure 12.1 The weak magnetic properties of a solid can be determined by its behaviour in the field generated by an electromagnet, in a Gouy balance: (a) sample with electromagnet turned off; (b) diamagnetic sample with electromagnet turned on (the sample appears to weigh less); and (c) paramagnetic sample with the electromagnet turned on (the sample appears to weigh more)

field. For materials that are isotropic, a group that includes gases and liquids as well as glasses, cubic crystals and polycrystalline solids, the magnetic susceptibility, χ, is defined by:

$$\boldsymbol{M} = \chi \boldsymbol{H} \tag{12.1}$$

where $\boldsymbol{M}$ is the magnetisation of the sample and $\boldsymbol{H}$ is the magnetic field, which are usually defined as vectors. The magnetic susceptibility is a dimensionless quantity. In nonisotropic solids, $\boldsymbol{M}$ and $\boldsymbol{H}$ are not necessarily parallel. The value of the magnetic susceptibility will then vary with direction in the crystal. The units used in magnetism are given in Section S4.4.

These weak magnetic materials can also be characterised by the extent to which the magnetic field is able to penetrate into the sample, the magnetic permeability. The magnetic permeability of a compound, μ, is defined by:

$$\mu = \mu_0(1 + \chi) \tag{12.2}$$

where μ_0 is a fundamental constant, the permeability of free space. Diamagnetic materials have a value of μ less than μ_0, whereas paramagnetic materials have value of μ greater than μ_0. These values are equivalent to field enhancement in a paramagnetic substance, and field reduction in a diamagnetic material (Figure 12.2).

12.1.2 Types of magnetic material

Magnetic materials can be classified in terms of the arrangements of magnetic dipoles in the solid. These dipoles can be thought of, a little imprecisely, as microscopic bar magnets attached to the various atoms present.

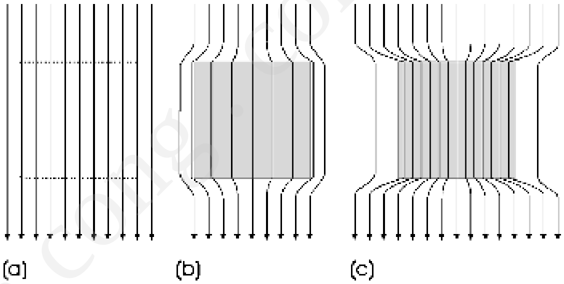

Figure 12.2 Weak magnetic materials differ in their response to an external magnetic field: (a) no solid present; (b) a diamagnetic solid repels the external field and the density of field lines in the solid decreases; (c) a paramagnetic solid attracts the external field and the density of the magnetic field lines in the sample increases. $\boldsymbol{B}$ (induction) and $\boldsymbol{H}$ (magnetic field) decrease inside a diamagnetic solid and increase inside a paramagnetic solid

Materials with no elementary magnetic dipoles at all are diamagnetic (Figures 12.3a and 12.3b). The imposition of a magnetic induction generates weak magnetic dipoles that oppose the applied induction. The magnetic susceptibility, χ, of a diamagnetic substance is negative and very slightly less than 1. There is no appreciable variation of diamagnetism with temperature.

Paramagnetic solids are those in which some of the atoms, ions or molecules making up the solid possess a permanent magnetic dipole moment. These dipoles are isolated from one another. The

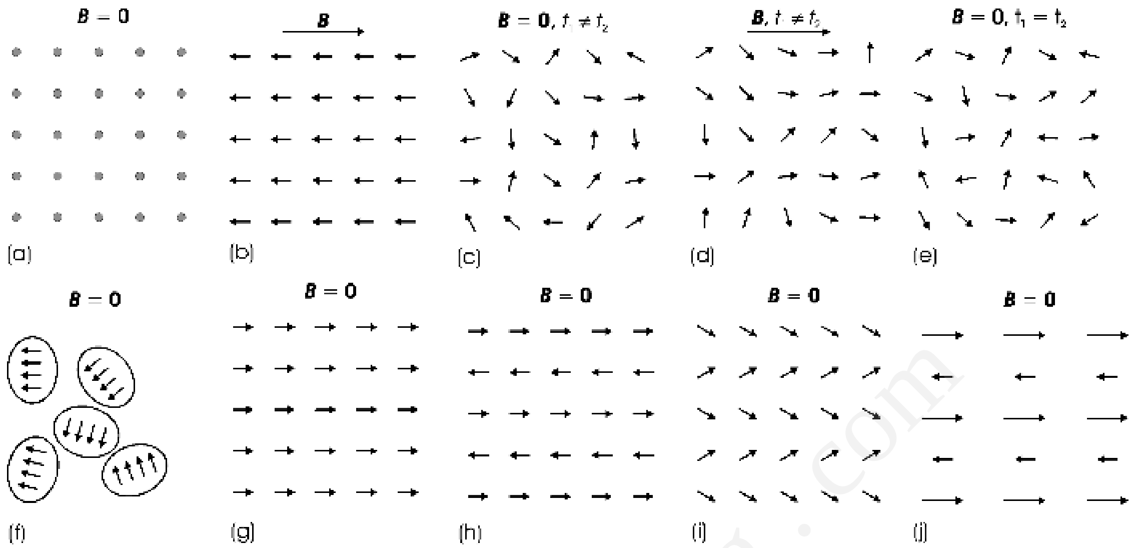

Figure 12.3 The effect of an applied magnetic field, ***H***, or induction, ***B***, on a solid. (a) and (b) A diamagnetic material has no dipoles present in the absence of magnetic induction; weak dipoles are induced that oppose the field to give a weak repulsion. (c) and (d) In the absence of magnetic induction, the elementary magnetic dipoles present are random; in a field, there is a tendency to align in the induction direction to give a weak attraction. The diagrams apply only for an instant, at time t_1. The dipoles continually change orientation and will be differently disposed at another time t_2. (e), A spin glass is similar to (c), but below a temperature T_f, the orientation of the dipoles changes slowly. (f) A cluster glass has oriented dipoles in small volumes below a temperature T_f. (g) A ferromagnetic solid has aligned dipoles in the absence of induction. (h) An antiferromagnetic solid has dipoles in an antiparallel arrangement in the absence of magnetic induction. (i) A canted magnetic material has dipoles arranged in a canted fashion in the absence of a field. (j) A ferrimagnetic solid has two opposed dipole arrays

solid, in effect, contains small, noninteracting atomic magnets. In the absence of a magnetic field, these are arranged at random and the solid shows no net magnetic moment. In a magnetic field, the elementary dipoles will attempt to orient themselves parallel to the magnetic induction in the solid, and this will enhance the internal field within the solid and give rise to the observed paramagnetic effect (Figures 12.3c and 12.3d). The alignment of dipoles will not usually be complete, because of thermal effects and interaction with the surrounding atoms in the structure. Thus the situation shown in Figures 12.3(c) and 12.3(d) is a snapshot at any instant, t_1. At any other instant, t_2, the orientation of the spins would still be random but it would be different from that drawn. The magnetic effect is much greater than diamagnetism, and the magnetic susceptibility, χ, of a paramagnetic solid is positive and slightly greater than 1.

The partial orientation of the elementary dipoles in a paramagnetic solid will be counteracted by thermal agitation, and it would be expected that at high temperatures the random motion of the atoms in the solid would cancel the alignment resulting from the magnetic field. The paramagnetic susceptibility would therefore be expected to vary with temperature. The temperature dependence is given by the Curie law:

$$\chi = \frac{C}{T} \tag{12.3}$$

where χ is the magnetic susceptibility, T is the absolute temperature, and C is the Curie constant. Curie law dependence in a solid (Figure 12.4a), is indicative of the presence of isolated paramagnetic ions or atoms in the material.

Interacting magnetic dipoles can produce a variety of magnetic properties in a solid. The

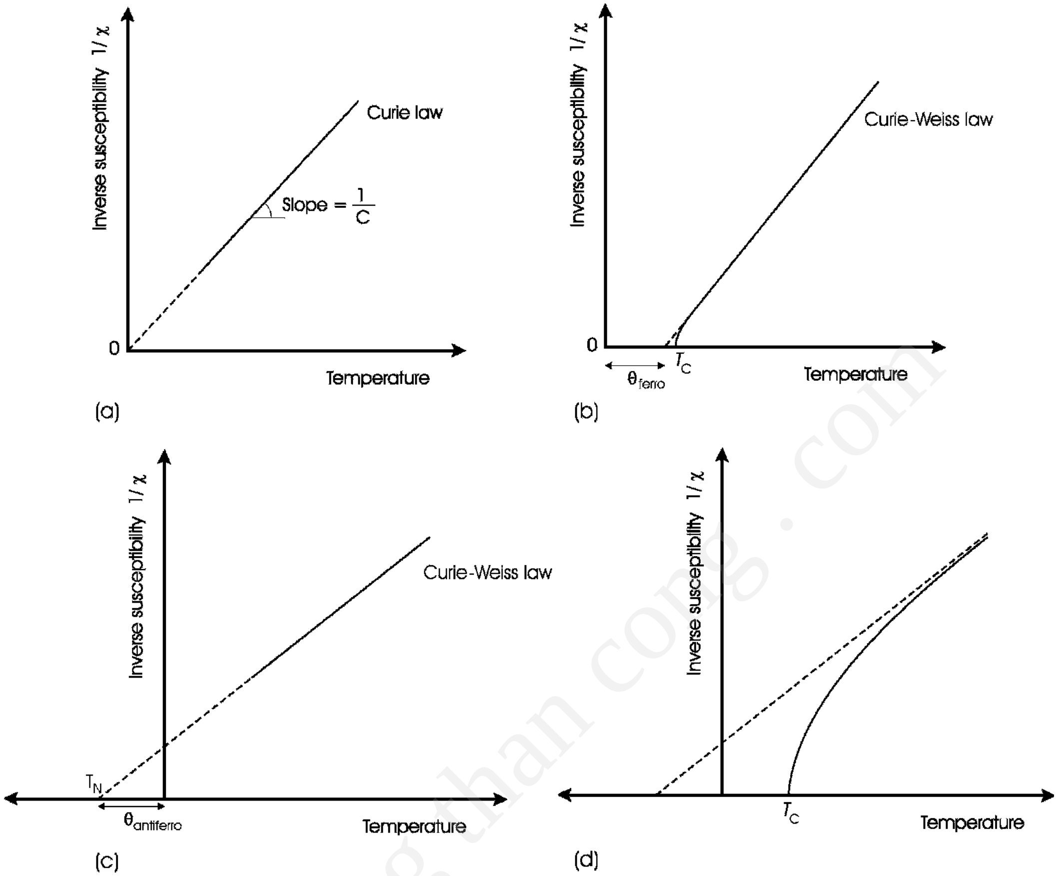

Figure 12.4 The temperature dependence of the reciprocal magnetic susceptibility: (a) Curie law behaviour of a paramagnetic solid; (b) Curie–Weiss law behaviour of a ferromagnetic solid above the Curie temperature, in the paramagnetic state; (c) Curie–Weiss law behaviour of an antiferromagnetic solid; and (d) behaviour of a ferrimagnetic solid

interactions can increase sufficiently that at low temperatures the random reorientation of the dipoles is restricted and changes only slowly with time. The directions of the spins are said to become frozen below a freezing temperature, T_{f}, to produce a spin glass (Figure 12.3e). In other materials, the interactions below T_{f} are strong enough for local ordering but because of the crystal structure, the localised regions are restricted and no long-range order occurs (Figure 12.3f). This arrangement is called a cluster glass, and is found at low temperatures in compounds such as Prussian blue, $KFe_2(CN)_6$, which has a magnetic freezing point of approximately 25 K.

Ferromagnetic materials are those in which the magnetic moments align parallel to each other over considerable distances in the solid (Figure 12.3g). An intense external magnetic field is produced by this alignment. Ferromagnetism is associated with the transition elements, with unpaired d electrons, and the lanthanides and actinides with unpaired f electrons.

Above a temperature called the Curie temperature, T_{C}, all ferromagnetic materials become paramagnetic. The transition to a paramagnetic state comes about when thermal energy is greater than the magnetic interactions, and causes the dipoles to disorder. *Well above* the Curie temperature,

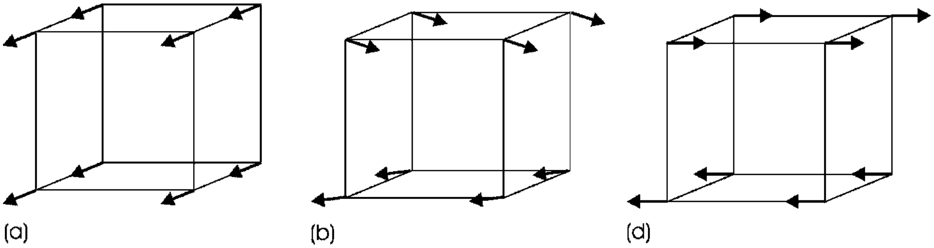

Figure 12.5 The relationship between the ordered arrays of magnetic dipoles arranged on a square lattice: (a) ferromagnetic configuration, (b) canted antiferromagnetic configuration and (c) antiferromagnetic configuration

ferromagnetic materials obey the Curie–Weiss law:

$$\chi = \frac{C}{T - \theta} \tag{12.4}$$

The Curie–Weiss constant, θ, is positive, has the dimensions of temperature, and a value usually close to, but not quite identical to, the Curie temperature, T_C, (Figures 12.4b). The transition is reversible, and on cooling, ferromagnetism returns when the magnetic dipoles align parallel to one another as the temperature drops through the Curie temperature.

It is energetically favourable in some materials for the elementary magnetic moments to align in an antiparallel fashion (Figure 12.3h). These are called antiferromagnetic compounds. Above a temperature called the Néel temperature, T_N, this arrangement disorders and the materials revert to paramagnetic behaviour. Well above the Néel temperature, antiferromagnetic materials obey the Curie–Weiss law:

$$\chi = \frac{C}{T - \theta} \tag{12.5}$$

In this case, the constant, θ, is negative (Figure 12.4c). Cooling the sample through the Néel temperature causes the antiferromagnetic ordering to reappear.

Ferromagnetic ordering and antiferromagnetic ordering represent the extremes of dipole orientation. In a number of solids, neighbouring magnetic dipoles are not aligned parallel to one another, but at an angle, referred to as a canted arrangement (Figure 12.3i). Such canted arrangements can be thought of as an intermediate configuration between ferromagnetic and antiferromagnetic states. For example, a ferromagnetic ordering of magnetic dipoles arranged on a square lattice (Figure 12.5a) can be transformed by canting of alternate layers (Figure 12.5b) into an antiferromagnetic configuration (Figure 12.5c).

An important group of solids has two different magnetic dipoles present, one of greater magnitude than the other. When these line up in an antiparallel arrangement they behave rather like ferromagnetic materials (Figure 12.3j). They are called ferrimagnetic materials. A ferrimagnetic solid shows a more complex temperature dependence. This is because the distribution of the magnetic ions over the available sites is sensitive both to temperature and to the spin interactions. The behaviour can be approximated by the equation

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} + \frac{\xi}{T - \theta}$$

where the parameters χ_0, θ, and ξ depend on the population of the available cation sites and the spin interactions. These are often taken as constants and a graph of $1/\chi$ against temperature is a straight line except near the Curie temperature, T_C (Figure 12.4d).

Although magnetic solids are generally thought to be inorganic compounds or metals, there is much current interest in organic magnetic materials.

12.1.3 Atomic magnetism

Magnetic properties reside in the subatomic particles that make up atoms. Of these, electrons make the biggest contribution, and only these will be considered in this chapter. Each electron has a magnetic moment due to the existence of a magnetic dipole, which can be thought of as a minute bar magnet linked to the electron. There are two contributions to the magnetic dipole moment of an electron bound to an atomic nucleus, which, in semiclassical models, are attributed to orbital motion and spin, related to the two quantum numbers l and s, introduced in Chapter 1.

The magnetic properties of electrons are described in terms of an atomic unit of magnetic dipole called the Bohr magneton, μ_B. It is given by:

$$\mu_B = \frac{eh}{4\pi m_e} \tag{12.6}$$

where e is the electron charge, m_e is the electron mass, and h is Planck's constant. The magnitude of the total magnetic dipole moment of a single electron associated with the orbital quantum number, l, the orbital component, is given by:

$$\boldsymbol{m}_{\text{orbital}} = \mu_B[l(l+1)]^{1/2}$$

The magnitude of the total contribution to the magnetic dipole moment of a single electron associated with the spin, s, the spin component, is given by:

$$\boldsymbol{m}_{\text{spin}} = g\mu_B[s(s+1)]^{1/2}$$

where g is called the free electron g value, equal to 2.0023, and s can take a value of $\frac{1}{2}$.

The orbital and spin components are linked, or coupled, on isolated atoms or ions to give an overall magnetic dipole moment for the atom, as explained in Section 1.4.2. The commonest procedure for calculating the resultant magnetic dipole moment is called Russell–Saunders coupling (see Section S1.3). In summary, individual electron spin quantum numbers, s, are added to give a many-electron total spin quantum number, S, and the individual orbital quantum numbers, l, are added to give a many-electron total orbital angular momentum quantum number, L. The many-electron quantum numbers L and S are further combined to give a total angular momentum quantum number, J. More detail is given in Section 12.2.2 for the lanthanides and transition metals of interest here.

The magnetic dipole moment of the atom is given by Equation (12.7):

$$\boldsymbol{m}_{\text{atom}} = g_J\mu_B[J(J+1)]^{1/2} \tag{12.7}$$

where g_J is called the Landé g factor, given by:

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{12.8}$$

The method of calculating S, L and J is described in Section S1.3.

A completely filled orbital contains electrons with opposed spins and, in this case, the value of S is zero. Similarly, a completely filled s, p, d or f orbital set has L equal to zero. This means that atoms with filled closed shells have no magnetic moment. The only atoms that display a magnetic moment are those with incompletely filled shells. These are found particularly in the transition metals, with incompletely filled d shells, and the lanthanides and actinides, which have incompletely filled f shells.

12.2 Weak magnetic materials

12.2.1 Diamagnetic materials

None of the atoms in a diamagnetic material has magnetic dipoles. A magnetic field, however, will induce a small magnetic dipole that is present only for as long as the magnetic field persists. The induced dipole is opposed to the magnetic induction, $\boldsymbol{B}$, as sketched in Figure 12.3. The effect is analogous to the effect on a macroscopic conductor brought into a magnetic field, described by Lenz's Law. (A conducting electrical circuit brought into a magnetic field will contain an induced current such as to yield a magnetic field opposed to the inducing field.) This very small effect gives rise to the typical diamagnetic response.

12.2.2 Paramagnetic materials

The magnetic dipole moment of a paramagnetic solid containing paramagnetic atoms or ions will be given by Equations (12.7) and (12.8). To obtain values for S, L and J that are of interest in understanding the magnetic behaviour (following Section 1.4.3 and Section S1.3.2):

1. Draw a set of boxes corresponding to the number of orbitals available, seven for the lanthanides and five for the transition metals.

2. Label each box with the value of m_l, highest on the left and lowest on the right. For lanthanides these run 3, 2, 1, 0, −1, −2, −3. For transition metals these run 2, 1, 0, −1, −2.

3. Fill the boxes with electrons, from left to right. When all boxes contain one electron, start again at the left.

4. Sum the m_s values of each electron, $+\frac{1}{2}$ or $-\frac{1}{2}$. This is equal to the maximum value of S.

5. Sum the m_l values of each electron to give a maximum value of L.

6. Calculate the J values, $J = L + S$, to $J = L - S$. The ground state is the lower value if the shell is up to half full and the higher value if the shell is over half full.

Equations (12.7) and (12.8) work well for many compounds, such as the salts of lanthanide ions, as can be judged from Table 12.1. Lanthanide ions have a partly filled 4f shell, and these orbitals are well shielded from any interaction with the surrounding atoms by filled 5s, 5p and 6s orbitals, so that, with the notable exceptions Eu^{3+} and Sm^{3+}, they behave like isolated ions.

For the transition metals, especially those of the 3d series, interaction with the surroundings is considerable. This has two important consequences. One is the curious fact that 3d transition metal ions in paramagnetic solids often have magnetic dipole moments corresponding only to the electron spin contribution, given by the quantum number S. The orbital moment, L, is said to be 'quenched'. In such materials, Equation (12.8) reduces to

$$g_J = 1 + \frac{S(S+1) + S(S+1)}{2S(S+1)} = 2$$

Table 12.1 Calculated and observed magnetic dipole moments for the lanthanides

Ion	Configuration[a]	S	L	J	Magnetic dipole moment[b] calc.	 meas.
La^{3+}, Ce^{4+}	f^0	0	0	0	0	Dia.[c]
Ce^{3+}, Pr^{4+}	f^1	$\frac{1}{2}$	3	$\frac{5}{2}$	2.54	~2.5
Pr^{3+}	f^2	1	5	4	3.58	3.5
Nd^{3+}	f^3	$\frac{3}{2}$	6	$\frac{9}{2}$	3.62	3.5
Pm^{3+}	f^4	2	6	4	2.68	–
Sm^{3+}	f^5	$\frac{5}{2}$	5	$\frac{5}{2}$	0.84	1.5
Sm^{2+}, Eu^{3+}	f^6	3	3	0	0	3.4[d]
Eu^{2+}, Gd^{3+}, Tb^{4+}	d^7	$\frac{7}{2}$	0	$\frac{7}{2}$	7.94	~8.0
Tb^{3+}	f^8	3	3	6	9.72	9.5
Dy^{3+}	f^9	$\frac{5}{2}$	5	$\frac{15}{2}$	10.63	10.6
Ho^{3+}	f^{10}	2	6	8	10.61	10.4
Er^{3+}	f^{11}	$\frac{3}{2}$	6	$\frac{15}{2}$	9.59	9.5
Tm^{3+}	f^{12}	1	5	6	7.57	7.3
Yb^{3+}	f^{13}	$\frac{1}{2}$	3	$\frac{7}{2}$	4.54	4.5
Yb^{2+}, Lu^{3+}	f^{14}	0	0	0	0	Dia.[c]

[a] The configurations of the lanthanide metals are given in Section S1.2.3.
[b] Units: Bohr magnetons; calc., calculated from Equation (12.7) in text; meas., measured value.
[c] Diamagnetic.
[d] Eu^{3+}

To a good approximation, Equations (12.7) and (12.8) can then be replaced by a spin only formula:

$$\boldsymbol{m} = g_J[S(S+1)]^{1/2}\mu_B \qquad (12.9)$$

where $g_J = 2$, S is the total spin quantum number, equal to $s_1 + s_2 + s_3 + \cdots$ for the unpaired electrons, and μ_B is the Bohr magneton. In the case of n unpaired electrons on each ion, each of which has s equal to $\frac{1}{2}$,

$$S = s_1 + s_2 + s_3 \cdots s_n = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \cdots = \frac{n}{2}$$

The spin-only formula can then be written:

$$\boldsymbol{m} = [n(n+2)]^{1/2}\mu_B \qquad (12.10)$$

The magnetic dipole moments calculated in this way are compared with the experimental values in Table 12.2. It is seen that in many cases the agreement is very good. In cases where the experimental value is considerably different from the spin-only value, orbital effects are significant.

The second feature of the transition metal ions, especially noticeable in the 3d series, is that many ions have two apparent spin states: high spin and low spin. For example, Fe^{3+}, with a $3d^5$ electron configuration, sometimes appears to have five unpaired spins and sometimes only one. This behaviour is found for 3d ions with configurations between $3d^4$ and $3d^7$. The explanation of this phenomenon lies with crystal field splitting of the d-electron energy levels, explained in Section S4.5. In summary, when the ions are in octahedral surroundings, the d-electron levels are split into two groups, one of lower energy, containing three levels, labelled t_{2g}, and one of higher energy, containing two levels, called e_g. If the splitting is large, the d electrons preferentially occupy the lower, t_{2g}, group. Spin pairing occurs for more than three d electrons, giving rise to a low spin state. In the alternative case, when the splitting is small, the electrons occupy all of the d orbitals. Spin pairing is avoided, and the ion has a high spin state.

The crystal field splitting energy between the t_{2g} and e_g set of orbitals is generally similar to the energy of visible light. This means that the magnetic behaviour of a material can be changed by irradiation with light of a suitable wavelength, which will promote electrons from the lower to the upper energy state. Molecules in which this state of affairs can occur are known as spin-crossover complexes. In them, a magnetic state can be switched from, say, diamagnetic to paramagnetic, by irradiation,

Table 12.2 The magnetic properties of the 3d transition metal ions

			Magnetic dipole moment[b]	
Ion	Configuration[a]	S	calc.	meas.
Sc^{3+}, Ti^{4+}, V^{5+}	d^0	0	0	Dia.[c]
Ti^{3+}, V^{4+}	d^1	$\frac{1}{2}$	1.73	1.7–1.8
Ti^{2+}, V^{3+}	d^2	1	2.83	2.8–2.9
Cr^{3+}, Mn^{4+}, V^{2+}	d^3	$\frac{3}{2}$	3.87	3.7–4.0
Cr^{2+}, Mn^{3+}	d^4	2	4.9	4.8–5.0
Mn^{2+}, Fe^{3+}	d^5	$\frac{5}{2}$	5.92	5.7–6.1
Co^{3+}, Fe^{2+}	d^6	2	4.9	5.1–5.7
Co^{2+}	d^7	$\frac{3}{2}$	3.87	4.3–5.2
Ni^{2+}	d^8	1	2.83	2.8–3.5
Cu^{2+}	d^9	$\frac{1}{2}$	1.73	1.7–2.2
Cu^{+}, Zn^{2+}	d^{10}	0	0	Dia.[c]

[a] The configuration of the 3d transitions metals are given in Section S1.2.2.

[b] Units: Bohr magnetons; calc., calculated from Equation (12.9) in text; meas., measured value.

[c] Diamagnetic.

resulting in photoinduced magnetism. The application of this photoinduced spin-crossover is being studied in single molecules, with the aim of making ever-smaller data storage devices.

12.2.3 The temperature dependence of paramagnetic susceptibility

As described in Section 12.1.2, the temperature dependence of the susceptibility of paramagnetic compound is given by the Curie law, Equation (12.3). The Curie law is indicative of the presence of isolated paramagnetic ions or atoms in the material.

In classical physics, the magnetic dipole can lie in any direction with respect to the magnetic field. In real atoms this is not possible, and the direction of the magnetic moment vector can only take values such that the projection of the vector on the magnetic field direction, z, has values of M_J, where M_J is given by:

$$\mathrm{M}_J = J, J-1, J-2, \cdots -J$$

There are $(2J+1)$ values of M_J. These orientations can be represented as a set of energy levels, as sketched in Figure 12.6. The separation of the energy levels is:

$$\Delta E = g_J \mu_{\mathrm{B}} B$$

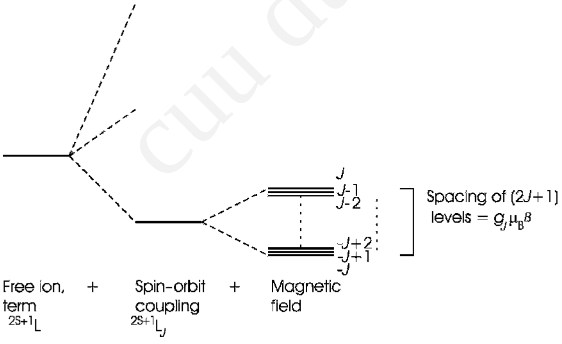

Figure 12.6 The splitting of atomic energy levels. The Russell–Saunders free ion term (left) becomes more complex when the spin and orbital contributions couple (centre). In a magnetic field each spin–orbit level splits into a further $(2J+1)$ equally spaced levels (right)

where g_J is the Landé g factor, of Equation (12.8), and B is the magnitude of the magnetic induction. The average value of the magnetic dipole moment, $\langle \boldsymbol{m} \rangle$, will depend on the population of these levels when at thermal equilibrium. The bulk magnetisation will then be given by:

$$\boldsymbol{M} = N\langle \boldsymbol{m} \rangle$$

where N is the number of magnetic dipoles per unit volume.

It is found that the value of $\boldsymbol{M}$ is:

$$\boldsymbol{M} = N g_J \mu_{\mathrm{B}} J\, B_J(x) \tag{12.11}$$

where $B_J(x)$ is the Brillouin function:

$$B_J(x) = \frac{2J+1}{2J}\coth\left\{\frac{2J+1}{2J}x\right\} - \frac{1}{2J}\coth\left\{\frac{x}{2J}\right\} \tag{12.12}$$

and

$$x = g_J \mu_{\mathrm{B}} \frac{JB}{kT}$$

The classical case, in which the magnetic dipole moments can rotate freely, is equivalent to a continuum of energy levels with J tending to infinity. In this case, the magnetisation is given by:

$$\boldsymbol{M} = N\boldsymbol{m}L(x) = N\boldsymbol{m}\left(\coth x - \frac{1}{x}\right) \tag{12.13}$$

where

$$x = \frac{mB}{kT}$$

and the function $L(x)$ is the Langevin function.

The rather complex equation for the magnetisation of a paramagnetic substance can be simplified for the case of $x \ll 1$, which holds in the case of higher temperatures and lower magnetic fields. In fact, even when the magnetic induction is equal to 1 T, a temperature of 300 K is sufficient to make $x \ll 1$). In this case, the magnetisation is given by:

$$\boldsymbol{M} = \frac{N g_J^2 \mu_B^2 B J(J+1)}{3kT} \tag{12.14}$$

Substituting $\boldsymbol{B} = \mu_0 \boldsymbol{H}$, for paramagnetic materials and rearranging, gives:

$$\frac{\boldsymbol{M}}{\boldsymbol{H}} = \chi = \frac{N\mu_0 g_J^2 \mu_B^2 J(J+1)}{3kT} \qquad (12.15)$$

This has the same form as the Curie equation, and the Curie constant is given by:

$$C = \frac{N\mu_0 g_J^2 \mu_B^2 J(J+1)}{3k} \qquad (12.16)$$

The value of χ is proportional to the number of magnetic dipoles present. The susceptibility is thus given in several forms. In the derivation above, N is the number of dipoles per unit volume, and the susceptibility is called the volume susceptibility, χ_v in m^{-3}. The mass susceptibility, χ_m, in which N refers to the number of magnetic dipoles per unit mass, is given by χ_v/ρ, where ρ is the density in $kg\,m^{-3}$. The susceptibility of one mole of the substance, the molar susceptibility, χ_{molar}, is given by $(\chi_v V_m)$, where V_m is the molar volume of the material.

12.3 Ferromagnetic materials

12.3.1 Ferromagnetism

The most important temperature effect is shown by just a small number of paramagnetic materials. In these, below a temperature called the Curie temperature, T_C, the material takes on quite new magnetic properties and is no longer paramagnetic, but strongly ferromagnetic. The change is reversible, and heating above the Curie temperature causes the material to revert to paramagnetic behaviour. Below the Curie temperature, the magnetic susceptibility is found to be 10^4 or more times higher than that of a normal paramagnetic substance. This state of affairs is found in only four elements – Fe, Co, Ni and Gd – at room temperature. Two lanthanides, Tb and Dy, have a temperature range (well below room temperature) over which they are ferromagnetic, as given in Table 12.3. However, in the second half of the 20th century, many other ferromagnetic compounds have been synthesised, notably oxides and alloys of the 3d transition metals and lanthanides.

Table 12.3 Ferromagnetic and antiferromagnetic compounds

Ferromagnetic compound	T_C/K	Antiferromagnetic compound	T_N/K
Fe	1043	Cr	310
Co	1388	α-Mn	100
Ni	627	α-Fe_2O_3	950
Gd	293	CuF_2	69
Tb	220–230	MnF_2	67
Dy	87–176	$CoCO_3$	18
CrO_2	386	NiO	523
$SmCo_5$	973	CoO	293
$Nd_2Fe_{14}B$	573	FeO	198
		MnO	116
		K_2NiF_4	97
		$LaFeO_3$	750

Note: T_C, Curie temperature; T_N, Néel temperature.

The magnetisation of a compound, $\boldsymbol{M}$, is the dipole moment per unit volume. For ferromagnetic compounds, the saturation magnetisation, $\boldsymbol{M}_s$, when all of the dipoles are aligned, can be measured and used to estimate the effective magnetic moment on the atoms in the structure when the unit cell is known.

$$\begin{aligned}\boldsymbol{M}_s &= (\text{number of dipoles per unit volume}) \\ &\quad \times (\text{effective magnetic moment on each dipole}) \\ &= N_{unpaired}\, \boldsymbol{m}_{eff}\, \mu_B\end{aligned}$$

In addition, the equation for the inductance (see Section S4.4),

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} + \mu_0 \boldsymbol{M}$$

can be approximated to:

$$\boldsymbol{B} = \mu_0 \boldsymbol{M}$$

as $\boldsymbol{B}$ is much greater than $\boldsymbol{H}$ in most of these materials.

The first theory to account for the existence of ferromagnetic solids was proposed by Weiss. He suggested that an internal 'molecular' field existed inside the magnetic compound and that this acted to align the magnetic moments of neighbouring atoms. The result was that a magnetisation was present even when the magnetic field was zero. Equation (S4.11) in Section S4.4 is replaced by Equation (12.17):

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \lambda \boldsymbol{M}) \tag{12.17}$$

where λ is the molecular field constant that indicates the strength of the molecular field. The resulting magnetisation of the solid is then given by Equation (12.11).

The Brillouin function, $B_J(x)$, is now a function of M:

$$x = \frac{g_J \mu_B J B}{kT} = \frac{g_J \mu_B J(H + \lambda M)}{kT}$$

Equation (12.11) cannot be solved analytically and, in the past, graphical solutions have been utilised. Nowadays, it is easier to use a computer to give numerical results. The way in which the value of M_s varies with temperature is shown in Figure 12.7. There are three special cases to note.

- Case 1: $T = 0\,\text{K}$, $M = M_{\text{sat}} = N g_J \mu_B J$

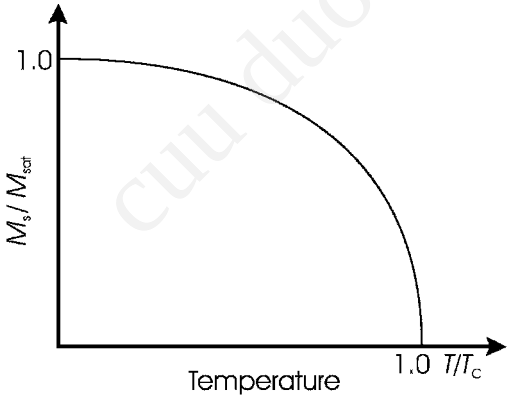

Figure 12.7 Variation of the relative spontaneous magnetisation, M_s/M_{sat}, as a function of relative temperature, T/T_C. When $T = 0$ the magnetisation is equal to the saturation magnetisation, M_{sat}. When $T = T_C$, the Curie temperature, the spontaneous magnetisation is zero

- Case 2: $T = T_C$, $M = 0$,

$$T_C = \frac{N \mu_0 g_J^2 \mu_B^2 J(J+1)\lambda}{3k} = \lambda C \tag{12.18}$$

- Case 3: $T \gg T_C$,

$$\chi = \frac{N \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k(T - \lambda C)} = \frac{C}{T - T_C} \tag{12.19}$$

The theory gives good agreement with the observations. Equation (12.18) shows that a high molecular field corresponds to a high Curie temperature, as one would expect. When there is a high interaction between the magnetic dipoles, it will be harder to disrupt the ordering by temperature effects alone. Equation (12.19) shows that ferromagnetic compounds obey the Curie–Weiss law well above a transition temperature, T_C, at which the material loses its ferromagnetic properties.

12.3.2 Exchange energy

The interaction that leads to the molecular field is quantum mechanical in origin and is related to the electron interactions that lead to chemical bonding. It is called the exchange interaction, giving rise to the exchange energy. To illustrate this concept we will focus on the important 3d orbitals. The electron distribution in an atom or an ion with several d electrons results from electrostatic repulsion between these electrons. This interaction is equivalent to the classical Coulomb repulsion between like charges, and is called the Coulomb repulsion. The total contribution to the energy is obtained by summing all the various electron–electron interactions, and is summarised as the Coulomb integral. This energy term is decreased if the electrons avoid each other as much as possible. Now, electrons with opposite spins tend to occupy near regions of space, whereas electrons with parallel spins tend to avoid the same regions of space. Thus, the electrostatic energy is decreased if the electrons all have parallel spins. In this case, as we know, they occupy different d orbitals, as far as possible. The energy decrease due to the preference for parallel spins is called the exchange energy. This idea has been encountered as Hund's first rule (Section S1.3.2) which says that in a free atom the state of lowest energy, the ground state, has as many electrons as possible with parallel spins. This is the same as saying that the ground state of a free atom has a maximum value of the spin multiplicity, or the equivalent quantum number *S*.

However, when the atom is introduced into a solid or a molecule another interaction, chemical bonding, is important. Chemical bonding is the result of placing electrons from neighbouring atoms into bonding orbitals. For bonding to occur, and the energy of the pair of atoms to be lowered, the electron spins must be antiparallel. However, the exchange interaction between electrons on neighbouring atoms is still present, tending to make the electron spins adopt a parallel orientation. In general, bonding energy is greater than the exchange energy, and paired electrons are more often found in solids and molecules. However, if the bonding forces are weak, the exchange energy can dominate, and unpaired electrons with parallel spins are favoured.

The 3d transition metals are notable in that the d orbitals do not extend far from the atomic nucleus, and so bonding between d orbitals is weak and the exchange energy is of greater importance. As one moves along the 3d-elements, it is found the d orbitals become more compact, making bonding less favourable and increasing the exchange energy. The interplay between bonding energy and exchange energy can be pictured in terms of the ratio of *D*/*d*, where *D* is atomic separation of the interacting atoms, and *d* is the diameter of the interacting *d* orbitals. A plot of *D*/*d*, against exchange interaction, a Bethe–Slater diagram, is shown in Figure 12.8. If the value of the exchange interaction is positive then ferromagnetism is to be expected. Of all of the 3d transition metals, only Fe, Co and Ni have positive values of *D*/*d*, and these are the only ferromagnetic 3d transition elements. The lanthanides have slightly positive values of *D*/*d* and are expected to be weakly ferromagnetic.

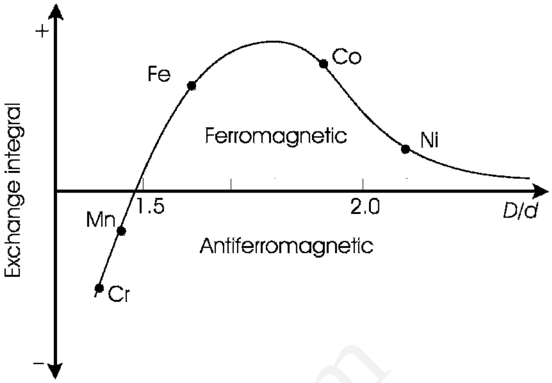

Figure 12.8 The Bethe–Slater curve for the magnitude of the exchange integral as a function of D/d, where D is the separation of the atoms in a crystal, and d is the diameter of the 3d orbital

12.3.3 Antiferromagnetism and superexchange

The interaction between the d orbitals giving rise to the conflict between the exchange energy and the bonding energy does not operate so simply in many compounds. In these, the transition metal ions are separated by a nonmetal such as oxygen, and the compounds are antiferromagnetic. The interaction of the d orbitals on the cations via the intermediate anion is called superexchange. It occurs in transition metal oxides such as nickel oxide, NiO, which is a typical antiferromagnetic.

In nickel oxide, the Ni^{2+} ions have eight d electrons. The oxide would be expected to be paramagnetic, as the Ni^{2+} ions are separated from each other by nonmagnetic oxygen ions. Instead, antiferromagnetic ordering occurs, and the magnetic susceptibility increases with temperature up to 250 °C before showing paramagnetic behaviour. The coupling between the ions leading to an antiferromagnetic ordering is related to a degree of covalent bonding between the Ni^{2+} and O^{2-} ions. The nickel atoms in NiO have an octahedral coordination, and the d orbitals are split by the crystal field (Section S4.5), so that the $d_{x^2-y^2}$ and d_{z^2} orbitals each contain one unpaired electron. As drawn schematically in Figure 12.9, an unpaired d electron in

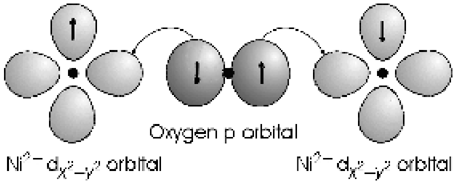

Figure 12.9 Superexchange leading to antiferromagnetic alignment of spins on cations

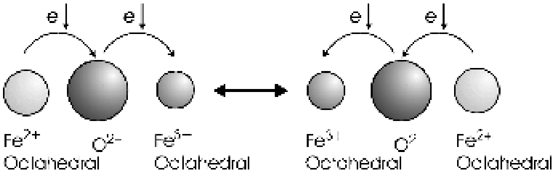

Figure 12.10 Double exchange, possible only with ferromagnetic alignment of spins on cations

the $3d_{x^2-y^2}$ orbital can have a covalent interaction with an electron in a filled p orbital, but only if the electrons have opposed spins. The oxygen 'spin down' electron will interact with a d orbital in which the electron is 'spin up'. This is true for both Ni^{2+} ions either side of an oxygen ion. In this case, as shown, the arrangement leads to an antiferromagnetic alignment of the unpaired d electrons on the Ni^{2+} ions. This is generally true, and superexchange tends to lead to an antiferromagnetic ordering in a solid.

It would be expected that the Néel temperature would increase with the degree of covalency, and this is found to be so. Table 12.3 shows that the Néel temperature for the series of 3d transition metal oxides MnO, FeO, CoO and NiO increases in the direction from MnO to NiO, as the covalent nature of the solids increase. Additionally, the dumbbell shape of the p orbitals suggests that the interaction should be greatest for a linear *M*–O–*M* configuration and minimum for a 90° angular *M*–O–*M* configuration. The oxides MnO, FeO, CoO and NiO all have the *halite* structure in which the linear *M*–O–*M* configuration holds, with metal ions at the corners of the cubic unit cell and oxygen ions at the centre of the cell edges. Thus, it becomes apparent that both chemical bonding and crystallography have a part to play in deciding on the effectiveness of magnetic interactions. This aspect is marked in the ferrimagnetic compounds.

12.3.4 Ferrimagnetism and double exchange

In ferrimagnetic materials two subsets of magnetic moments exist, with one of the subsets in an antiparallel arrangement with respect to the first, as illustrated in Figure 12.3(j). The observed magnetic moment is due to the difference between the two sets of magnetic dipoles. Many of the magnetic ceramics are ferrimagnetic materials. The ancient 'lodestone', Fe_3O_4, is a ferrimagnetic. Above the Néel temperature (858 °C for Fe_3O_4), the material reverts to paramagnetic behaviour.

In the ferrimagnetic state, there are several interactions between the spin subsets. As with the antiferromagnetic compounds, they can only be understood in terms of the crystal structures and the chemical bonding in the compounds. The most important feature of ferrimagnetic materials is that two valence states must exist for the cations. In the case of Fe_3O_4, these are Fe^{2+} and Fe^{3+}. Other ion pairs, such as Mn^{2+} and Mn^{3+}, can also behave in the same way. The coupling between these ions in called double exchange. In this mechanism, the two ions are separated by an anion such as oxygen (Figure 12.10). An Fe^{2+} ion, for example, transfers an electron to an adjacent O^{2-} ion which simultaneously transfers one of its electrons to a neighbouring Fe^{3+} ion. In essence, the electron hops from Fe^{2+} to Fe^{3+} via the intermediate oxygen ion. The charges on the Fe ions are reversed in the process. Because all of the orbitals on the oxygen ion are full, and electrons are spin paired, a 'spin-down' electron moving from Fe^{2+} will displace a 'spin-down' electron from O^{2-} onto Fe^{3+}. This double exchange is favourable only if there are parallel spins on the two cations involved. Thus, double exchange leads to ferromagnetic ordering.

The other important factor in ferrimagnetic compounds is the crystal structure of the compound. This can also be illustrated by the oxide Fe_3O_4, which adopts the inverse *spinel* structure (see Section 5.3.10). In this structure the cations are distributed between tetrahedral sites and octahedral sites in the following way, $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$, where (Fe^{3+}) represents cations in tetrahedral sites, and $[Fe^{2+}Fe^{3+}]$ represents cations in octahedral sites. In Fe_3O_4, the Fe^{2+} and Fe^{3+} cations that take part in double exchange are restricted to those that occupy the octahedral sites. The population of Fe^{3+} ions in the tetrahedral sites is not involved. The reason for this separation lies with the d-orbital energies, which are controlled by the crystal field splitting (see Section S4.5). The d-orbital energy of a cation in an octahedral site is quite different from that of a cation in a tetrahedral site. This difference in energy prevents double exchange between Fe^{2+} ions in octahedral sites and Fe^{3+} ions in tetrahedral sites. However, superexchange is possible between the occupants of the octahedral and tetrahedral sites, which tends to give an antiferromagnetic ordering between these cations.

The outcome of these two interactions is the ferrimagnetic structure. In general, therefore, ferrimagnetic compounds have a common cation in two valence states and two sets of different sites over which these cations are ordered. Many crystalline structures potentially fulfil these requirements, including the cubic and hexagonal ferrites, described in Sections 12.3.5 and 12.3.6.

The saturation magnetisation, $\boldsymbol{M}_s$, of ferrites, can be estimated by assuming the spin-only magnetic moments listed in Table 12.2 apply. It is necessary to determine, from the crystal structure, which spins cancel, and then assuming all the excess moments are completely aligned:

$$\begin{aligned}\boldsymbol{M}_s &= (\text{number of unpaired dipoles per unit volume}) \\ &\quad \times (\text{magnetic moment on each dipole}) \\ &= N_{\text{unpaired}}\ \boldsymbol{m}_{\text{ion}}\ \mu_B\end{aligned}$$

where $\boldsymbol{m}_{\text{ion}}$ is taken from Table 12.2. The equation for the inductance (see Section S4.4),

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} + \mu_0 \boldsymbol{M}$$

can be approximated to

$$\boldsymbol{B} = \mu_0 \boldsymbol{M}$$

as $\boldsymbol{B}$ is much greater than $\boldsymbol{H}$ in most of these materials.

12.3.5 Cubic spinel ferrites

Ferrites with the cubic *spinel* structure (see Section 5.3.10) are soft magnetic materials (see Section 12.4.3), widely used in electronic circuitry. The formula of all ferrites can be written as $A^{2+}Fe_2^{3+}O_4$, where A^{2+} can be chosen from a large number of medium-sized cations, for example Ni^{2+} or Zn^{2+}. The majority of the important ferrites are inverse *spinels*, in which the A^{2+} cations occupy the octahedral sites, together with half of the Fe^{3+} ions. The other half of the Fe^{3+} cations is found in the tetrahedral sites. Thus nickel ferrite would be written $(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4$, where the cations in octahedral sites are enclosed in square brackets and those in tetrahedral sites in parentheses. Lodestone, or magnetite, Fe_3O_4, described in Section 12.3.4, is an example in which the cations are Fe^{2+} and Fe^{3+}, and the cation distribution is $(Fe^{3+})[Fe^{2+}Fe^{3+}]_2O_4$.

The magnetic properties of the ferrites can be tailored by changing the A^{2+} cations present. This chemical manipulation of physical properties is widely used and is the cornerstone of silicon electronics. In the ferrites, dopant cations substitute for the A^{2+} and Fe^{3+} ions present. There is great flexibility in this, as not only can the ions be changed but also the distribution over the octahedral and tetrahedral sites. Some ions, such as Cr^{3+}, have a strong preference for octahedral sites and are rarely found in tetrahedral sites. Other ions, such as Fe^{3+}, can adapt to either geometry more easily. Complex mixtures of cations, for example $Ni_aMn_bZn_cFe_dO_4$, are often used to tailor quite specific magnetic behaviour. In all of these complex formulae, remember that the total of the cations must be in accord with the *spinel* formula, $A^{2+}B_2^{3+}O_4$, both with respect to the total numbers but also with respect to the charges.

In reality, the distribution of the cations is rarely perfectly normal or inverse, and the distribution tends to vary with temperature. As the magnetic properties depend sensitively on the cation distributions, processing conditions are important if the desired magnetic properties are to be obtained.

12.3.6 Hexagonal ferrites

An important group of ferrites is known that have hard magnetic properties (see Section 12.4.3). As in the case of the cubic ferrites, they are derived from a single structure type, this time that of magnetoplumbite, $Pb^{2+}Fe^{3+}_{12}O_{19}$. As can be seen, all of the Fe ions are trivalent. The unit cells of these phases are hexagonal, hence the general name of hexagonal ferrites. The variety of ferrites derived from magnetoplumbite is achieved in the same way as the cubic ferrites, by substitution of the cations present by others. The magnetic properties of the hexagonal ferrites can be changed by fine-tuning the amounts and types of M^{2+} and M^{3+} ions in the structure, which can substitute for the Pb^{2+} and the Fe^{3+} cations present. However, the system is more complex than that of the cubic *spinels*, in which only one parent structure forms. In the hexagonal ferrites hundreds of structures occur.

The two simplest hexagonal ferrites, $BaFe_{12}O_{19}$, known as ferroxdure, and $SrFe_{12}O_{19}$, are widely used as permanent magnets in many applications, especially in electric motors. The structure of both is the magnetoplumbite type. The structure can be illustrated by describing $BaFe_{12}O_{19}$, which is built from a close packing of oxygen and oxygen-plus-barium layers (Figure 12.11). There are 10 of these layers in the unit cell, which contains two $BaFe_{12}O_{19}$ formula units. Using the description of close-packed layers described in Section 5.4.1, the relative positions are:

$$A\ B'\ A\ B\ C\ A\ C'\ A\ C\ B$$

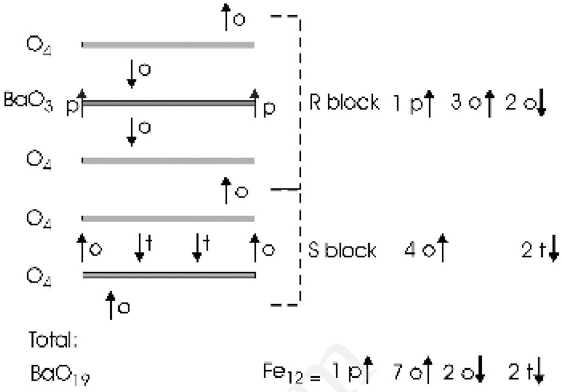

Figure 12.11 The idealised structure and spin arrangement of $BaFe_{12}O_{19}$. Half of the unit cell is drawn, composed of one R block and one S block. The composition of the cubic close-packed layers (wide lines) is indicated on the left-hand side. The spin directions on the cations are represented by arrows, and the coordination of the cations by letters; o = octahedral, t = tetrahedral, p = trigonal prismatic. The overall composition and spin status is summarised at the bottom of the diagram

where the symbols B′ and C′ represent mixed barium and oxygen, BaO_3, layers, and the other symbols represent oxygen-only, O_4 layers. These 10 layers are thought of as being arranged in a sequence of four alternating slices, two that resemble spinel, called S blocks, and two containing the BaO_3 layer, called R blocks. Half a unit cell, consisting of one R block and one S block, is drawn in Figure 12.11. [In the lower half of the cell the R and S blocks are inverted with respect to those shown, but the site geometries remain the same.] The Fe^{3+} cations occupy nine octahedral sites, two tetrahedral sites and one trigonal pyramidal (five-coordinate) site per $BaFe_{12}O_{19}$ unit. The arrangement of the spins on the Fe^{3+} ions in these sites is such that four point in one direction, parallel to the hexagonal *c* axis, and the other eight point in the opposite direction. The arrangement is different from that shown in Figure 12.3(j), because the spins are all of the same magnitude and, in this case, the numbers of spins are unbalanced. Because the spins are aligned along the crystallographic *c* axis, the materials show a high degree of anisotropy. The hexagonal ferrites are widely used in permanent ceramic magnets.

12.4 Microstructures of ferromagnetic solids(1)

12.4.1 Domains

So far, in this discussion, emphasis has been laid on the atomic interactions that lead to magnetic properties. Especially in ferromagnetic solids, the microstructure of the solid is of importance and dominates applications. The microstructures found are the result of long-range interactions between the elementary magnets. For an isolated atom or ion with unpaired electron spins, no interaction occurs between the elementary magnets, and magnetic properties are reflected in a Curie law type of dependence.

When the magnetic atoms are not isolated, as in ferromagnetic solids, interactions that are more complex arise. These are revealed by the way in which such materials respond to being magnetised in an external magnetic field. All ferromagnetic substances remain magnetised to some extent after the external field is removed, and this feature characterises ferromagnetism. Some materials retain a state of magnetisation almost indefinitely. These are called magnetically hard materials and are used to make permanent magnets. However, many ferromagnetic materials appear to lose most of their magnetisation rather easily. These are called magnetically soft materials.

If the ordering forces between the atomic magnetic moments are strong enough to lead to ferromagnetism, it is reasonable to ask why ferromagnetic materials often show no obvious magnetic properties. The answer lies in the microstructure of hard and soft magnetic solids. On a microscopic scale, all such crystals are permanently magnetised but are composed of magnetic domains or 'Weiss domains'. Domains are regions that have all of the elementary magnetic dipoles aligned (Figure 12.12a), but the directions in neighbouring domains are different, so that the net result is that the external magnetic field is very small. Domains are distinct from the grain structure of a metal and occur in single crystals as well as in polycrystalline ferromagnetic solids, and the geometry of the domains varies from one ferromagnetic solid to another. Ferromagnetic materials, like ferroelectrics, belong to the group of ferroic materials.

Two main interactions need to be considered in order to understand domain formation, an electrostatic interaction and a dipole–dipole interaction. The parallel ordering, as we know, is caused by the exchange energy. This is effectively electrostatic and short range, and is equivalent to the ionic bonding forces described in Section 2.1.2. The external magnetic field arising from the parallel dipoles gives rise to magnetostatic energy. This is reduced if the external field is reduced. One way of achieving this is to form the aligned dipoles into *closure domains* with antiparallel orientations (Figure 12.12b). This is achieved by the dipole–dipole interaction, which is one of the weak bonding forces described in Section 3.1.1. This interaction between the magnetic dipoles, which is long range, falls approximately as the cube of the distance between atoms. It leads to a preferred antiparallel arrangement of the dipoles.

When the two interactions are compared, it is found that at short ranges the electrostatic force is the most important, and an arrangement of parallel spins is of lowest energy. As the distance from any dipole increases, the short-range electrostatic interaction falls below that of the dipole–dipole interaction. At this distance, the system can lower its energy by reversing the spins (Figure 12.12c). The domains form as a balance between these two competing effects, short-range electrostatic and long-range dipolar. The balance is achieved for domains of 1–100 micrometers in size.

The alignment from one domain to the adjoining one is not abrupt but depends on the balance between the electrostatic and dipole interactions. The dipole orientation is found to change gradually over a distance of several hundred atomic diameters. This structure is called a domain or Bloch wall (Figure 12.13).

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(1) Ferromagnetic and ferrimagnetic materials behave in the same way with respect to the subject matter of this section. To avoid repetition, only the term ferromagnetic will be used, but it should be understood that ferrimagnetic materials are identical.

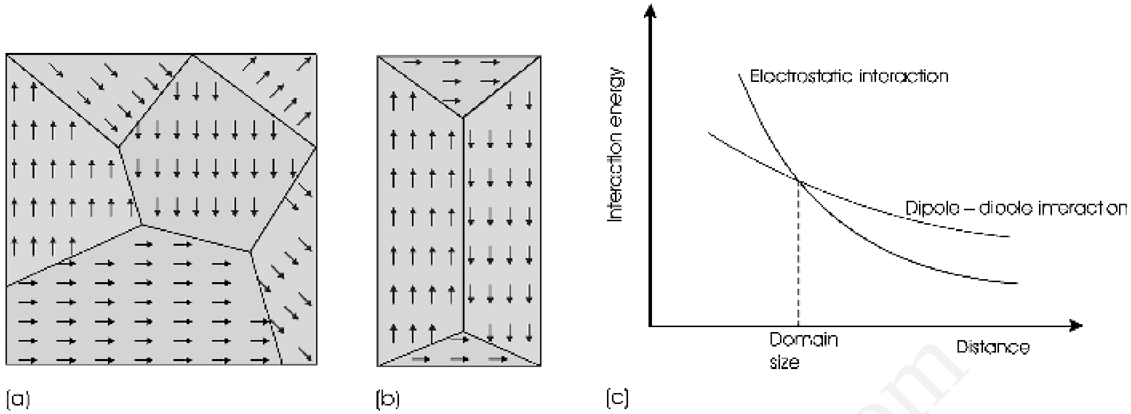

Figure 12.12 (a) Representation of Weiss domains; the magnetic dipoles are represented by arrows; (b) Domain closure; and (c) graph of interaction energy as a function of distance. The dipole–dipole interactions in the solid tend to produce antiparallel alignment of magnetic dipoles, and the electrostatic interactions a parallel alignment of magnetic dipoles. The domain size is a reflection of the point where these interactions balance

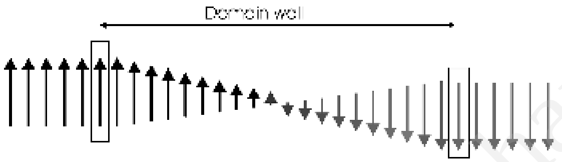

Figure 12.13 Schematic representation of a Bloch wall between two magnetic domains. On the far left the magnetic dipoles (arrows) point upwards. Moving the right they spiral through 180° until, at the for right, they point downwards. The extent of the wall is indicated by the magnetic dipoles enclosed in rectangles

The geometry of domains also depends on crystal structure. Most ferromagnetic solids are magnetically anisotropic. This means that the magnetic moments align more readily in some crystallographic directions than in others. These are known as 'easy' and 'hard' directions respectively. The domain geometry will reflect this crystallographic preference.

12.4.2 Hysteresis

In essence, the magnetic state of a ferromagnetic solid will depend on its history, a phenomenon called hysteresis. This is because the domain structure reflects the way in which the solid has previously been exposed to magnetic fields and to high temperatures. However, the state of magnetisation is reproducible and cycles in a constant fashion as a function of the direction and strength of an applied external magnetic field. Hysteresis is perhaps the most characteristic feature of strongly magnetic materials.

On placing a ferromagnetic material into a uniform external magnetic field, the dipoles tend to align themselves along the field direction. In a typical ferromagnetic solid, the alignment of some domains is favourable in that the magnetic moments of the constituents are already close to that of the external field. In other domains, the magnetic moments will be at an angle to the field or even opposed to it. The tendency to align with the field will be opposed by local effects in the solid, and at low field strengths little will happen. However, as the external field strength increases, some dipoles will rotate to align with the external field. The effect of this is that domains that are arranged so that the dipoles they contain are more or less aligned in the field direction will grow at the expense of those that are poorly aligned. Ultimately, all of the domains that remain will have parallel magnetic moments

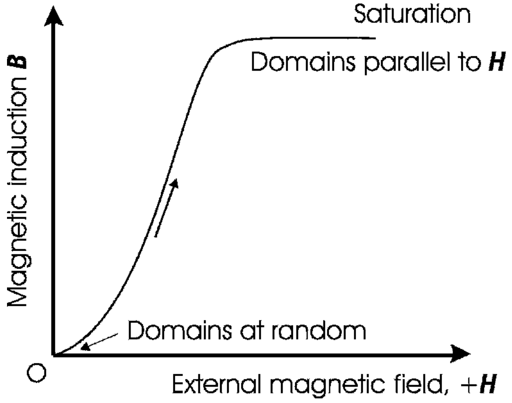

Figure 12.14 The initial part of a magnetic induction–external magnetic field (***B***–***H***) loop for a ferromagnetic solid

(Figure 12.14). At this point, the magnetisation of the sample will be a maximum and has reached saturation.

Reversal of the applied field will cause the magnetic moments to align in the opposite direction. Once again, this will be opposed by the internal energy of the solid, as new domain walls have to be created and domain walls must move. The ***B***–***H*** path will therefore not follow the original path, but will trace a new path that 'lags behind' (the definition of hysteresis) the old one (Figure 12.15). When the applied field reaches zero, the value of ***B*** is still positive, and this is called the remanence, B_r. The magnetic flux, ***B***, will be reduced to zero at a value of the applied field called the coercivity, H_c. Ultimately, domain alteration will cease when all the magnetic moments are now parallel to the reversed applied field and saturation is again reached. Reversal of the field once again will cause the value of ***B*** to trace a new path, but one that eventually reaches saturation in the initial direction. Repeated cycles now follow this outer pathway.

12.4.3 Hysteresis loops: hard and soft magnetic materials

The shape of the hysteresis loop for a ferromagnetic material is of importance. The area of the loop is a measure of the energy required to complete a hysteresis cycle. A soft magnetic material is one that is easily magnetised and demagnetised. The energy changes must be low, and the hysteresis loop has a small area (Figure 12.16). Soft magnetic materials are used in applications such as transformers, where the magnetic behaviour must mirror the variations of an electric current without large energy losses. Ferrites with the cubic *spinel* structure are generally soft magnetic

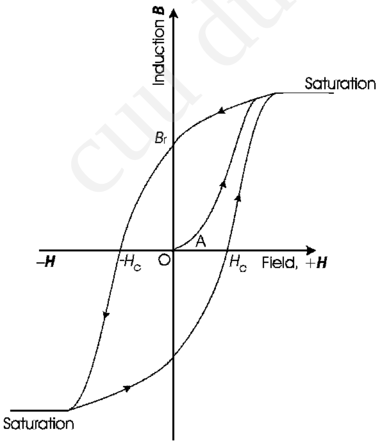

Figure 12.15 The complete ***B***–***H*** (hysteresis) loop of a ferromagnetic solid

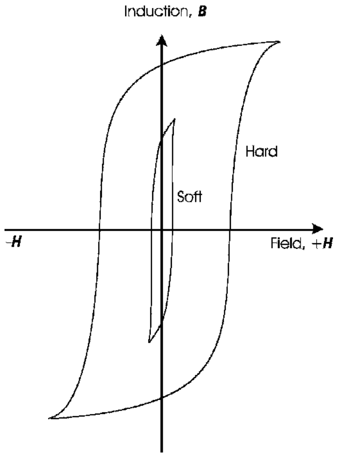

Figure 12.16 Schematic ***B***–***H*** loops for soft and hard magnetic solids

materials. The value of the saturation magnetisation is sensitive to the composition of the material, and the formulae of cubic ferrites are carefully tailored to give an appropriate value. However, the shape of the hysteresis loop is strongly influenced by the microstructure of the solid. Grain boundaries and impurities hinder domain wall movement and so change the coercivity and remanence of a sample. Ferrites for commercial applications not only have to have carefully chosen compositions but also have to be carefully fabricated in order to reproduce the desired magnetic performance.

Hard magnetic materials have rather rectangular, broad, hysteresis curves (Figure 12.16). These materials are used in permanent magnets, with applications from door catches to electric motors. The hexagonal ferrites are hard magnetic materials, as are alloys such as $SmCo_5$ and $Nd_2Fe_{14}B$.

Naturally, there is a continuum of magnetic materials between soft and hard magnetic materials, and the characteristics of any particular solid are tailored to the application. Of these, magnetic storage of information is of great importance. The data are stored by magnetising small volumes of the storage material, often a thin film deposited on a solid surface or a flexible tape. The magnetic material that receives the signal to be stored must be soft enough magnetically to respond quickly to small energising electric signals but be hard enough magnetically to retain the information for long periods.

12.5 Free electrons

So far, in this chapter, the band model of the solid has been ignored. This is because magnetism is associated with the d and f orbitals. These orbitals are not broadened greatly by interactions with the surroundings and even in a solid remain rather narrow. The resulting situation is quite well described in terms of localised electrons placed in d or f orbitals on a particular atom. However, some aspects of the magnetic properties of solids can be explained only by band theory concepts.

12.5.1 Pauli paramagnetism

Most metals show paramagnetic behaviour. It is rather small and independent of temperature and is quite different from the Curie law behaviour of a 'normal' paramagnetic ion. The cause of the weak paramagnetism was explained by Pauli in terms of the Fermi–Dirac statistics of electrons in solids. It is known as Pauli paramagnetism.

As outlined in Section 2.3, electrons in a normal metal occupy the (partly filled) uppermost band. All of the electrons are spin-paired, with two electrons being allocated to each energy state. In this state, the metal would be diamagnetic. A small change takes place when the metal is placed in a magnetic field. Those electrons with a spin parallel to the magnetic field have a slightly lower energy than those with a spin opposed to the magnetic field. Those electrons near the very top of the (partly filled) conduction band (i.e. those at the Fermi surface) can reorient themselves in the applied magnetic field. This results in an imbalance in the numbers of 'spin-up' and 'spin-down' electrons, and the metal becomes paramagnetic. Calculation shows that the number influenced is very small (for the same reason that the specific heat contribution of the electrons is very small) and so the magnetic susceptibility is small. The position is drawn in Figure 12.17. The paramagnetic susceptibility χ is

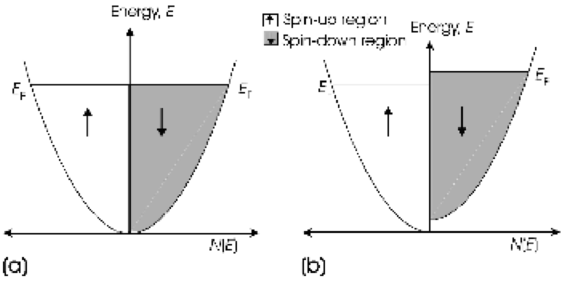

Figure 12.17 (a) The density of states, $N(E)$, for electrons in a metal is made up of equal numbers of spin-up and spin-down electrons. In the absence of a magnetic field, these are of equal energy. (b) The application of a magnetic field causes these to separate in energy. The electrons opposed to the field have a slightly higher energy than those parallel to the field

proportional to the density of states at the Fermi level, $N(E_F)$, and it is found that

$$\chi \propto \mu_0 \mu_B N(E_F),$$

where μ_0 is the permittivity of free space and μ_B the Bohr magneton. Thus, a measurement of the Pauli paramagnetism of a normal metal provides a method of assessing the density of states at the Fermi level. Temperature does not change the numbers of electrons at the Fermi surface appreciably, and so the paramagnetism is virtually temperature-independent.

All electrons not in the conduction band will be in filled shells, paired, and not magnetically active.

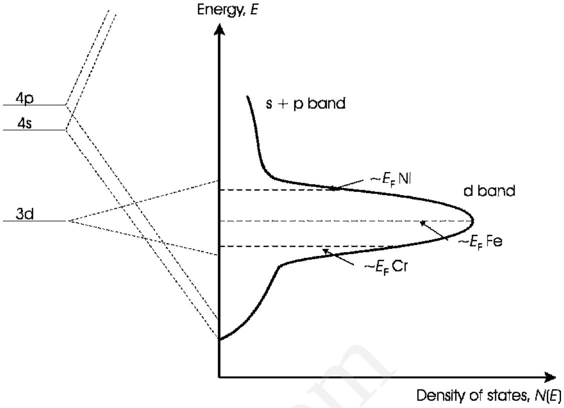

Figure 12.18 Energy band overlap of 3d, 4s and 4p orbitals for the 3d transition metals

12.5.2 Transition metals

The band model just outlined would lead to the expectation that all metals would show Pauli paramagnetism. However, three 3d transition metals, iron, cobalt and nickel, together with a few lanthanides, are ferromagnetic metals. The simple band picture must be expanded to account for this complication.

To illustrate this, consider the situation in the 3d transition metals. The electron configuration and measured magnetic moments of these metals is given in Table 12.4, and the band picture is illustrated in Figure 12.18. The d band is narrow and is overlapped by broad outer bands from the s and p orbitals. The s and d electrons will be allocated to this composite band. [However, it is still to be expected that the number of 'spin-up' and 'spin-down' electrons will be identical.] Now, a stable ferromagnetic state can arise only if there is an excess of spins that are parallel and maintained in this state by the exchange energy of the system. To obtain this, energy must be supplied to promote electrons at the Fermi energy so that they can reverse spins. The rather small energy needed to produce Pauli paramagnetism is donated by the magnetic field. When this is removed, the separation of the spin states vanishes. In a ferromagnetic metal, the exchange energy must be sufficient to counterbalance the increase in energy of the electrons at the Fermi level. The balance depends on the form of the $N(E)$ curve, especially in the region of the Fermi surface. The 4s and 4p bands are broad, with a low density of states at the Fermi level, so that relatively small numbers of electrons are promoted. The gain in exchange energy is not sufficient to balance the energy outlay, and the metal remains paramagnetic. In contrast, the 3d band is narrow, with a high density of states at the Fermi level. Larger numbers of electrons can be promoted and reverse spin, leading to greater exchange energy. This is sufficient to stabilise the ferromagnetic ordering.

Table 12.4 Magnetic moments and electron configurations of the ferromagnetic 3d transition metals

Element	Electron configuration	Magnetic moment/μ_B
Iron, Fe	[Ar] $3d^6$ $4s^2$	2.22
Cobalt, Co	[Ar] $3d^7$ $4s^2$	1.72
Nickel, Ni	[Ar] $3d^8$ $4s^2$	0.6

When the density of states at the Fermi surface is calculated with a high precision, it is found that only the three metals iron, cobalt and nickel will have sufficient exchange energy to retain a ferromagnetic state. The experimental value of the magnetic moment (Table 12.4) is also calculated to be equal to the number of holes in the d band. Thus, the d band of iron contains 7.78 electrons, (2.22 holes), that of cobalt contains 8.28 electrons (1.72 holes), and that of nickel contains 9.4 electrons (0.6 holes).

The magnetic properties of alloys of these ferromagnetic metals with nonmagnetic metals confirm this interpretation. For example, both copper and zinc have 10 d electrons. As they are alloyed with a ferromagnetic metal, the d band is filled and the ferromagnetic properties diminish. These vanish when the d band is just filled with electrons. A good example is provided by the nickel–copper system, because the alloys all have the same face-centred cubic crystal structure as the parent Ni and Cu phases (see Section 4.2.2). The electron configuration of copper is [Ar] $3d^{10}\,4s^1$, and in this metal the 3d band is filled. As copper is added to nickel to form the alloy, the excess copper electrons are added to the d band to gradually fill it. At 20 °C, the ferromagnetic–paramagnetic change occurs at a composition of 31.5 wt% copper, that is, approximately $Ni_{235}\,Cu_{100}$.

Exact details of the magnetic properties of most alloys depend on the crystal structures of the alloys and the form of the density of states curve at the Fermi level, as well as the relative proportions of the metals present.

12.6 Nanostructures

12.6.1 Small particles and data recording

The magnetic properties of very small particles have been of interest for a considerable period. The earliest applications of these properties arose in the use of magnetic particles for magnetic recording media. The essence of magnetic data storage is the existence of two easily distinguished magnetic states. Magnetic data storage uses a thin magnetisable layer laid down on a tape or disc. A ‘write head’ generates an intense magnetic field that changes the direction of magnetisation in the surface material. The induced magnetisation pattern in the layer is the stored data. The data are read by sensing the magnetic field changes by using a ‘read head’.

The data storage layers are composed mostly of small magnetic particles in a polymer film. The magnetic response of the film depends critically on the domain structure of the particles and the particle shape. Ideally, small single-domain particles are used, each of which has only two directions of magnetisation, directed along the + and − directions of a single crystallographic axis. The direction is switched by the ‘write head’ and sensed by the ‘read head’.

The commonest magnetic particles in use at present are γ-Fe_2O_3, or maghemite, cobalt doped γ-Fe_2O_3, and chromium dioxide, CrO_2, all of which have acicular (needle-shaped) crystals. Chromium dioxide is a ferromagnetic oxide with the rutile structure. The crystal structure of γ-Fe_2O_3 is curious. Despite its formula, it has the *spinel* structure, and is closely related to the inverse *spinel* magnetite, $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$, where round brackets enclose cations on tetrahedral sites and square brackets enclose cations on octahedral sites. γ-Fe_2O_3 is a ferrimagnetic *spinel* that has a formula $(Fe^{3+})[Fe^{3+}_{5/3}Va_{1/3}]O_4$, where Va represents vacancies on octahedral Fe^{2+} sites. It is thus a ferrite with an absence of M^{2+} ions. The direction of magnetisation in all of these compounds corresponds to the needle axis. The crystallites are aligned in a colinear array, with the needle axis parallel to the direction of motion of the tape or disc, by applying a magnetic field during the coating operation. This is called the longitudinal orientation or direction.

12.6.2 Superparamagnetism and thin films

Domain walls are created because of the competition between long-range dipole–dipole interactions, which lead to an antiparallel alignment of magnetic dipoles, and short-range electrostatic interactions, which tend to produce a parallel alignment of magnetic dipoles. When particles of a magnetic solid are below the domain size, the electrostatic interactions dominate (Figure 12.12c). The magnetic dipoles tend to align parallel to each other, and a *superparamagnetic* state results. This need not only occur in small particles. Isolated clusters of magnetic atoms or ions in a solid can also exhibit this feature. For example, nanoclusters of ferromagnetic particles embedded in polymers often show superparamagnetic behaviour, as can small magnetic precipitates in a nonmagnetic matrix. The same seems to be true of the magnetic particles that occur in certain bacteria that are able to navigate along the Earth's magnetic field gradient.

The same interactions lead to the observation that the magnetisation in thin films changes with film thickness. In thick films, of ordinary dimensions, domains form and the magnetic flux is trapped in the film (Figure 12.19a). When the thickness of a film is reduced to below single domain size, the magnetic dipoles align in a parallel direction in a longitudinal manner. The film has a north and a south pole at it extremities (Figure 12.19b). An external magnetic field is now detectable that runs more or less parallel to the film surface. Further reduction in film thickness to just a few atom layers results in the individual electron spins realigning normal to the film plane. North and south poles are now on the film surfaces, and the external magnetic field lies perpendicular to the film plane (Figure 12.19c). The implications of these scale effects are of importance in attempts to increase the density of magnetic recording media.

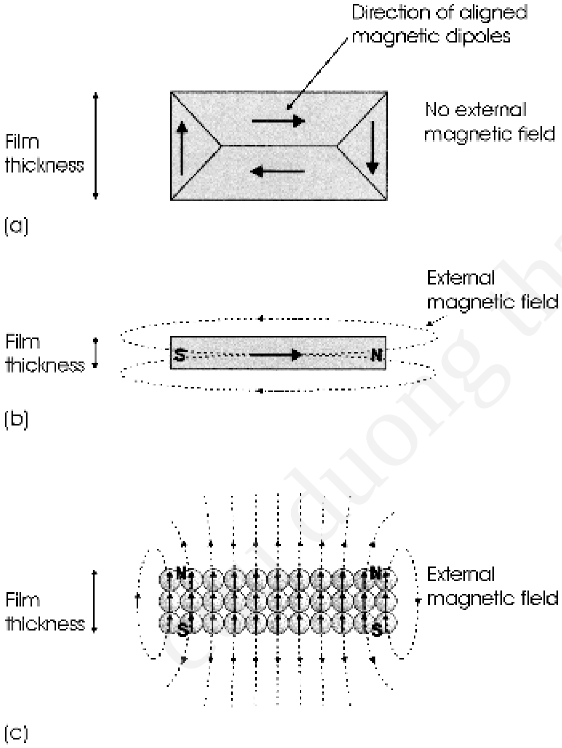

Figure 12.19 (a) Domain closure in a bulk film prevents magnetic flux from escaping. (b) A film less than a domain wide has magnetic dipoles aligned, so the flux escapes longitudinally; acicular crystals in magnetic recording media are ideally in this form. (c) A thin film of the order of one atomic thickness has elementary dipoles aligned perpendicular to the film, allowing flux to escape normal to the film

12.6.3 Molecular magnetism

The ultimate size limit for magnetic recording of data may well rest with magnetic molecules in which the cations show high-spin and low-spin states. For example, consider a single 3d transition metal ion such as Fe^{2+} in an octahedral crystal field (Section S4.5). There are two magnetic states, corresponding to the high-spin and the low-spin configurations (Figure 12.20). The low-spin state is diamagnetic, with the spin quantum number, S, zero, and the high-spin state is paramagnetic, with the spin quantum number, S, equal to two.

The crystal field-splitting energy between the t_{2g} and e_g set of orbitals is generally similar to the energy of visible light. This means that the magnetic

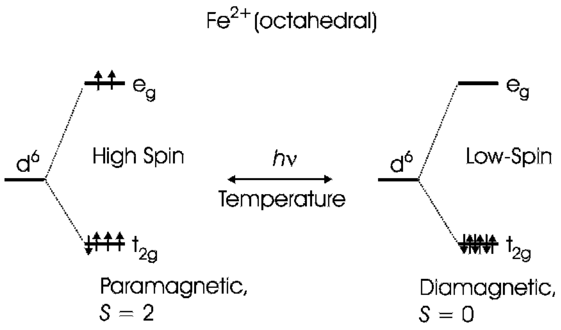

Figure 12.20 The Fe^{2+} ion in an octahedral crystal field can exist in either a high-spin or a low-spin state. These two states have different magnetic properties, and can be interconverted by radiation and heat energy

behaviour of a material can be changed by irradiation of light of a suitable wavelength, which will promote electrons from the lower-energy to the upper-energy state. Molecules in which this state of affairs can occur are known as spin-crossover complexes. In them, a magnetic state can be switched from, say, diamagnetic to paramagnetic, by irradiation, resulting in *photoinduced magnetism*. It is clearly possible to consider this as a potential data-storage unit.

In practice, Fe^{2+} ions are not isolated, but exist in compounds. The distribution of the ions between the high-spin and low-spin states will depend on molecular interactions and the temperature. If the transition-metal ions are linked by chemical bridges involving strong interactions, it is possible to induce a cooperative interaction between the cations, so that all cross over at once. There is still a long way to go before isolated ions are used to store bits of data, but research in this area is making rapid progress.

Answers to introductory questions

What atomic feature renders a material paramagnetic?

Paramagnetic solids are those in which some of the atoms, ions or molecules making up the solid possess a permanent magnetic dipole moment. These dipoles are isolated from one another. The solid, in effect, contains small, noninteracting atomic magnets. In the absence of a magnetic field, these are arranged at random and the solid shows no net magnetic moment. In a magnetic field, the elementary dipoles will attempt to orient themselves parallel to the magnetic induction in the solid, and this will enhance the internal field within the solid and give rise to the observed paramagnetic effect. The alignment of dipoles will not usually be complete, because of thermal effects and interaction with the surrounding atoms in the structure. Moreover, the orientation of the spins changes continuously. The magnetic susceptibility, χ, of a paramagnetic solid is positive and slightly greater than 1.

Why do ferromagnetic solids show a domain structure?

Two main interactions need to be considered in order to understand domain formation, a dipole–dipole interaction and an electrostatic interaction. The parallel arrangement of the spins is caused by the exchange energy. This is effectively electrostatic and short-range. The external magnetic field arising from the parallel dipoles gives rise to magnetostatic energy. This is reduced if the external field is reduced. One way of achieving this is to form the aligned dipoles into closure domains with antiparallel orientations. This is achieved by the dipole–dipole interaction, which is long-range, and leads to a preferred antiparallel arrangement of the dipoles. When the two interactions are compared, it is found that at short ranges the electrostatic force is the most important, and an arrangement of parallel spins is of lowest energy. As the distance from any dipole increases, the short-range electrostatic interaction falls below that of the dipole–dipole interaction. At this distance, the system can lower its energy by reversing the spins. The domains form as a balance between these two competing effects – short-range electrostatic and long-range dipolar. The balance is achieved for domains of 1–100 micrometers in size.

The alignment from one domain to the adjoining one is not abrupt but depends on the balance between the electrostatic and dipole interactions. The dipole orientation is found to change gradually over a distance of several hundred atomic diameters. This structure is called a domain or Bloch wall.

What is a ferrimagnetic material?

Ferrimagnetic materials behave rather like ferromagnetic materials. They have two different magnetic dipoles present, one of greater magnitude that the other. These line up in an antiparallel arrangement.

A ferrimagnetic solid shows complex temperature dependence because the distribution of the magnetic ions over the available sites is sensitive both to temperature and to the spin interactions.

Further reading

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Problems and exercises

Quick quiz

1 A Gouy balance cannot be used to investigate:
(a) Diamagnetic materials
(b) Paramagnetic materials
(c) Ferromagnetic materials

2 The material which is slightly attracted to a magnetic field is:
(a) Diamagnetic
(b) Paramagnetic
(c) Ferromagnetic

3 A material that does not contain any magnetic dipoles on atoms or ions is:
(a) A diamagnetic material
(b) A paramagnetic material
(c) An antiferromagnetic material

4 The Curie law describes the magnetic behaviour of:
(a) Paramagnetic solids
(b) Diamagnetic solids
(c) Ferrimagnetic solids

5 Above the Curie temperature, ferromagnetic materials become:
(a) Diamagnetic
(b) Paramagnetic
(c) Antiferromagnetic

6 The magnetic behaviour of ferromagnetic solids is described by the Curie–Weiss law:
(a) Above the Curie temperature
(b) Below the Curie temperature
(c) At low temperatures

7 The Néel temperature is the temperature at which an antiferromagnetic material becomes:
(a) Ferromagnetic
(b) Ferrimagnetic
(c) Paramagnetic

8 At high temperatures, the magnetic behaviour of ferrimagnetic materials can be described by:
(a) The Curie–Weiss law
(b) The Curie law
(c) Neither of these

9 A ferrimagnetic compound contains:
(a) All magnetic dipoles arranged parallel to one another
(b) Two sets of magnetic dipoles arranged antiparallel to each other
(c) One set of magnetic dipoles arranged in an antiparallel arrangement

10 The magnetic properties of electrons is due to:
(a) The electron spin only
(b) The orbital motion only
(c) Both the orbital motion and spin

11 Atoms and ions that show magnetic properties have:
(a) Only filled electron orbitals
(b) Only partly filled electron orbitals
(c) Some filled and some partly filled orbitals

12 The orbital contribution to the magnetic moment is quenched for:
(a) Lanthanide atoms and ions
(b) 3d transition metal atoms and ions
(c) Both lanthanides and transition metals

13 The number of room-temperature ferromagnetic elements is:
(a) Four
(b) Three
(c) Five

14 The Weiss molecular field constant describes:
(a) Magnetic interactions between dipoles in a ferromagnetic material
(b) Magnetic interactions between molecules in a paramagnetic material
(c) Bonding interactions between molecules in a ferromagnetic material

15 The exchange energy in a magnetic material is lower for electrons with:
(a) Parallel spins
(b) Antiparallel spins
(c) Paired electrons with no overall spin

16 The interaction of d orbitals and oxygen atoms that leads to antiferromagnetic ordering is called:
(a) Exchange
(b) Superexchange
(c) Double exchange

17 Ferrimagnetic compounds contain metal ions in:
(a) One valence state
(b) Two valence states
(c) Several valence states

18 The interaction between magnetic atoms in a ferrimagnetic material is called:
(a) Double exchange
(b) Superexchange
(c) Interaction exchange

19 Ferrites with the *spinel* structure are:
(a) Paramagnetic materials
(b) Ferromagnetic materials
(c) Ferrimagnetic materials

20 Most *spinel* structure ferrites have:
(a) A normal *spinel* structure
(b) An inverse *spinel* structure
(c) A ferromagnetic *spinel* structure

21 The general formula of cubic ferrites can be written:
(a) $A_2^{2+}\mathrm{Fe}_3^{3+}\mathrm{O}_4$
(b) $A^{2+}\mathrm{Fe}_2^{3+}\mathrm{O}_4$
(c) $A^{2+}\mathrm{Fe}_3^{3+}\mathrm{O}_4$

22 The general formula of hexagonal ferrites is:
(a) $A^{2+}\mathrm{Fe}_{12}\mathrm{O}_{19}$
(b) $A_2^{2+}\mathrm{Fe}_{12}\mathrm{O}_{19}$
(c) $\mathrm{BaFe}_{12}\mathrm{O}_{19}$

23 Hexagonal ferrites are:
(a) Paramagnetic materials
(b) Ferromagnetic materials
(c) Ferrimagnetic materials

24 Materials that lose their magnetism easily are called:
(a) Soft magnetic materials
(b) Hard magnetic materials
(c) Impermanent magnetic materials

25 Hexagonal ferrites are:
(a) Hard magnetic materials
(b) Soft magnetic materials
(c) Intermediate magnetic materials

26 The significant microstructure of a ferromagnetic solid is the presence of:
(a) Magnetic grains
(b) Magnetic domains
(c) Hysteresis

27 A magnetic domain is a region within which:
(a) All magnetic dipoles are parallel to the crystal axis
(b) All magnetic dipoles are parallel to the magnetic field
(c) All magnetic dipoles are aligned parallel to each other

28 A Bloch wall in a ferromagnetic solid:
(a) Is the external surface of the ferromagnetic region

(b) Is the region between two domains

(c) Is another name for a grain boundary

29 The walls between magnetic domains are the result of:

(a) Competition between long-range interactions and thermal energy

(b) Competition between short-range interactions and chemical bonding

(c) Competition between long-range and short-range interactions

30 Hysteresis is caused by:

(a) Rearrangement of magnetic domains in an applied magnetic field

(b) Rearrangement of grains in an applied magnetic field

(c) Disordering of magnetic dipoles in an applied magnetic field

31 Pauli paramagnetism refers to:

(a) The paramagnetic behaviour of ions

(b) The paramagnetic behaviour of ferromagnetic metals above the Curie temperature

(c) The paramagnetic behaviour of metals

32 The ferromagnetic properties of the 3d transition metals are explained by:

(a) The overlap of 3s and 3d orbitals

(b) The overlap of 3p and 3d obitals

(c) The overlap of 3d and 4s orbitals

33 Superparamagnetism can be observed in:

(a) Very small ferromagnetic particles

(b) Very small paramagnetic particles

(c) Paramagnetic particles in a nonmagnetic matrix

Calculations and questions

12.1 Determine the ground-state values of S, J, L and $\boldsymbol{m}$ for the f^3 ion Nd^{3+}.

12.2 Determine the ground-state values of S, J, L and $\boldsymbol{m}$ for the f^7 ion Gd^{3+}.

12.3 Determine the ground-state values of S, J, L and $\boldsymbol{m}$ for the d^4 ion Mn^{3+} in (a) the high-spin state and (b) the low-spin state.

12.4 Determine the ground-state values of S, J, L and $\boldsymbol{m}$ for the d^7 ion Co^{2+} in (a) the high-spin state and (b) the low-spin state.

12.5 Why don't lanthanide ions possess high-spin and low-spin states? [Note: answer is not provided at the end of this book.]

12.6 Show that the 'spin-only' formula

$$\boldsymbol{m} = g[S(S+1)]^{1/2}$$

is equivalent to

$$\boldsymbol{m} = [n(n+2)]^{1/2},$$

where n is the number of unpaired spins. [Note: derivation is not given in the answers at the end of this book.]

12.7 Estimate the saturation magnetisation, M_s, for a sample of ferromagnetic nickel metal (a) assuming only the unpaired d electrons contribute to the magnetism and the spins can be added as if the material were paramagnetic and (b) using the measured magnetic moment per nickel atom of 0.58 μ_B. The metal has an A1 structure with a cubic unit cell parameter of 0.3524 nm.

12.8 Estimate the saturation magnetisation, M_s, for a sample of ferromagnetic cobalt metal (a) assuming only the unpaired d electrons contribute to the magnetism and the spins can be added as if the material were paramagnetic and (b) using the measured magnetic moment per cobalt atom of 1.72 μ_B. The metal has an A3 structure with a hexagonal unit cell parameter of $a_0 = 0.2507$ nm, and $c_0 = 0.4069$ nm.

12.9 Iron has a saturation magnetisation of 1.72×10^6 A m^{-1}. What is the measured magnetic moment, in Bohr magnetons, of an iron atom. Iron has an A2 structure, with a cubic unit cell parameter of 0.2867 nm.

12.10 Nickel has a saturation magnetisation of 0.489×10^6 A m^{-1}. What is the measured magnetic moment, in Bohr magnetons, of a nickel atom. Nickel has the A1 structure, with a cubic unit cell parameter of 0.3524 nm.

12.11 The magnetic moment of Fe^{3+} ions in the species $[Fe(H_2O)_6]^{3+}$ is 5.3 μ_B. What is the likely electron configuration of the Fe^{3+} ion?

12.12 The magnetic moment of Fe^{3+} ions in the species $[Fe(CN)_6]^{3-}$ is 2.3 μ_B. What is the likely electron configuration of the Fe^{3+} ion? What can you conclude about the orbital contribution to the magnetic moment for this species?

12.13 The species $[Co(NH_3)_6]^{3+}$, containing Co^{3+} ions, gives rise to diamagnetic solids, whereas the species $[CoF_6]^{3-}$, also containing Co^{3+} ions, has a strong magnetic moment and gives rise to paramagnetic solids.

(a) What is the likely electron configuration of the Co^{3+} ions in these two species?

(b) Calculate the expected magnetic moment of Co^{3+} in $[CoF_6]^{3-}$.

12.14 The species $[Fe(CN)_6]^{4-}$, containing Fe^{2+} ions, gives rise to diamagnetic solids, whereas the species $[Fe(NH_3)_6]^{2+}$, also containing Fe^{2+} ions, has a strong magnetic moment and gives rise to paramagnetic solids.

(a) What is the likely electron configuration of the Fe^{2+} ions in these two species?

(b) Calculate the expected magnetic moment of Fe^{2+} in $[Fe(NH_3)_6]^{2+}$.

12.15 The relationship between the energy of a light photon, E, and its frequency, ν, is $E = h\nu$ [see Section 1.2.2, Equation (1.3)]. The crystal field splitting of diamagnetic $[Co(NH_3)_6]^{3+}$, containing Co^{3+} ions (see Question 12.13) is 4.57×10^{-19} J. What wavelength light would produce photoinduced paramagnetism in this molecule?

12.16 The relationship between the energy of a light photon, E, and its frequency, ν, is $E = h\nu$ [see Section 1.2.2, Equation (1.3)]. The crystal field splitting of diamagnetic $[Fe(CN)_6]^{4-}$, containing Fe^{2+} ions (Question 12.14) is 4.57×10^{-19} J. What wavelength light would produce photoinduced paramagnetism in this molecule?

12.17 Calculate (a) the paramagnetic energy level splitting for a Pr^{3+} ion in a magnetic induction of 0.5 T and (b) the corresponding wavelength of radiation for a transition between these energy levels.

12.18 Calculate (a) the paramagnetic energy level splitting for a Ho^{3+} ion in a magnetic induction of 0.75 T and (b) the corresponding wavelength of radiation for a transition between these energy levels.

12.19 (a) Calculate the paramagnetic energy level splitting for a V^{4+} ion in a magnetic induction of 0.25 T if the orbital contribution is quenched and (b) calculate the corresponding wavelength of radiation for a transition between these energy levels.

12.20 (a) Calculate the paramagnetic energy level splitting for a Ni^{2+} ion in a magnetic induction of 0.6 T if the orbital contribution is quenched and (b) calculate the corresponding wavelength of radiation for a transition between these energy levels.

12.21 Calculate the mass susceptibility of $NiSO_4 \cdot 7H_2O$ at 20 °C (in units of kg^{-1}), which contains isolated Ni^{2+} ions. The density of the compound is 1980 kg m^{-3}. Assume that the spin-only formula is adequate.

12.22 Calculate the mass susceptibility of $CuSO_4 \cdot 5H_2O$ at 20 °C, (in units of kg^{-1}), which contains isolated Cu^{2+} ions. The density of the compound is 2284 kg m^{-3}. Assume that the spin-only formula is adequate.

12.23 Calculate the volume susceptibility of $MnSO_4 \cdot 4H_2O$ at 20 °C, (in units of m^{-3}), which contains isolated Mn^{2+} ions. The density of the compound is 1980 kg m^{-3}.

Assume that the spin-only formula is adequate.

12.24 (a) Calculate the value of x in the Brillouin function $B_J(x)$, where $x = g_J\mu_B JB/kT$, for an Mn^{2+} ion with five unpaired electrons in an inductance of 0.5 T. Assume that the orbital angular momentum is quenched, so that $L = 0$. Take S as 5/2, from Table 12.2. The Curie law requires that $x \ll 1$. (b) Estimate the temperature at which x is 0.01.

12.25 (a) (i) Calculate the value of x in the Brillouin function $B_J(x)$, where $x = g_J\mu_B JB/kT$, for a Ti^{3+} ion with one unpaired electron in an inductance of 0.45 T. Assume that the orbital angular momentum is quenched, so that $L = 0$, and take S as 1/2, from Table 12.2. The Curie law requires that $x \ll 1$. (ii) Estimate the temperature at which x is 0.005. (b) Repeat the calculation assuming that the orbital angular momentum is not quenched, and $L = 2$, $J = 3/2$. (iii) Estimate the temperature at which x is 0.005.

12.26 The saturation magnetisation of iron is $1.752 \times 10^6\ \mathrm{A\,m^{-1}}$. Calculate the effective magnetic moment on an iron atom. Iron adopts the A2 structure with a unit cell edge of 0.2867 nm.

12.27 The saturation magnetisation of nickel is $0.510 \times 10^6\ \mathrm{A\,m^{-1}}$. Calculate the effective magnetic moment on a nickel atom. Nickel adopts the A1 structure with a unit cell edge of 0.3524 nm.

12.28 The saturation magnetisation of cobalt is $1.446 \times 10^6\ \mathrm{A\,m^{-1}}$. The crystal structure of cobalt is disordered in normal circumstances (see Section 6.1.1).

(a) Calculate the number of magnetic dipoles per unit volume in cobalt, knowing the effective magnetic moment per atom is 1.72 μ_B.

(b) If it is assumed that there is one atom per primitive cubic unit cell, determine the length of the unit cell edge.

12.29 Estimate (a) the saturation magnetisation and (b) the magnetic inductance for the cubic ferrite $CoFe_2O_4$ with the inverse spinel structure. Co^{2+} is a d^7 ion. The cubic unit cell has a lattice parameter of 0.8443 nm and contains eight formula units. Assume that the orbital angular momentum is completely quenched in this material.

12.30 Estimate (a) the saturation magnetisation and (b) the magnetic inductance for the cubic ferrite $NiFe_2O_4$ with the inverse spinel structure. Ni^{2+} is a d^8 ion. The cubic unit cell has a lattice parameter of 0.8337 nm and contains eight formula units. Assume that the orbital angular momentum is completely quenched in this material.

12.31 Estimate (a) the saturation magnetisation and (b) the magnetic inductance for the hexagonal ferrite ‘ferroxdur’, $BaFe_{12}O_{19}$. The hexagonal unit cell has parameters $a_0 = 0.58836$ nm, $c_0 = 2.30376$ nm and volume $7.128 \times 10^{-28}\ \mathrm{m^3}$. There are two formula units in the unit cell. Assume that the orbital angular momentum is completely quenched in this material.

12.32 Estimate (a) the saturation magnetisation and (b) the magnetic inductance for the hexagonal ferrite $SrFe_{12}O_{19}$. The hexagonal unit cell contains two formula units and has a volume $7.975 \times 10^{-28}\ \mathrm{m^3}$. Assume that the orbital angular momentum is completely quenched in this material.

12.33 Derive a formula for the saturation magnetisation of a cubic ferrite $A^{2+}Fe_2O_4$, which is only partly inverse. The fraction of Fe^{3+} ions on tetrahedral sites is given by λ, where $0 < \lambda < 0.5$ (see Section 5.3.10). [Note: derivation is not given in the answers at the end of this book.]