CHAPTER W2

The magnetic properties of solids

Explanation

This chapter is a supplement to the book:

Understanding the properties of matter

by Michael de Podesta.

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CHAPTER W2

The magnetic properties of solids

W2.1 Introduction

All substances respond to an applied magnetic field by becoming magnetised i.e. they behave as if they were a bar magnet themselves. The quantitative measure of the extent to which they behave like a bar magnet is called the *magnetisation* of the substance. The responses of different substances to applied magnetic fields normally falls in one of three broad categories:

- The 'bar magnet' created in the sample lines up so that the magnetic field inside the material is increased. The energy of the atoms in the material is lowered by applying a field and so the sample tries to move into regions of high magnetic field. Such materials are called *paramagnets*.
- The 'bar magnet' created in the sample lines up so that the field inside the material is decreased. The energy of the atoms in the material is increased by applying a field and so the sample tries to move away from regions of high magnetic field. Such materials are called *diamagnets*.

By far the majority of substances fall into one or other of these two categories. In either category, when the sample is removed from the magnetic field, the magnetisation returns to zero. In the third category the sample can possess a non-zero magnetisation *in the absence of any applied magnetic field.* Such materials are called *ferromagnets.* Other more unusual forms of magnetic response do exist, but their phenomenology is rather complex and it is not appropriate to discuss them here. The response of diamagnetic and paramagnetic substances to an applied magnetic field is shown schematically in Figure W2.1. The key feature of ferromagnetic behaviour is illustrated in Figure W2.2

This short supplementary chapter is structured as follows:

- we begin by discussing the data on the magnetic properties of the elements. However, in order to do this we need to acquaint ourselves with some of the terminology of magnetism and immediately we come face to face to face with the vexed issue of magnetic units. All I wish to say on this matter is that things are better now than they used to be, but any scientist using non-SI units to describe their results should be ashamed of themselves.

- We then take a look at the data on the elements and move on to try to understand the basic phenomena which we observe. We need to consider many features of the electronic structure of solids in order to arrive at even a semi-quantitative understanding of the data. We will see that the magnetic response of any particular substance can be considered as the sum of many different contributions.

- Finally, we mention briefly the truly astounding phenomenon of ferromagnetism. In my experience as a physicist I have seen nothing which continually fascinates and astounds me more than the strange repulsion and attraction of ferromagnets.

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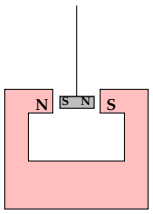
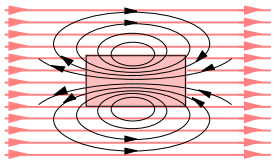
Figure W2.1 Illustration of the response of diamagnetic and paramagnetic substances to an applied magnetic field. Note that both types of substance have no magnetic moment in the absence of an applied field.

DIAMAGNETIC RESPONSE

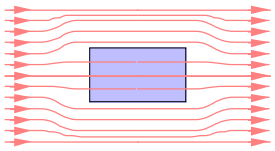
(a) A diamagnetic sample suspended in a magnetic field. Notice the sense of the of magnet moment induced by the applied magnetic field.



(b) The *applied* magnetic field is indicated by the shaded arrowed lines. The magnetic field induced in the sample — indicated by full black lines — has the form of the field due to a bar magnet whose lines of flux tend to *decrease* the field inside the material, and *increase* the field on either side of the material.

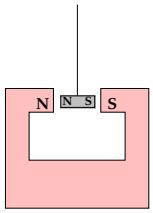


(c) The net magnetic field. The flux density inside the material is *less* than the flux density of the applied field i.e. the sample has 'repelled' flux lines.

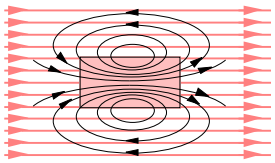


PARAMAGNETIC RESPONSE

(a) A paramagnetic sample suspended in a magnetic field. Notice the sense of the of magnet moment induced by the applied magnetic field.



(b) The *applied* magnetic field is indicated by the shaded arrowed lines. The magnetic field induced in the sample — indicated by full black lines — has the form of the field due to a bar magnet whose lines of flux tend to *increase* the field inside the material, and *decrease* the field on either side of the material.



(c) The net magnetic field. The flux density inside the material to *greater* than the flux density of the applied field i.e. the sample has 'concentrated' flux lines.

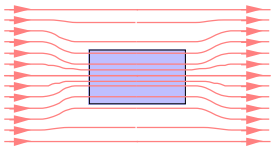
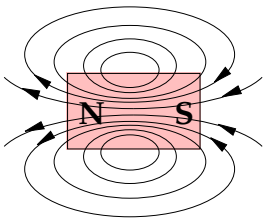


Figure W2.2 Illustration of the key properties of a ferromagnetic material. (a) shows a sample suspended in free space showing a magnetic moment in the absence of an applied field. (b) shows the lines of magnetic flux around a ferromagnetic material. Notice that there is no applied magnetic field.



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W2.2 Quantitative magnetic measurements

Magnetic field

The magnetic field in a region of space (also referred to as the *magnetic induction*) has the symbol **B** and is measured in tesla. One may also define a second field **H**, known as the *applied magnetic field* which is measured in Am^{-1}. The existence of two ways of describing magnetic phenomena has led to enormous confusion. From the point of view of the solid-state physicists, there are two points to bear in mind:

- Microscopically, the magnetic field to which electrons, protons and neutrons respond is the *local* value of **B**, the *magnetic induction* in their vicinity.
- Inside a sample exposed to a magnetic field, the value of **B** differs from the value outside the sample because of the magnetic response of the substance. This effect is illustrated for diamagnets and paramagnets in Figure 7.55 (a) and Figure 7.55 (b) respectively, although the effect is largest in ferromagnets (Figure 7.56) which can experience large values of internal magnetic field in the absence of *any* applied field. Thus the value of **B** inside the sample is not the same as the value of **B** which was applied to the sample.

In the context of magnetic measurements, the field **H** may be regarded as a fictional field which is not affected by the magnetisation of the material.

The magnetic field **B** inside a material is given by:

$$\mathbf{B} = \mu_o(\mathbf{H} + \mathbf{M}) \qquad \text{(W2.1)}$$

where μ_o is a constant with the value $4\pi \times 10^{-7}$ henry per metre ($H\ m^{-1}$), and **M** is the magnetisation of material, defined below.

There are several ways of specifying the extent of the magnetic effect induced in a sample of material:

Magnetic moment

The extent of the magnetic response of a sample can be determined by measuring the distortion of the magnetic field around the edge of a magnetised sample. The 'magnetic strength' exhibited in a particular sample is specified in terms of the equivalent distortion that would be achieved by an electric current flowing in a small loop at the position of the sample. The strength of the magnetic field created by a current loop is specified in terms of its *magnetic moment*, **m**, (sometimes called its *magnetic dipole moment*) given by:

$$\mathbf{m} = \mathbf{i} \times \mathbf{A} \quad [Am^2] \qquad \text{(W2.2)}$$

Thus the magnetic moment is measured in $A\ m^2$ and points in the direction indicated by a right-hand screw rotating in the same sense as the current.

Magnetisation

In a fixed applied field, the magnetic moment (defined in Equation W2.2) of a large sample will be larger than the magnetic moment of a small sample of the same substance. Thus one defines the *magnetic moment per unit volume*, the *magnetic moment per kilogram* and the *magnetic moment per mole*. The most common of these is the specification of the magnetic moment per unit volume known as the *magnetisation*, **M**.

$$\mathbf{M} = \frac{\mathbf{m}}{V} \quad \left[\frac{A\ m^2}{m^3} = A\ m^{-1} \right] \qquad \text{(W2.3)}$$

Susceptibility

Both the magnetic moment (W2.2) and the magnetisation (W2.3) of a sample depend on the magnetic field that the sample experiences: the magnetisation in a large magnetic field will be larger than in a small magnetic field. If we divide the magnetisation by the applied field **H**, then we obtain a measure of the strength of magnetic response which does not depend on applied field or sample size. If this is done one obtains the *magnetic susceptibility per unit volume*, or the *volume susceptibility* for short. However frequently one encounters:

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- the *mass susceptibility*, which is the magnetic moment per kg, divided by the applied field, or:
- the *molar susceptibility*, which is the magnetic moment per mole, divided by the applied field.

All these susceptibilities are given the symbol χ, pronounced 'khi', subscripted with an appropriate letter. We thus have:

- χ_V, the *Volume susceptibility*, which is the *magnetic moment per unit volume*, divided by the applied field **H**, or:

$$\chi_V = \frac{m}{Sample\ \ volume \times H} \qquad \left[\text{Units}: \frac{\text{A m}^2}{\text{m}^3 \times \text{A m}^{-1}} = \text{dimensionless}\right] \qquad \text{(W2.4)}$$

$$\chi_V = \frac{M}{H} \qquad \left[\text{Units}: \frac{\text{A m}^{-1}}{\text{A m}^{-1}} = \text{dimensionless}\right] \qquad \text{(W2.5)}$$

- χ_m, the *Molar susceptibility*, which is the *magnetic moment per mole*, divided by the applied field H, or:

$$\chi_m = \frac{m}{\text{Number moles in sample} \times H} \qquad \left[\text{Units}: \frac{\text{A m}^2}{\text{mol} \times \text{A m}^{-1}} = \text{m}^3\ \text{mol}^{-1}\right] \qquad \text{(W2.6)}$$

- χ_{kg}, the *Mass susceptibility*, which is the *magnetic moment per unit mass*, divided by the applied field H, or:

$$\chi_{kg} = \frac{m}{\text{Sample mass} \times H} \qquad \left[\text{Units}: \frac{\text{A m}^2}{\text{kg} \times \text{A m}^{-1}} = \text{m}^3\ \text{kg}^{-1}\right] \qquad \text{(W2.7)}$$

W2.3 Data on the elements

For paramagnetic and diamagnetic substances the magnetic moment induced by an applied field is in general proportional to the applied magnetic field, at least for weak applied fields. From the definitions of magnetic susceptibility (Equations W2.4 to W2.7), it can be seen that the susceptibility will than be independent of the strength of the applied magnetic field.

The *magnetic molar susceptibility*, χ_M (W2.6) of the elements at around room temperature is shown in Table W2.1 and summarised in Figure W2.3. The shading in Table W2.1 corresponds to the shaded regions in Figure W2.3(a). The shaded data indicated by *B*, *C* and *D* on Figure W2.3 mark the first and second row of transition elements, and the lanthanide series respectively. The unshaded band *A* marks the ferromagnetic elements Fe, Co and Ni.

The data indicate that some elements exhibit weak diamagnetism and others a rather stronger paramagnetism. Ferromagnetism appears to be a relatively rare magnetic phenomenon – at least at room temperature. However the clearest feature of Figure W2.3 is that elements with atomic numbers Z from 57 to 70 (known as the lanthanide series of elements) have by far the strongest magnetic response, and this magnetic response is *paramagnetic*. Further it is clear that first row (Z = 21 to 30) and second row (Z = 39 to 48) transition elements also have a relatively strong paramagnetic response. The third row transition series (Z = 71 to 80) also has a relatively strong response, but this does not show up so clearly in comparison with the nearby lanthanide series.

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In large magnetic fields, the proportionality between the induced magnetic moment and applied field is *sometimes* broken. However, the characteristic deviations from direct proportionality with field vary with temperature in a complex manner.

The main questions raised by our preliminary examination of the experimental data on the magnetic properties of solids are:

- Why is paramagnetism strongest in elements belonging to the transition series, and the especially strong in the lanthanide series of elements?
- Why are elements outside the transition series either slightly diamagnetic or slightly paramagnetic?
- Why do most elements acquire only small magnetic moments in an applied magnetic field, but a few elements, such as iron, can exhibit permanent magnetic moments?

Example W2.1

The molar susceptibility of copper and cerium are is -6.87×10^{-11} m^3mol^{-1} and 3.04×10^{-8} m^3mol^{-1} respectively. Samples of each substance are subjected to a magnetic induction of $B_o = 0.1$ tesla. What is the magnetic field inside each sample?

In order to calculate the field B inside the sample we need to use Equation W2.1:

$$B = \mu_o(H + M)$$

and so we need first to calculate the applied field H and the magnetisation M. The applied field is unaffected by the presence of a sample and so is the same as the field which would be there in the absence of sample i.e. $M = 0$. Thus:

$$H = \frac{B}{\mu_o}$$

The magnetisation is not quite so straightforward to calculate. We are given the molar susceptibility χ_M i.e. the magnetic moment per mole. In order to calculate the magnetic moment per unit volume — the magnetisation M — we need to know the density ρ and molar mass A of the substance. The molar susceptibility χ_V is then given in terms of χ_M by:

$$\chi_V = \frac{\rho\chi_M}{A} = \frac{M}{H}$$

We thus find:

$$\mathbf{M} = \frac{\mathbf{H}\rho\chi_M}{A}$$

and hence the magnetic induction field inside the sample is given by:

$$\mathbf{B} = \mu_o\left[\frac{\mathbf{B}_o}{\mu_o} + \frac{\mathbf{B}_o\rho\chi_M}{\mu_o A}\right]$$

$$= \mathbf{B}_o + \frac{\mathbf{B}_o\rho\chi_M}{A}$$

For copper, we find from Table W2.1 that 1 mole of copper has a mass of $A = 63.55 \times 10^{-3}$ kg and a density of $\rho = 8933$ kg m^{-3} and hence the difference in magnetic field between the inside and outside ($\mathbf{B} - \mathbf{B_o}$) of a sample of copper — given by the second term in the equation above — is:

$$\Delta B = \frac{B_o\rho\chi_M}{A} = \frac{0.1\times 8933\times(-6.87\times10^{-11})}{63.55\times10^{-3}}$$

$$= -9.66\times10^{-7} \text{ T}$$

Similarly, for cerium, we find from Table 7.19that 1 mole of cerium has a mass of $A = 63.55 \times 10^{-3}$ kg and a density of $\rho = 8933$ kgm^{-3} and hence the difference in magnetic field between the inside and outside ($\mathbf{B} - \mathbf{B_o}$) of a sample of cerium — given by the second term in the equation above — is:

$$\Delta B = \frac{B_o\rho\chi_M}{A} = \frac{0.1\times 6711\times(+3.04\times10^{-11})}{140.1\times10^{-3}}$$

$$= +1.46\times10^{-4} \text{ T}$$

Thus for a sample of copper in an applied field of 0.1 T, the field inside the sample is slightly less than the field outside the sample by around 10^{-6} T, or roughly 1 part in 10^5 of the applied field. For the cerium sample, the field inside the sample is slightly more than the field outside the sample by around 10^{-4} T, or roughly 1 part in 10^3 of the applied field.

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Table W2.1 Molar magnetic susceptibility of the elements at around room temperature. The data are summarised in Figure W2.3. The shading in the table corresponds to the shading in Figure and highlights elements with a large susceptibilities.

Z	Element, atomic mass (u) and density (kg m^{-3})			χ_M (m^3 mol^{-1})
1	Hydrogen, H	1.008	89	—
2	Helium, He	4.003	120	—
3	Lithium, Li	6.941	533	1.78×10^{-10}
4	Beryllium, Be	9.012	1846	-1.17×10^{-10}
5	Boron, B	10.81	2466	-8.43×10^{-11}
6	Carbon, C	12.01	2266	-7.57×10^{-11}
7	Nitrogen, N	14.01	1035	—
8	Oxygen, O	16	1460	—
9	Fluorine, F	19	1140	—
10	Neon, Ne	20.18	1442	-8.48×10^{-11}
11	Sodium, Na	22.99	966	2.02×10^{-10}
12	Magnesium, Mg	24.31	1738	1.65×10^{-10}
13	Aluminium, Al	26.98	2698	2.08×10^{-10}
14	Silicon, Si	28.09	2329	-5.06×10^{-11}
15	Phosphorus, P	30.97	1820	-3.41×10^{-10}
16	Sulphur, S	32.06	2086	-1.95×10^{-10}
17	Chlorine, Cl	35.45	2030	—
18	Argon, A	39.95	1656	—
19	Potassium, K	39.1	862	2.62×10^{-10}
20	Calcium, Ca	40.08	1530	5.61×10^{-10}
21	Scandium, Sc	44.96	2992	3.96×10^{-9}
22	Titanium, Ti	47.9	4508	1.92×10^{-9}
23	Vanadium, V	50.94	6090	3.20×10^{-9}
24	Chromium, Cr	52	7194	2.31×10^{-9}
25	Manganese, Mn	54.94	7473	6.59×10^{-9}
26	Iron, Fe	55.85	7873	Ferro
27	Cobalt, Co	58.93	8800	Ferro
28	Nickel, Ni	58.7	8907	Ferro
29	Copper, Cu	63.55	8933	-6.87×10^{-11}
30	Zinc, Zn	65.38	7135	-1.44×10^{-10}
31	Gallium, Ga	69.72	5905	-2.72×10^{-10}
32	Germanium, Ge	72.59	5323	-9.64×10^{-11}
33	Arsenic, As	74.92	5776	-6.87×10^{-11}
34	Selenium, Se	78.96	4808	-3.16×10^{-10}
35	Bromine, Br	79.9	3120	—
36	Krypton, Kr	83.8	3000	—
37	Rubidium, Rb	85.47	1533	2.13×10^{-10}
38	Strontium, Sr	87.62	2583	1.16×10^{-9}
39	Yttrium, Y	88.91	4475	2.40×10^{-9}
40	Zirconium, Zr	91.22	6507	1.53×10^{-9}
41	Niobium, Nb	92.91	8578	2.56×10^{-9}
42	Molybdenum, Mo	95.94	10222	1.15×10^{-9}
43	Technetium, Tc	97	11496	3.01×10^{-9}
44	Ruthenium, Ru	101.1	12360	5.43×10^{-10}
45	Rhodium, Rh	102.9	12420	1.40×10^{-9}
46	Palladium, Pd	106.4	11995	7.13×10^{-9}
47	Silver, Ag	107.9	10500	-2.45×10^{-10}
48	Cadmium, Cd	112.4	8647	-2.48×10^{-10}
49	Indium, In	114.8	7290	-8.04×10^{-10}
50	Tin, Sn	118.7	7285	-4.75×10^{-10}
51	Antimony, Sb	121.7	6692	-1.22×10^{-9}
52	Tellurium, Te	127.6	6247	-4.98×10^{-10}
53	Iodine, I	126.9	4953	-5.58×10^{-10}
54	Xenon, Xe	131.3	3560	-5.51×10^{-10}
55	Caesium, Cs	132.9	1900	3.72×10^{-10}
56	Barium, Ba	137.3	3594	2.61×10^{-10}
57	Lanthanum, La	138.9	6174	1.53×10^{-9}
58	Cerium, Ce	140.1	6711	3.04×10^{-8}
59	Praseodymium, Pr	140.9	6779	6.30×10^{-8}
60	Neodymium, Nd	144.2	7000	7.07×10^{-8}
61	Promethium, Pm	145	7220	—
62	Samarium, Sm	150.4	7536	2.29×10^{-8}
63	Europium, Eu	152	5248	4.27×10^{-7}
64	Gadolinium, Gd	157.2	7870	Ferro
65	Terbium, Tb	158.9	8267	1.83×10^{-6}
66	Dysprosium, Dy	162.5	8531	1.30×10^{-6}
67	Holmium, Ho	164.9	8797	9.05×10^{-7}
68	Erbium, Er	167.3	9044	5.57×10^{-7}
69	Thulium, Tm	168.9	9325	3.21×10^{-7}
70	Ytterbium, Yb	173	6966	3.13×10^{-9}
71	Lutetium, Lu	175	9842	2.28×10^{-10}
72	Hafnium, Hf	178.5	13276	9.46×10^{-10}
73	Tantalum, Ta	180.9	16670	1.94×10^{-9}
74	Tungsten, W	183.9	19254	7.36×10^{-10}
75	Rhenium, Re	186.2	21023	8.49×10^{-10}
76	Osmium, Os	190.2	22580	1.24×10^{-10}
77	Iridium, Ir	192.2	22550	3.21×10^{-10}
78	Platinum, Pt	195.1	21450	2.54×10^{-9}
79	Gold, Au	197	19281	-3.51×10^{-10}
80	Mercury, Hg	200.6	13546	—
81	Thallium, Tl	204.4	11871	-6.40×10^{-10}
82	Lead, Pb	207.2	11343	-2.88×10^{-10}
83	Bismuth, Bi	209	9803	-3.52×10^{-9}
84	Polonium, Po	209	9400	—
85	Astatine, At	210	—	—
86	Radon, Rn	222	4400	—
87	Francium, Fr	223	—	—
88	Radium, Ra	226	5000	—
89	Actinium, Ac	227	10060	—
90	Thorium, Th	232	11725	1.67×10^{-9}
91	Protactinium, Pa	231	15370	—
92	Uranium, U	238	19050	5.14×10^{-9}
93	Neptunium, Np	237	20250	—
94	Plutonium, Pu	244	19840	7.73×10^{-9}
95	Americium, Am	243	13670	1.22×10^{-8}

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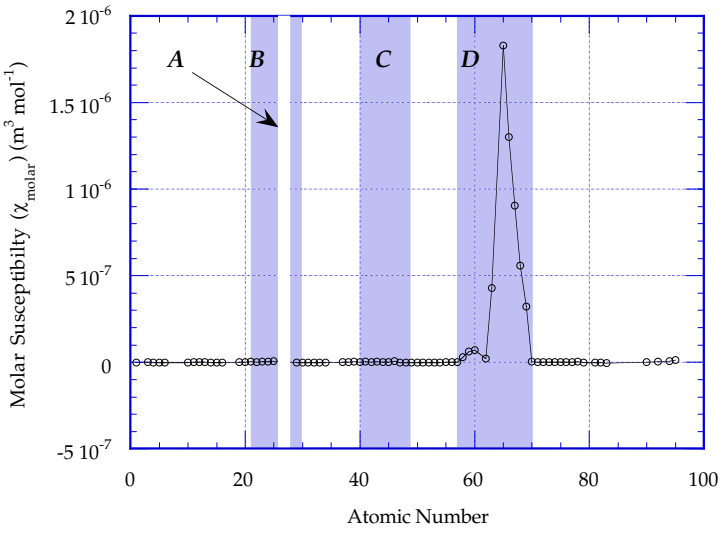
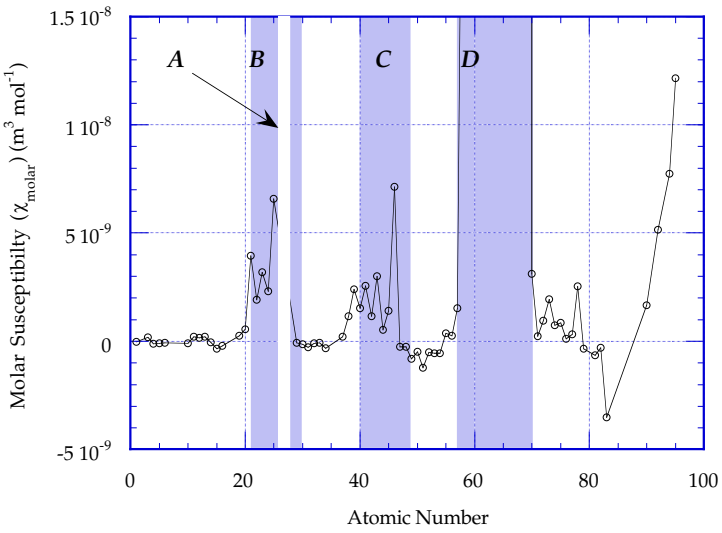
Figure W2.3 Summary of molar magnetic susceptibility data for the solid elements shown (a) at a large scale and (b) on a detailed scale. The bands *B*, *C* and *D* mark the first and second row of transition elements, and the lanthanide series. The band *A* marks the ferromagnetic elements Fe, Co and Ni. **Note:** points greater than zero correspond to a paramagnetic response and points less than zero correspond to a diamagnetic response.

(a)



(b)



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W2.4 Understanding the magnetic properties of the elements

We will analyse the magnetic response of solids as the sum of several relatively independent terms, some of which are diamagnetic, some paramagnetic, and some ferromagnetic. In any particular case the balance between the different terms determines the overall response. The different magnetic responses arise from electrons in different situations within the solid. In general we can categorise electrons as either being :

- Core electrons, in filled electron shells,
- Core electrons, in partially-filled electron shells,
- Conduction electrons.

However for both core electrons and conduction electrons, we have to consider:

- the alteration of the motion of charged particles in an applied magnetic field, and
- the re-orientation of the intrinsic magnetic moment of electrons in an applied magnetic field.

These two contributions, generally referred to as the *orbital* and *spin* contributions respectively, must be considered for both core electrons and conduction electrons. For example, conduction electrons generally have a diamagnetic orbital response, but a paramagnetic spin response.

The diversity of magnetic properties is so great, that it will be as well to map out where our discussion will lead before we actually begin. Table W2.2 summarises the magnetic responses of non-interacting electrons in solids. In any particular material the balance between paramagnetic and diamagnetic responses is slightly different.

The origin of the ferromagnetic response seen in just a few elements lies in the *electrical* interaction between electrons, often, but not exclusively, *core electrons*. This is discussed briefly at the end of this chapter (Page W2.18). Our discussion of the magnetic properties of solids will therefore discuss each of the three 'sub-systems' first assuming no electrical interaction between electrons on neighbouring atoms.

1. Filled electron shells

The *spin response* of a filled electron shell is easy to calculate: it is zero i.e. filled electron shells do not acquire any net magnetic moment in the presence of an applied field due to electron spin. This can be seen by noting that in any filled shell, electrons occupy quantum states in pairs with opposite spin. Thus in zero applied field the net magnetic moment due to spin is zero. Further, the Pauli exclusion principle prevents the spins from re-orienting and thus the spins are not able to acquire a magnetic moment in an applied field.

A semi-classical calculation

The orbital response of a filled electron shell is not so straightforward to calculate but we can approach the problem semi-classically as follows. We consider electrons in atomic orbitals to move in circles of radius r. The magnetic moment due a current flowing in a circle of area A is:

Table W2.2 Summary of the response of non-interacting electrons to applied magnetic fields. Table W2.3 at the end of this section has more details. The type of response is listed with the name of the scientist most closely associated with it.

	Core Electrons (Filled Shells)	Core Electrons (Partly-Filled Shells)	Conduction Electrons
Spin Response	No Response	Paramagnetism (Curie)	Paramagnetism (Pauli)
Orbital Response	Diamagnetism (Larmor)	Paramagnetism (Curie)	Diamagnetism (Landau)

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$$\text{magnetic moment} = iA \qquad \text{(W2.8)}$$

If the 'current' is due to the rapid orbit with angular frequency ω of an electron with charge q moving around a circular path of radius r (Figure W2.4 (a)) then Equation W2.8 becomes:

$$\text{magnetic moment} = \frac{q\omega}{2\pi} \times \pi r^2 \qquad \text{(W2.9)}$$

which simplifies to:

$$\text{magnetic moment} = \tfrac{1}{2} q\omega r^2 \qquad \text{(W2.10)}$$

Now the electron moves in a circular path due to a centripetal force F_o which in our case will be the electrical attraction between the electron and its ion core. We can relate F_o and ω by the standard relationship:

$$F_o = mr\omega^2 \qquad \text{(W2.11)}$$

where m is the electron mass. Now consider the situation when a magnetic field B is applied perpendicular to the orbit (Figure W2.4 (b)). In the presence of an applied magnetic field there is an extra force on the particle which may act either with F_o or against it. In either case its effect is mainly to alter the orbital frequency — the area of the orbit remains unaffected to first order. Thus we write:

$$F_o - qvB = mr(\omega + \Delta\omega)^2 \qquad \text{(W2.12)}$$

Expanding to first order in $\Delta\omega$:

$$F_o - qr\omega B = mr\omega^2 + 2mr\omega\Delta\omega + \ \ldots \qquad \text{(W2.13)}$$

and recalling that $F_o = mr\omega^2$ we write:

$$-qr\omega B = 2mr\omega\Delta\omega + \ \ldots \qquad \text{(W2.14)}$$

and solving for $\Delta\omega$ we arrive at:

$$\Delta\omega = \frac{-qB}{2m} \qquad \text{(W2.15)}$$

$\Delta\omega$ is a frequency commonly encountered in studies of magnetic phenomena as is known as the *cyclotron* or *Larmor* frequency. Now the increased (or decreased) orbital frequency causes a change in the magnetic moment of the orbital since the magnetic moment = $\tfrac{1}{2} q\omega r^2$ (Equation W2.10). Substituting Equation W.15 in Equation W2.10 we write:

$$\begin{aligned} \Delta(\text{magnetic moment}) &= \tfrac{1}{2} q\Delta\omega r^2 \\ &= \tfrac{1}{2} q \frac{-qB}{2m} r^2 \\ &= -\frac{q^2 B}{4m} r^2 \end{aligned} \qquad \text{(W2.16)}$$

which yields the change in magnetic moment of an orbital due to an applied magnetic field B. Notice that in the case shown in Figure W2.4:

- The magnetic moment of the orbit initially points in the opposite direction to the magnetic field.
- The effect of the magnetic field (Figure W2.5 (a) and (c)) is to *increase* the orbital speed of the electron, and hence to increase the current, and hence to increase the size of the magnetic moment that opposes the applied magnetic field. The field effect on the orbit is therefore diamagnetic.

Figure W2.4 (a) The force F_o keeps a charged particle in a circular orbit of radius r at speed v.

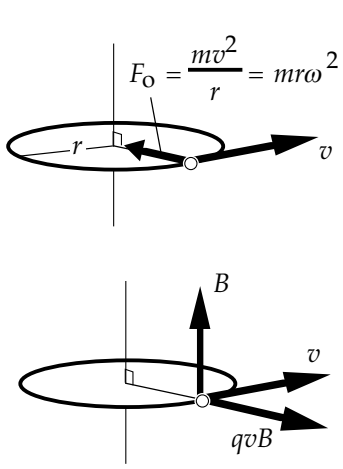

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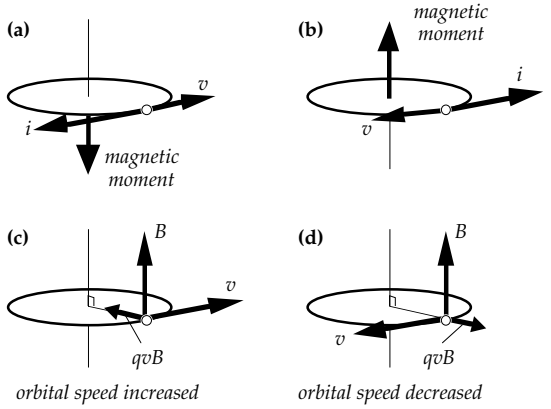
Figure W2.5 (a) The directions of the magnetic moment resulting from electron orbits in opposite directions. In the presence of a magnetic field **B** the additional force (Figure W2.4b) acts (c) to increase the orbital speed of the electron whose moment opposes **B** and (d) to decrease the orbital speed of the electron whose moment is parallel to **B.** The sign of the electron charge has been taken account in calculating the directions shown.



However in fully-filled electron shells, for every electron orbiting in one sense there is an equivalent electron orbiting in the opposite sense. For an electron orbiting the opposite sense to that in Figure W2.4:

- The magnetic moment of the orbit initially points in the same direction as the magnetic field.
- The effect of the magnetic field (Figure W2.5 (b) and (d)) is to *decrease* the orbital speed of the electron, and hence to decrease the current, and hence to decrease the size of the magnetic moment in the same sense as the applied magnetic field. The field effect on the orbit is therefore diamagnetic.

Thus no matter what the orientation of the magnetic field, its effect on the orbital moment is net diamagnetic. Notice that the magnetic moment of the orbital is generally much larger than the diamagnetic alteration to its value. However in filled electron shells, each orbital moment is paired with an equal and opposite one, and so only the diamagnetic effect is observed. Diamagnetism arising from this origin is known as *Larmor* diamagnetism.

More detailed predictions

Now electron orbits in an atom are not simple circles, but three-dimensional charge distributions. To take account of this in place of r^2 we write $\overline{r^2}$ which is the average radius of an orbit perpendicular to the magnetic field:

$$\Delta(\text{magnetic moment}) = -\tfrac{1}{4}\frac{q^2B}{m} \times \overline{r^2} \qquad \text{(W2.17)}$$

If the electron orbital has no particular orientation with respect to the direction of a field applied along, say, $\hat{\mathbf{z}}$, then we expect to find $\overline{x^2} = \overline{y^2} = \overline{z^2}$. Since $\overline{r^2} = \overline{x^2} + \overline{y^2}$, if the average radius of the orbital is $\overline{\rho}$ then $\overline{\rho^2} = \overline{x^2} + \overline{y^2} + \overline{z^2}$ and so $\overline{r^2} = \tfrac{2}{3}\overline{\rho^2}$. We can thus rewrite Equation W2.17 as:

$$\Delta(\text{magnetic moment}) = -\tfrac{1}{4}\frac{q^2B}{m} \times \tfrac{2}{3}\overline{\rho^2} \qquad \text{(W2.18)}$$

$$\Delta(\text{magnetic moment}) = -\frac{q^2B}{6m}\overline{\rho^2} \qquad \text{(W2.19)}$$

If we express this in terms of the applied field H this becomes:

$$\Delta(\text{magnetic moment}) = -\frac{q^2\mu_o H}{6m}\overline{\rho^2} \qquad \text{(W2.20)}$$

Now each atom has $\approx Z$ filled electron orbitals and so we expect each orbital to acquire a moment:

$$\Delta(\text{magnetic moment}) = -\frac{Zq^2\mu_o H}{6m}\overline{\rho^2} \qquad \text{(W2.21)}$$

where $\overline{\rho^2}$ is now an average value for each type of atom. In one mole of substance we have N_A such magnetic moments, and so dividing by H we obtain :

$$\chi_{\text{molar}} = -\frac{N_A Zq^2\mu_o}{6m}\overline{\rho^2} \qquad \text{(W2.22)}$$

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Approximating $\rho \approx 0.1$ nm for all orbitals (likely to be correct within a factor 2 or 3 either way) Equation W2.22 evaluates to:

$$\chi_{\text{molar}} \approx -Z\frac{6.02\times10^{23}\times(1.6\times10^{-19})^2\times4\pi\times10^{-7}}{6\times9.1\times10^{-31}}\times(10^{-10})^2$$

$$\chi_{\text{molar}} \approx 3.6Z\times10^{-11} \quad \text{m}^3\,\text{mol}^{-1} \qquad \text{(W2.23)}$$

This rough prediction for the Larmor diamagnetic response of all atoms is compared with the experimental data in Figure W2.6. We see that the prediction appears to be slightly greater than diamagnetic response of any particular element, but does form a conceivable 'baseline' (or background) diamagnetic susceptibility. In order to make a more realistic calculation of this background diamagnetic response found in all matter, one can consult tabulations of the calculated values of $\overline{\rho^2}$ for atomic orbitals. These values would show more realistic variations across the periodic table.

2. Partly-filled electron shells

As we mentioned in the text following Figure W2.5, the magnetic moment due to an electron in an orbital is generally much larger than the diamagnetic change in the magnetic moment when a magnetic field is applied. If the magnetic moment is not compensated by an equivalent orbital, then the main effect of the applied field is to apply a *torque* to the magnetic moment which tends to align it with the applied field. This paramagnetic response can only occur in partly-filled electron shells, but when it does occur it is generally considerably stronger than the background diamagnetic response of the filled orbitals on the atom or ion.

Thus if we have partially-filled electron shells, in the absence of an applied field, the magnetic moments on each atom or ion will point randomly in all directions (Figure W2.7). An applied magnetic field will tend to align the magnetic moments to some extent, in competition with the thermal disorder that tends to randomise the atomic orientations

Curie Law

If all the magnetic moments (m) in one mole of substance were parallel to one another, then the total magnetic moment would be $N_A m$. The effect of the thermal disorder reduces the total magnetic moment below this figure and so we can write:

$$\text{molar magnetic moment} = \text{fraction} \times N_A m \qquad \text{(W2.24)}$$

where the *fraction* is zero in the absence of a magnetic field, and has a maximum value of one when

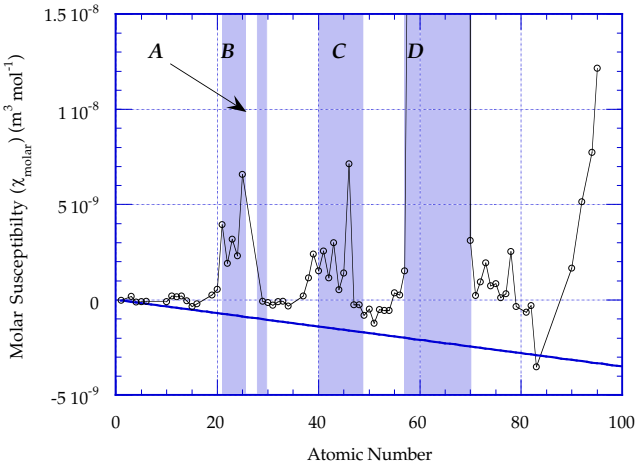

Figure W2.6 (a) The directions of the magnetic moment resulting from electron orbits in opposite directions. In the presence of a magnetic

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the all the atomic magnetic moments are aligned. The value of the *fraction* will depend on the ratio of the magnetic energy of a magnetic dipole in a field to the thermal energy of the magnetic dipole. As an approximation we therefore write:

$$\text{molar magnetic moment} = \frac{\text{magnetic energy}}{\text{thermal energy}} \times N_A m \qquad \text{(W2.25)}$$

Recalling that the potential energy of a magnetic dipole in a field is $-\mathbf{m}.\mathbf{B}$ which is $\approx mB$ and the thermal energy associated with atomic rotation is $\approx k_B T$, we write:

$$\text{molar magnetic moment} \approx \left[\frac{mB}{k_B T}\right] \times N_A m \qquad \text{(W2.26)}$$

We expect this expression to be valid only when $mB << k_B T$. In this case we can write $B \approx \mu_o H$:

$$\text{molar magnetic moment} \approx \left[\frac{\mu_o mH}{k_B T}\right] \times N_A m \qquad \text{(W2.7)}$$

and so the molar susceptibility (Equation W2.6) is given by:

$$\chi_{\text{molar}} \approx \frac{\mu_o N_A m^2}{k_B T} \qquad \text{(W2.28)}$$

A more detailed theory (*Bleaney and Bleaney*) predicts an expression which differs from W2.28 by a factor $\frac{1}{3}$

$$\chi_{\text{molar}} \approx \frac{1}{3}\frac{\mu_o N_A m^2}{k_B T} \ \text{m}^3\,\text{mol}^{-1} \qquad \text{(W2.29)}$$

The expression W2.29 expresses the *Curie law* of magnetic susceptibility. The law is incidentally named after *Pierre* Curie the husband of Marie.

Figure W2.7 An illustration of the random orientations of permanent magnetic moments on atoms. The magnetic moment is represent schematically by an arrow and a loop indicating the sense in which an equivalent current would flow.

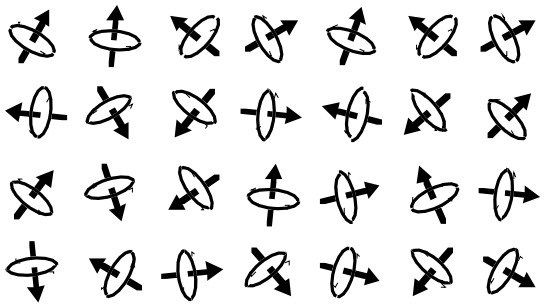
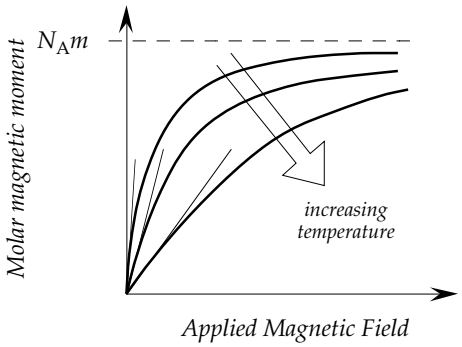
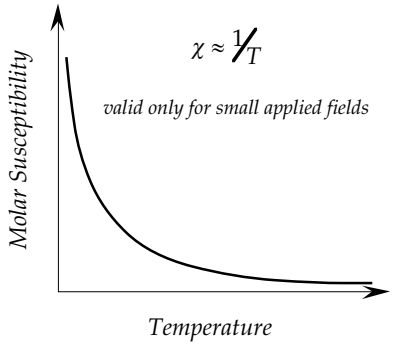


Figure W2.8 Illustration of (Pierre) Curie Law behaviour. (a) shows three magnetisation curves at three different temperatures. Notice that at the highest fields the magnetic moment eventually saturates. (b) shows the variation of the initial slopes in (a) with temperature.

(a)



(b)



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Example W2.2

Vanadium is an element which has unfilled electronic orbitals. Estimate the magnetic moment on each atom?

If we rearrange Equation W2.2.29 to solve for m we can write:

$$m = \sqrt{\frac{3k_B}{\mu_o N_A}} \times \sqrt{\chi_{molar} T}$$

Enumerating this yields:

$$m = \sqrt{\frac{3 \times 1.38 \times 10^{-23}}{4\pi \times 10^{-7} \times 6.02 \times 10^{23}}} \times \sqrt{\chi_{molar} T}$$

which evaluates to:

$$m = 7.40 \times 10^{-21} \sqrt{\chi_{molar} T} \quad \text{J T}^{-1}.$$

Substituting the value of the molar susceptibility of vanadium (Table W2.1) = 3.20×10^{-9} m^3 mol^{-1} at 293 K we arrive at:

$$m = 7.40 \times 10^{-21} \sqrt{3.20 \times 10^{-9} \times 293}$$
$$= 7.17 \times 10^{-24} \quad \text{J T}^{-1}$$

Magnetic moments on atoms and ions are normally expressed in smaller units than JT^{-1} known as Bohr magnetons defined by:

$$Bohr \;\; magneton(\mu_B) = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} \text{ J T}^{-1}$$

In these units the magnetic moments of the atoms of a substance may be written as:

$$m = 798\sqrt{\chi_{molar} T} \text{ Bohr magneton}$$

which evaluates to:

$$m = 0.77 \;\; \mu_B$$

Note: In this answer we have neglected to take account of the weak diamagnetic contribution to the molar susceptibility arise from filled shells.

The magnitudes of atomic magnetic moments

As we saw in Example W2.2, typical values of atomic magnetic moments deduced from a Curie Law analysis of the transition series elements are of the order of a Bohr magneton (μ_B). The magnetic moments arise because of the orbital and spin orientations of electrons in partially-filled electron shells.

Each electron within a shell chooses its orbit so as to minimise the strong *electrical* repulsion between itself and the other electrons in the shell. In partially-filled shells with several electrons, the minimum energy configuration of electrons can have a considerable resultant magnetic moment.

Example W2.3

Atoms which possess intrinsic magnetic moments typically have moments of the order of one Bohr magneton. Estimate the current i which must flow around an area A of the same order as an atomic cross-sectional area in order to produce a magnetic moment of one μ_B.

We remind ourselves of Equation W2.2,

$$m = iA.$$

We can estimate A as being $\approx \pi \langle r^2 \rangle$ which for $r \approx 10^{-10}$ m is $\approx 10^{-20}$ m^2. Since $\mu_B = 9.27 \times 10^{-24}$ Am^2 we have:

$$i = \frac{m}{A} \approx \frac{9.27 \times 10^{-24}}{10^{-20}}$$
$$\approx 10^{-3} \;\; A$$

Thus to produce a magnetic moment typical of the values found in atoms requires currents of the order of a milliamp to flow around a loop of atomic dimensions.

3. Conduction electrons

We have described in the previous section the magnetic response of electrons in orbitals around atoms or ions. This response occurs in all matter. However in metals and semiconductors there are additional contributions to the magnetic response of a substance due to the conduction electrons. It is found that this response is generally rather weak, but that the orbital motion of conduction electrons respond diamagnetically and the spins of the conduction electrons respond paramagnetically.

Conduction electron diamagnetism

In section 5 of chapter 6 we described the way in

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which conduction electrons occupied plane wave quantum states. Each of these quantum states corresponded to a electron travelling in a straight line. We envisaged that electrons would stay in a quantum state until a *scattering event* occurs after an average time τ which will transfer the electron to a new quantum state. However when a magnetic field **B** is applied, the Lorentz force $q\mathbf{v}\times\mathbf{B}$ causes the electron paths to change from straight lines to arcs of circles as shown in Figure W2.9.

In FigureW2.9 (c) it is clear that at high fields the electron trajectories have become significantly curved and one can imagine at much larger fields electrons will travel in complete circles before scattering. The magnetic force which acts perpendicular to the electron trajectories causes electrons into circular orbits with an angular frequency ω_c given by Equation W2.15 (where the symbol $\Delta\omega$ is used instead of ω_c):

$$\omega_c = \frac{eB}{2m_e} \qquad \text{(W2.15* and W2.30)}$$

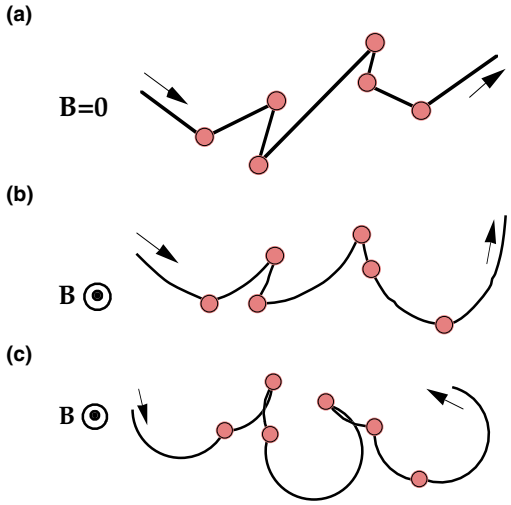
Thus the number of radians that an electron orbits before scattering is on average $\omega_c\tau$. If the magnetic field is such that $\omega_c\tau >> 1$ then a variety of interesting phenomena occur that we do not have time to discuss further here.

The magnitude of the diamagnetic effect of is extremely difficult to calculate. Here we merely note that it is (a) relatively small, and (b) typically one third of the paramagnetic response of the electrons described in the following section.

Conduction electron (Pauli) paramagnetism

Now we consider the effect of a magnetic field on the spin of conduction electrons. The origin of this interaction with the field is that electrons have an magnetic moment which is described in relation to an internal 'spin' degree of freedom. The magnetic moment μ_e points in the opposite direction to the spin and is given by:

Figure W2.9 Illustration of the effect of a magnetic field on typical conduction electron trajectory (a) shows the trajectory in zero field. The spheres indicate a scattering event. In (b) a weak field is applied causing slight curvature of the electron paths. In (c) a much stronger field is applied which significantly affects the electron trajectories.



Example W2.4

How large must a magnetic field be in order to ensure the condition $\omega_c\tau >> 1$ is satisfied?

We must have (From Equation W2.15)

$$\frac{eB\tau}{2m} >> 1$$

which requires:

$$B >> \frac{2m}{e\tau}$$

Recalling from our studies of the resistivities of metals that at room temperature $\tau \approx 10^{-14}$ seconds we write:

$$B >> \frac{2\times 9.1\times 10^{-31}}{1.6\times 10^{-19}\times 10^{-14}} \approx 1100 \text{ tesla}$$

It is currently technology impossible to achieve a field of this magnitude (except transiently through the use of exploding and imploding coils of wire). Steady field values of limited to less than 20 or 30 T, and pulsed values to $<\approx$ 100 T. Thus in order to study matter when $\omega_c\tau >> 1$ the scattering time τ must be reduced by using pure samples of substances at low temperatures (≈ few K or less).

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$$\mu_e = \frac{g_s \mu_B}{\hbar}\mathbf{S} \qquad \text{(W2.31)}$$

where:

- g_s is the spin *g*-factor which has a value 2.002: which is usually taken to be 2 for work in solids. The significance of the spin *g*-factor taking the value 2 is that magnetic moments arising from the intrinsic spin of electrons are twice as large would be expected from the equivalent amount of non-spin, i.e. *orbital,* angular momentum.
- μ_B is a Bohr magneton = 9.274×10^{-24} (A m^2 or J T^{-1})
- **S** is the spin of the electron which has values of $\pm\hbar/2$

The electron spin can orient itself in one two ways with respect to applied field, and the energy of interaction with the magnetic field **B** is therefore:

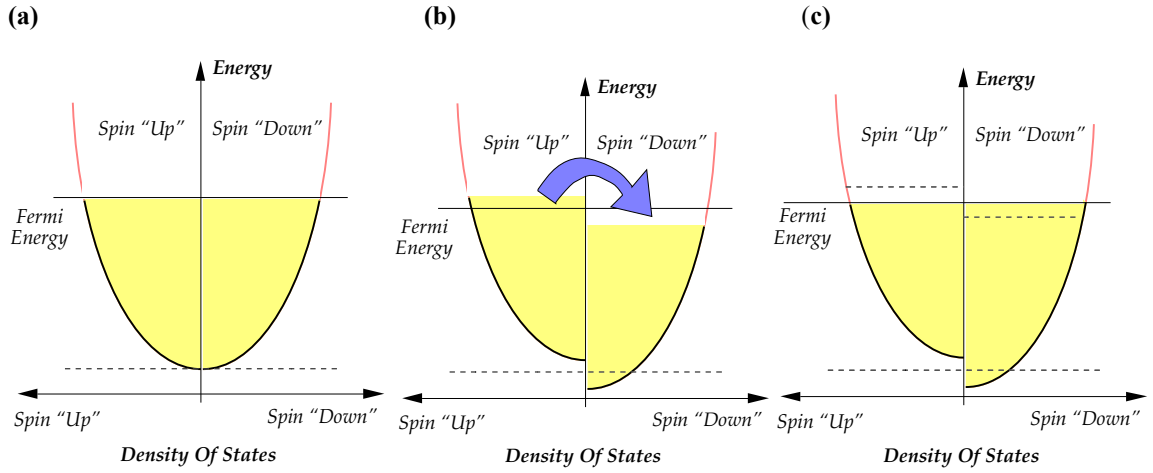
$$\begin{aligned} u &= \mu_e \cdot \mathbf{B} \\ &= +\frac{g_s \mu_B}{\hbar}\mathbf{S}\cdot B \end{aligned} \qquad \text{(W2.32)}$$

and an electron can lower its energy if it orients itself so that its magnetic moment is *parallel* to **B** i.e. so that its spin is *anti-parallel* to **B**. Since **S** takes the value of $\pm\hbar/2$ the energy of electron will be:

$$\begin{aligned} u &= +\frac{2\mu_B}{\hbar}\left[\pm\frac{\hbar}{2}\right]B \\ &= \pm\mu_B B \end{aligned} \qquad \text{(W2.33)}$$

Now conduction electrons in a metal are not able to just change their spin orientation at will because, as outlined in §6.5, the electrons are 'packed' two at a time into **k**-states, one spin up and one spin down. In general the *exclusion principle* prevents an electron from changing its spin state because the quantum state with the same **k**-state but opposite spin is al-

Figure W2.10 Illustration of the origin of conduction electron (Pauli) paramagnetism. In (a) no magnetic field is applied, and so as many electrons have spin up as spin down because the energy of these two states is the same. In (b) electrons with spins parallel to the magnetic field **B** have a lower energy than electrons with spins anti-parallel to **B**. The Figure shows a hypothetical situation that might occur if the field were applied suddenly before the electrons had a chance to change their spin state. In the situation shown, the metal would still have no net magnetic moment. However clearly the 'spin up' electrons can lower their energy by reversing their spin and occupying 'spin down' states with a higher *kinetic energy*. In (c) the process described in (b) has been completed. There is now a net excess of electrons having 'spin down' i.e. spin anti-parallel to **B**. It is this imbalance that we can detect as the paramagnetic response of conduction electrons. The magnitude of the response will clearly be larger if we have a large density of states at the Fermi energy.



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ready occupied. As shown in Figure W2.10, only those electrons in **k**-states close to the Fermi energy can change their spin state. They do this by occupying k-states with higher *kinetic energy*, but opposite spin.

When the electrons change spin, the balance between 'spin up' and 'spin down' is altered and the metal acquires a net magnetic moment. Since more electron magnetic moments are parallel to the magnetic field than anti-parallel to the field, the metal has a paramagnetic response, normally called the *Pauli paramagnetism*. We can calculate the magnetisation if we look at the imbalance between 'spin up' and 'spin down' electrons.

Net magnetic moment per unit volume =
[Extra 'Spin Down' Electrons] × [$+\mu_B$]
–[Lost 'Spin Up' Electrons] × [$-\mu_B$]
(W2.34)

$$M = \underbrace{\left[\frac{g(E_F)}{2}\times\mu_B B\right]}_{\substack{\text{number of extra}\\ \text{'spin–down'}\\ \text{electrons}}}\times\left[\mu_B\right] - \underbrace{\left[\frac{g(E_F)}{2}\times\mu_B B\right]}_{\substack{\text{number of lost}\\ \text{'spin–up'}\\ \text{electrons}}}\times\left[-\mu_B\right] \quad \text{(W2.35)}$$

$$\begin{aligned} M &= \left[\frac{g(E_F)\mu_B B}{2} + \frac{g(E_F)\mu_B B}{2}\right]\times\left[\mu_B\right] \\ &= \left[g(E_F)\mu_B B\right]\times\left[\mu_B\right] \\ &= g(E_F)\mu_B^2 B \end{aligned} \quad \text{(W2.36)}$$

where $g(E_F)$ is the density of states at the Fermi Energy and so $g(E_F)/2$ is the density of either 'spin up' or 'spin down' states at the Fermi Energy.

This Pauli contribution has no (or only a weak) temperature-dependence. It is of a similar order of magnitude, but rather smaller than, the diamagnetic contribution $\chi_{molar} \approx -3.6Z\times10^{-11} = -104.4 \times 10^{-11}$ m^3 mol^{-1} (Equation W2.23). Notice that in general the experimental molar susceptibility -6.87×10^{-11} m^3 mol^{-1} is the result of several contributions mentioned above, and no single contribution dominates unless there are unfilled electronic orbitals.

Nuclei.

The nuclei at core of atoms consists of *nucleons*, i.e. neutrons and protons, arranged in a structure determined by a balance between the strong nuclear force and the electric force. Both protons and, surprisingly, neutrons, possess intrinsic magnetic moments, in general nuclei possess orbital angular momentum as well. It is thus common for nuclei to possess magnetic moments. However the magnitude of the magnetic moments are typically 1000 times smaller than the magnitude of electronic magnetic moments. As a result of this the nuclear contribution to the magnetic moment is usually negligible.

Example W2.5

Estimate the molar susceptibility due to the spins of the conduction electrons in copper according to EquationW2.36

We first note that the susceptibility will eventually be shown to be rather small, and so we may equate the magnetic induction field B in Equation W2.36 with $\mu_o H$. Hence the molar susceptibility $\chi_m = M/H$ may be written as:

$$\chi_{molar}^{Pauli} = \frac{M}{H} = \mu_o \mu_B^2 g_m(E_F)$$

The density of electronic states at the Fermi energy $g(E_F)$ is given in the Free Electron Approximation by:

$$g(E_F) = \frac{V\sqrt{2m^3 E_F}}{\pi^2\hbar^3}$$

This has been evaluated for copper in Example 7.14. where we estimated the electronic contribution to the heat capacity of copper. Using that estimate of:

$$g(E_F) = 8.026 \times 10^{41} \text{ states J}^{-1} \text{ mol}^{-1}$$

and recalling that a Bohr magneton μ_B has a value 9.27×10^{24} J T^{-1} we estimate the Pauli contribution to the magnetic susceptibility of copper as:

$$\begin{aligned} \chi_{molar}^{Pauli} &= 4\pi\times10^{-7}\times\left(9.274\times10^{-24}\right)^2\times8.026\times10^{41} \\ &= 8.67\times10^{-11} \text{ m}^3\text{ mol}^{-1} \end{aligned}$$

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$$\text{nuclear magneton}(\mu_N) = \frac{e\hbar}{2m_p}$$
$$= 5.051\times10^{-27}\ \text{J T}^{-1}$$
$$\mu_N = 5.45\times10^{-4}\,\mu_B \qquad \text{(W2.37)}$$

The interaction between magnetic moments is extremely weak and so the nuclei obey the Curie Law (W2.29) extremely well. Thus at low temperatures (< 1 K), in materials with an otherwise weak magnetic response, it is possible to detect the magnetic response of the nuclei. Indeed the extremely weak interactions between the nuclei cause them to order magnetically at temperatures below 1μK.

Summary.

The main questions raised by our preliminary examination of the experimental data on the magnetic properties of solids were:

The strength of paramagnetism in the transition and lanthanide series

We saw that in all matter there is a weak background diamagnetic response due to filled electron shells, and that in addition to this there is a paramagnetic response from electrons in partially-filled shells. In the transition series of elements the 3*d*, 4*d* and 5*d* electron shells are partially -filled and so we can understand that the paramagnetism of the elements in these series should be rather strong. Understanding the detailed behaviour requires a theory of the origin atomic magnetic moments which is beyond the scope of this text.

Figure W2.3 shows that the lanthanide elements displayed an especially strong paramagnetic response. This response is due to the partial-filling of the 4*f* electron shell. We recall from our discussion of the density anomalies in the lanthanide series (§7.2) that the 4*f* lies *inside the atom* and is not involved in bonding with neighbouring atoms. This is in contrast with the transition elements in which the *d*-shells that are involved in the strong magnetic response are also involved in bonding to neighbouring atoms. Electrons involved in bonding are not able to re-orient their orbital motion in order to align with the field. This is because the electric forces of bonding are much stronger than the magnetic forces trying to orient the orbits so that their magnetic moment aligns with the field. So for electrons in *d*-orbitals, only the spin magnetic moment aligns with the applied field. The inability of the orbital angular momentum of bonded electrons to reorient themselves is known as *quenching* of orbital magnetic moment.

However in the lanthanide series, there is no quenching of the orbital angular momentum. When coupled with the fact that orbital angular momentum of electrons in the 4*f* shells is rather large this gives rise to the extraordinarily large magnetic susceptibilities of the lanthanide series.

In conclusion we note the measured values of susceptibility and the inferred values of the magnetic moments give many clues about the detailed occupancy of electronic orbitals in solids.

The occurrence of para- and dia-magnetism outside the transition series

Outside the transition series, there are no contributions to the magnetic response from partially-filled orbitals. The susceptibility is therefore determined by the balance between the remaining modes of response. In insulators we have only the Larmor diamagnetic response. In metals we have additional due to the conduction electrons which are generally slightly paramagnetic.

The smallness of most susceptibilities

The magnetic responses of substances that we have discussed so far are in general rather weak. The basic reason for this that the magnetic energy is general rather small in comparison with other energies involved in the magnetic response of the substance. In Larmor diamagnetism, the magnetic force on the electron competes with the electronic forces on the electron (F_o in Equation W2.11). In Curie paramagnetism, there is competition between thermal disor-

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Table W2.3 Summary of the response of non-interacting electrons to applied magnetic fields. The type of response is listed with the name of the scientist most closely associated with it.

	Core electrons (filled shells)	Core electrons (partly-filled shells)	Conduction electrons	Nuclei
Spin response	No response	Paramagnetism (Curie) $\chi \approx 1/T$	Paramagnetism (Pauli)	Weak paramagnetism (Curie) $\chi \approx 1/T$
Orbital response	Diamagnetism (Larmor)	Paramagnetism (Curie) $\chi \approx 1/T$	Diamagnetism (Landau)	Weak paramagnetism (Curie) $\chi \approx 1/T$

der and magnetic torques on atoms. Thus at low temperatures the Curie susceptibility can become much larger than Figure W2.8 would indicate. Similarly in Pauli paramagnetism, the competition is between the magnitude of the magnetic energy and the Fermi energy. And finally in Landau diamagnetism the competition is between the magnitude of electronic speeds of the order of the Fermi velocity, and the Lorentz force on the electrons. In all these responses, the magnetic energy is generally small compared with the other (mainly electronic) energies involved.

Ferromagnets

For the reasons mentioned above, we can be even more surprised at the gigantic magnitude of the magnetic response of ferromagnets. This is not the place to discuss the experimental data at length, however it is important to note that the origin of this behaviour is in the *coulomb* interaction *between* electrons in the solid, *not* the magnetic interaction of these electrons with an external magnetic field.

The Curie theory of the paramagnetic properties of the atoms with partially-filled orbitals implicitly assumes that there are no interactions of any kind between neighbouring magnetic moments. Inevitably there will of course be some kind of interaction between the atomic magnetic moments. In ferromagnets these interactions cause neighbouring atomic magnetic moments to align parallel to one another (Figure W2.11)

However — and this is frequently not appreciated — the interactions between neighbouring magnetic moments *are* ***not*** *magnetic*. they arise from consideration both of quantum mechanics and the coulomb electrical interactions. That magnetic forces cannot give rise to ferromagnetism may be appreciated by anyone who has played with a pair of bar magnets. Such magnets will spontaneously try to align such that that north-seeking and south-seeking poles of the magnet are together (Figure W2.1 (b)) which in atomic terms correspond to neighbouring atomic magnetic moments pointing *in opposite directions* (Figure W2.1 (c)). Clearly such forces cannot give rise to the ferromagnetic structure illustrated in Figure W2.1 (a).

The interactions which give rise to ferromagnetism are off the same nature as those which cause magnetic moments *within atoms*. Consider two electrons in a partially-filled orbital on an atom. Since the electrons repel one another, they correlate their motion so as to minimise this repulsion. In classical terms, one way of doing this is to orbit the atom in the same sense, but 180° out of phase so that they are always on opposite sides of the atom. Quantum mechanically this corresponds to occupying quantum states with parallel angular momenta. It is considerations of this type which give rise to the occurrence of permanent magnetic moments on atoms with partially filled orbitals.

In a ferromagnetic substance, these correlations persist from each atom to its immediate neighbour. For example, electrons on one atom may be able to minimise their coulomb repulsion of electrons on a neighbouring atom by arranging that their orbits are in the same sense as those of electrons on

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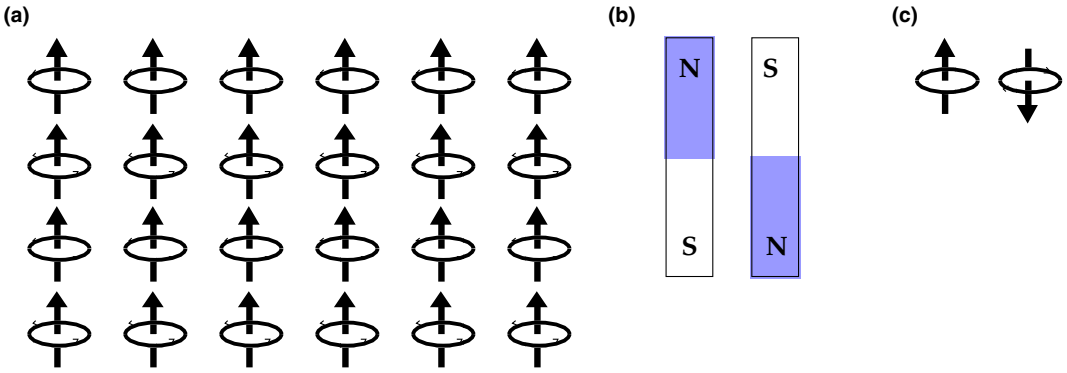
Figure W2.11 (a) the magnetic moments on neighbouring atoms within a ferromagnet are aligned my the *electrical* interaction of the electrons on each atom. Note that *magnetic* interactions would tend to cause alignment as indicated in (c). This is familiar to us as the propensity of bar magnets to align as indicated in (b). Thus magnetic interactions would never give rise to ferromagnetism.



neighbouring atom. If this is so for all neighbours within the solid, then the magnetic dipoles on each atom will be aligned *despite* the fact that magnetically they would rather be oriented anti-parallel to their neighbours. This essentially coulomb-driven alignment of neighbouring orbitals is known as *ferromagnetism*. This is the mechanism whereby a substance possess a permanent magnetic dipole moment, in the absence of an applied field. The ferromagnetically-ordered arrangement of atomic dipole moments may be destroyed if the temperature is raised sufficiently. The temperature required to destroy the spontaneous magnetisation of a substance is known as the *Curie temperature*, and is large for substances in which there is a large coulomb interaction between electrons on neighbouring atoms (known technically as the *exchange* interaction). Many substances have weak exchange interactions and become magnetically ordered at low temperatures. Only rare substances have sufficiently strong exchange interactions to allow ferromagnetism to survive at room temperature and above.

Sometimes electrons on one atom may minimise their coulomb repulsion of electrons on neighbouring atoms by arranging that their orbits are in the opposite sense as those of electrons on neighbouring atoms i.e. they have a negative exchange energy. This phenomena gives rise to a different (but related) type of magnetic order known as *antiferromagnetism*.

Finally, we note that in commonly occurring ferromagnets such iron, steel and iron oxides, the observed magnetic properties depend strongly on the so-called *domain structure* of the magnet. A domain is small region of ferromagnet (typically 10 nm to 1000 nm in size) within which the magnetic moments are aligned as illustrated in Figure W2.11(a). However neighbouring domains are typically aligned with their magnetic moments opposite to one another in order to minimise the magnetic interaction between the domains (Figure W2.11(b)). The bulk magnetic properties of these materials depend on the way in which an applied field causes domains to either

- grow,
- shrink or
- stay the same size,

when an magnetic field is applied to the sample.

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W2.5 Exercises

P1. List three diamagnetic and three paramagnetic elements. (Table W2.1)

P2. What is the maximum susceptibility of an element in the second transition row of the periodic table (Y to Cd) (Figures 2.2 and W2.3 and Table W2.1)

P3. Estimate the Larmor diamagnetic susceptibility (Equation W2.23) for (a) scandium (b) neodymium and (c) germanium.

P4. What is the magnetic susceptibility of titanium? What is the expected magnetic moment of a titanium sample of volume 1 mm^3 held in a magnetic field of 1 tesla? What is the magnetisation M of the titanium? What is the applied field H inside the sample? What is magnetic field B inside the sample? What is the magnetic moment per atom?

P5. Superconductors can display perfect diamagnetism i.e. the internal magnetic field B is always zero. Use Equations W2.1 and W2.5 to show that the volume susceptibility $\chi_V = -1$.

P6. In a magnetic field B, a magnetic moment **m** is subject to a torque Γ given by

$$\Gamma = \mathbf{m} \times \mathbf{B}$$

Explain why the torque on a sample of copper in a large magnetic field is essentially zero.

P7. In a vibrating sample magnetometer (*VSM*) a sample is subjected to magnetic field and then vibrated sinusoidally inside a coil of wire. The magnetic moment acquired by the sample induces a voltage in the coil. At room temperature a sample of ferromagnetic nickel has a magnetic moment of 3×10^{-3} Am^{-2} and induces an *rms* voltage of 1.3 V in a *VSM* pickup coil. What voltage would you expect from samples of (a) silicon and (b) uranium each with a volume of 10 mm^3 in a magnetic field of 1 tesla. (Table W2.19).

P8. Explain to a colleague who is not studying physics that all substances, even apparently non-magnetic ones (such as plastics) become magnetised in the presence of an applied magnetic field. How would you demonstrate this to them using apparatus costing less than £100? (Hint: think of the principle of "null methods" or "balance methods" used for detecting small changes described in Chapter 3).

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