

## Paramagnetism

"A grocer is attracted to his business by a magnetic force as great as the repulsion which renders it odious to artists."

Honoré De Balzac, *Les célibataires*. 1841.

In the previous chapter we discussed the diamagnetic effect, which is observed in all materials, even those in which the constituent atoms or molecules have no permanent magnetic moment. Next we are going to discuss the phenomenon of paramagnetism, which occurs in materials that have net magnetic moments. In paramagnetic materials these magnetic moments are only weakly coupled to each other, and so thermal energy causes random alignment of the magnetic moments, as shown in Fig. 5.1(a). When a magnetic field is applied, the moments start to align, but only a small fraction is deflected into the field direction for all practical field strengths. This is illustrated in Fig. 5.1(b).

Many salts of transition elements are paramagnetic. In transition metal salts, each transition metal cation has a magnetic moment resulting from its partially filled d shell, and the anions ensure spatial separation between cations. Therefore the interactions between the magnetic moments on neighboring cations are weak. The rare earth salts also tend to be paramagnetic. In this case the magnetic moment is caused by highly localized f electrons, which do not overlap with f electrons on adjacent ions. There are also some paramagnetic metals, such as aluminum, and some paramagnetic gases, such as oxygen,  $O_2$ . All ferromagnetic materials (which we will discuss in the next chapter) become paramagnetic above their Curie temperature, when the thermal energy is high enough to overcome the cooperative ordering of the magnetic moments.

At low fields, the flux density within a paramagnetic material is directly proportional to the applied field, so the susceptibility,  $\chi = M/H$ , is approximately constant. Generally  $\chi$  is between around  $10^{-3}$  and  $10^{-5}$ . Because the susceptibility is only slightly greater than zero, the permeability is slightly greater than 1 (unlike

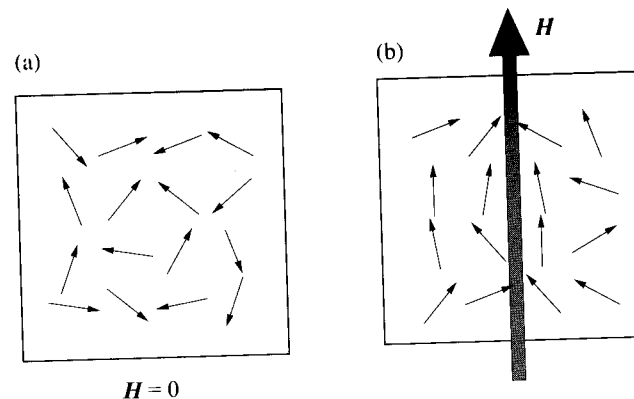


Figure 5.1 Schematic of the alignment of magnetic moments in a paramagnetic material: (a) shows the alignment in the absence of an external field, and (b) shows the response when a field of moderate strength is applied.

paramagnets, where it was slightly less than 1). In many cases, the susceptibility is inversely proportional to the temperature. This temperature dependence of  $\chi$  can be explained by the Langevin localized moment model<sup>10</sup> which we will discuss in the next section. However in some metallic paramagnets the susceptibility is independent of the temperature – these are the Pauli paramagnets. The paramagnetism in the Pauli paramagnets results from a quite different mechanism, and is well described by the band structure theory of collective electrons. We will discuss Pauli paramagnetism in Section 5.4.

### 5.1 Langevin theory of paramagnetism

The Langevin theory explains the temperature dependence of the susceptibility in paramagnetic materials by assuming that the non-interacting magnetic moments on atomic sites are randomly oriented as a result of their thermal energy. When an external magnetic field is applied, the orientation of the atomic moments shifts slightly towards the field direction as shown schematically in Fig. 5.1. We will derive the expression for the susceptibility using a classical argument, then extend it to the quantum mechanical case at the end of the derivation.

For a moment which makes an angle  $\theta$  to the applied field  $H$ , the probability of occupying an energy state,  $E$ , is (by Boltzmann statistics)

$$e^{-E/k_B T} = e^{m \cdot H / k_B T} = e^{m H \cos \theta / k_B T}. \quad (5.1)$$

(Here the un-bold  $m$  and  $H$  represent the magnitude of the magnetic moment and field vectors respectively, and  $k_B$  is Boltzmann's constant). We can calculate the number of moments lying between angles  $\theta$  and  $\theta + d\theta$  with respect to the field

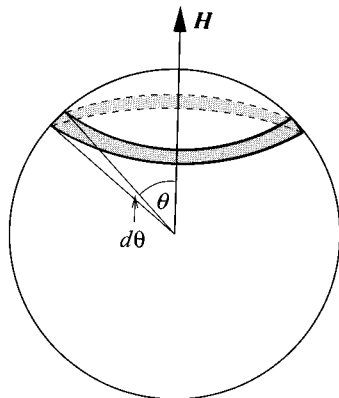


Figure 5.2 The fraction of paramagnetic moments between angles  $\theta$  and  $\theta + d\theta$  around an axis is equal to the fractional area that the angle  $d\theta$  sweeps out on the surface of the sphere as shown.

$H$ , by noticing that it is proportional to the fractional surface area of a surrounding sphere, as shown in Fig. 5.2. This fractional surface area,  $dA = 2\pi r^2 \sin \theta d\theta$ .

So the overall probability,  $p(\theta)$ , of an atomic moment making an angle between  $\theta$  and  $\theta + d\theta$  is

$$p(\theta) = \frac{e^{mH \cos \theta / k_B T} \sin \theta d\theta}{\int_0^\pi e^{mH \cos \theta / k_B T} \sin \theta d\theta}, \quad (5.2)$$

where the denominator is the *total* number of atomic magnetic moments, and the factors of  $2\pi r^2$  cancel out.

Each moment contributes an amount  $m \cos \theta$  to the magnetization parallel to the magnetic field, and so the magnetization from the whole system is

$$M = Nm \langle \cos \theta \rangle \quad (5.3)$$

$$= Nm \int_0^\pi \cos \theta p(\theta) d\theta \quad (5.4)$$

$$= Nm \frac{\int_0^\pi e^{mH \cos \theta / k_B T} \cos \theta \sin \theta d\theta}{\int_0^\pi e^{mH \cos \theta / k_B T} \sin \theta d\theta}. \quad (5.5)$$

$$(5.6)$$

Carrying out the nasty integrals (or looking them up in tables!) gives

$$M = Nm \left[ \coth \left( \frac{mH}{k_B T} \right) - \frac{k_B T}{mH} \right] \quad (5.7)$$

$$= Nm L(\alpha), \quad (5.8)$$

where  $\alpha = mH/k_B T$  and  $L(\alpha) = \coth(\alpha) - 1/\alpha$  is called the Langevin function. The form of  $L(\alpha)$  is shown in Fig. 5.3. If  $\alpha$  were made large enough, for example

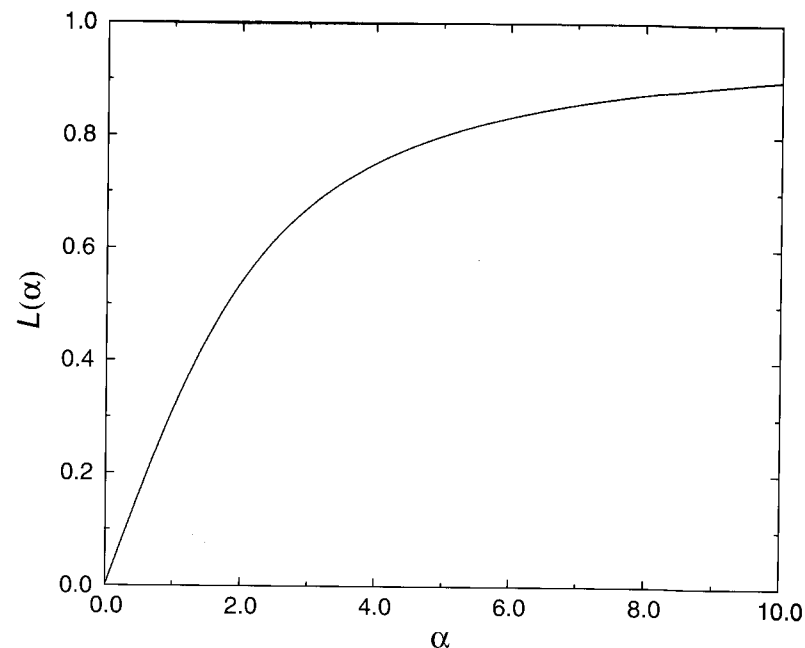


Figure 5.3 The Langevin function,  $L(\alpha)$ .

by applying a very large field, or lowering the temperature towards zero kelvin, then  $M$  would approach  $Nm$ , and complete alignment of the magnetic spins could be achieved.

Now what about our earlier statement that  $\chi \propto 1/T$ ? We were expecting to see  $M = \text{some constant} \times H/T$  and we've ended up with something far more complicated. Well, the Langevin function can be expanded as a Taylor series:

$$L(\alpha) = \frac{\alpha}{3} - \frac{\alpha^3}{45} + \dots \quad (5.9)$$

So, keeping only the first term, (which dominates at all practical fields and temperatures since  $\alpha$  is very small),

$$M = \frac{Nm\alpha}{3} = \frac{Nm^2 H}{3k_B T}. \quad (5.10)$$

(The equivalent expression in SI units is  $M = (N\mu_0 m^2 / 3k_B)(H/T)$ , since  $E = -\mu_0 \mathbf{m} \cdot \mathbf{H}$ ). The magnetization is proportional to the applied field and inversely proportional to the temperature, as we expected. This gives the susceptibility

$$\chi = \frac{M}{H} = \frac{Nm^2}{3k_B T} = \frac{C}{T}, \quad (5.11)$$

where  $C = Nm^2/3k_B$  is a constant. This is Curie's law – the susceptibility of a paramagnet is inversely proportional to the temperature.

So far we have assumed that the magnetic dipole moment can take all possible orientations with respect to the applied magnetic field, whereas in reality it can have only discrete orientations because of spatial quantization. If we incorporate the quantization into the derivation of the total magnetization, we obtain:

$$M = NgJ\mu_B \left[ \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\alpha\right) - \frac{1}{2J} \coth\left(\frac{\alpha}{2J}\right) \right] \quad (5.12)$$

$$= NgJ\mu_B B_J(\alpha). \quad (5.13)$$

$B_J(\alpha)$  is the Brillouin function, which is equal to the Langevin function in the limit that  $J \rightarrow \infty$ . The Brillouin function can also be expanded in a Taylor series:

$$B_J(\alpha) = \frac{J+1}{3J}\alpha - \frac{[(J+1)^2 + J^2](J+1)}{90J^3}\alpha^3 + \dots \quad (5.14)$$

where  $\alpha = Jg\mu_B H/k_B T$ .

Keeping only the first term in the expansion, the quantum mechanical expression for the susceptibility becomes

$$\chi = \frac{Ng^2 J(J+1)\mu_B^2}{3k_B T} = \frac{C}{T}. \quad (5.15)$$

Again, to obtain the susceptibility in SI units, this expression is multiplied by  $\mu_0$ . The overall form of the response is the same as in the classical case, but this time the proportionality constant,  $C$ , is given by  $Ng^2 J(J+1)\mu_B^2/3k_B = Nm_{\text{eff}}^2/3k_B$  where  $m_{\text{eff}} = g\sqrt{J(J+1)}\mu_B$ .

## 5.2 The Curie–Weiss law

In fact many paramagnetic materials do not obey the Curie law which we just derived, but instead follow a more general temperature dependence given by the Curie–Weiss law:

$$\chi = \frac{C}{T - \theta}. \quad (5.16)$$

Paramagnets which follow the Curie–Weiss law undergo spontaneous ordering and become ferromagnetic below some critical temperature, the Curie temperature,  $T_C$  (which we'll see later is for all practical purposes equal to  $\theta$ ).

In our derivation of the Curie law we assumed that the localized atomic magnetic moments do not interact with each other at all – they are just reoriented by the applied magnetic field. Weiss explained the observed Curie–Weiss behavior by postulating the existence of an internal interaction between the localized moments which he called a 'molecular field'. He did not speculate as to the origin of his molecular

field, beyond suggesting that it is a mutual interaction between the electrons which tends to align the dipole moments parallel to each other. (We can't really criticize Weiss for this – remember that the electron had been discovered only 10 years earlier, and quantum mechanics hadn't been 'invented' yet!)

Weiss assumed that the intensity of the molecular field is directly proportional to the magnetization:

$$H_W = \gamma M, \quad (5.17)$$

where  $\gamma$  is called the *molecular field constant*. So the total field acting on the material is

$$H_{\text{tot}} = H + H_W. \quad (5.18)$$

We just derived

$$\chi = \frac{M}{H} = \frac{C}{T}, \quad (5.19)$$

so, replacing  $H$  by  $H_{\text{tot}} = H + \gamma M$ ,

$$\frac{M}{H + \gamma M} = \frac{C}{T} \quad (5.20)$$

or

$$M = \frac{CH}{T - C\gamma}. \quad (5.21)$$

Therefore

$$\chi = \frac{M}{H} = \frac{C}{T - \theta}, \quad (5.22)$$

the Curie–Weiss law!

When  $T = \theta$  there is a divergence in the susceptibility, which corresponds to the phase transition to the spontaneously ordered phase. A positive value of  $\theta$  indicates that the molecular field is acting in the same direction as the applied field, and tending to make the elementary magnetic moments align parallel to one another and to the applied field. This is the case in a ferromagnetic material.

We can estimate the size of the Weiss molecular field. Below the critical temperature,  $T_C$ , paramagnetic materials exhibit ferromagnetic behavior. Above  $T_C$ , the thermal energy outweighs  $H_W$ , and the ferromagnetic ordering is destroyed. Therefore at  $T_C$ , the interaction energy,  $\mu_B H_W$ , must be approximately equal to the thermal energy,  $k_B T_C$ . So  $H_W \approx k_B T_C / \mu_B \approx 10^{-16} 10^3 / 10^{-20} \approx 10^7$  Oe. This is extremely large! In the next chapter we will apply Weiss's molecular field theory below the Curie temperature to understand the ferromagnetic phase, and we will discuss the origin of the molecular field.

The Langevin theory and the Curie–Weiss law give accurate descriptions of many paramagnetic materials. Next, we will look at two cases where they don't do so well. The first is not really a problem with the theory, but a difference in the size of the measured and predicted magnetic moments of the ions. The second is an example of a class of materials (the Pauli paramagnets) where the assumptions of the Langevin localized moment theory no longer apply.

### 5.3 Quenching of orbital angular momentum

The total magnetization in a paramagnet depends on the magnetic moment,  $m$ , of the constituent ions. Once we know the  $g$ -factor of an ion, and the  $J$  value, we can calculate its magnetic moment – it's just  $m = g\mu_B\sqrt{J(J+1)}$ . (This after all was the whole purpose of Chapter 3!) In general this formula works very well for paramagnetic salts, even though the ions have formed into crystals and are no longer 'free'. As an example we show the calculated and experimental values for the rare earth ions in Table 5.1. In all cases (except for the  $\text{Eu}^{3+}$  ion) the agreement is very good. In  $\text{Eu}^{3+}$  the calculated magnetic moment for the ground state is zero, however there are low-lying excited states which do have a magnetic moment and which are partially occupied at practical temperatures. Averaging over

Table 5.1 *Calculated and measured effective magnetic moments for the rare earth ions.*

(From Ref. 16, Kittel, *Introduction to solid state physics*, 7th edn. Copyright 1995 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

ion	configuration	$g\sqrt{J(J+1)}$	$m/\mu_B$
$\text{Ce}^{3+}$	$4f^1 5s^2 5p^6$	2.54	2.4
$\text{Pr}^{3+}$	$4f^2 5s^2 5p^6$	3.58	3.5
$\text{Nd}^{3+}$	$4f^3 5s^2 5p^6$	3.62	3.5
$\text{Pm}^{3+}$	$4f^4 5s^2 5p^6$	2.68	–
$\text{Sm}^{3+}$	$4f^5 5s^2 5p^6$	0.84	1.5
$\text{Eu}^{3+}$	$4f^6 5s^2 5p^6$	0.00	3.4
$\text{Gd}^{3+}$	$4f^7 5s^2 5p^6$	7.94	8.0
$\text{Tb}^{3+}$	$4f^8 5s^2 5p^6$	9.72	9.5
$\text{Dy}^{3+}$	$4f^9 5s^2 5p^6$	10.63	10.6
$\text{Ho}^{3+}$	$4f^{10} 5s^2 5p^6$	10.60	10.4
$\text{Er}^{3+}$	$4f^{11} 5s^2 5p^6$	9.59	9.5
$\text{Tm}^{3+}$	$4f^{12} 5s^2 5p^6$	7.57	7.3
$\text{Yb}^{3+}$	$4f^{13} 5s^2 5p^6$	4.54	4.5

Table 5.2 *Calculated and measured effective magnetic moments for the first row transition metal ions.*

(From Ref. 16, Kittel, *Introduction to solid state physics*, 7th edn. Copyright 1995 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

ion	configuration	$g\sqrt{J(J+1)}$	$g\sqrt{S(S+1)}$	$m/\mu_B$
$\text{Ti}^{3+}, \text{V}^{4+}$	$3d^1$	1.55	1.73	1.8
$\text{V}^{3+}$	$3d^2$	1.63	2.83	2.8
$\text{Cr}^{3+}, \text{V}^{2+}$	$3d^3$	0.77	3.87	3.8
$\text{Mn}^{3+}, \text{Cr}^{2+}$	$3d^4$	0.00	4.90	4.9
$\text{Fe}^{3+}, \text{Mn}^{2+}$	$3d^5$	5.92	5.92	5.9
$\text{Fe}^{2+}$	$3d^6$	6.70	4.90	5.4
$\text{Co}^{2+}$	$3d^7$	6.63	3.87	4.8
$\text{Ni}^{2+}$	$3d^8$	5.59	2.83	3.2
$\text{Cu}^{2+}$	$3d^9$	3.55	1.73	1.9

the calculated magnetic moments for these excited states gives a value which is in agreement with the measured value.

However for the first row transition metals, things do not work out quite so nicely, and in fact the measured magnetic moment is closer to that which we would calculate if we completely ignored the *orbital* angular momentum of the electrons. Table 5.2 lists the measured magnetic moments, and the calculated values using the total and spin-only angular momenta. It's clear that the spin-only values are in much better agreement with experiment than the values calculated using the total angular momentum. This phenomenon is known as *quenching* of the orbital angular momentum, and is a result of the electric field generated by the surrounding ions in the solid. Qualitatively, these electric fields cause the orbitals to be coupled strongly to the crystal lattice, so that they are not able to reorient towards an applied field, and so do not contribute to the observed magnetic moment. The spins, on the other hand are only weakly coupled to the lattice – the result is that only the spins contribute to the magnetization process, and, consequently, to the resultant magnetic moment of the specimen. For a more detailed discussion see Ref. 16.

### 5.4 Pauli paramagnetism

In the Langevin theory we assumed that the electrons in the partially occupied valence shells (which cause the net atomic magnetic moments) were fully localized on their respective atoms. We know that, in metals, the electrons are able to wander through the lattice and give rise to electrical conductivity. So the localized moment approximation is unlikely to be a good one. This is in fact the case, and in

Curie law. We do not see the  $1/T$  susceptibility dependence characteristic of Langevin paramagnets. Instead the susceptibility is more or less independent of temperature – a phenomenon known as Pauli paramagnetism. Before we can explain Pauli paramagnetism we need to understand the concept of energy bands.

### 5.4.1 Energy bands in solids

As we saw in Chapter 3 that the electrons in atoms occupy discrete energy levels known as atomic orbitals. When atoms are brought together to form a solid, the wavefunctions of their outermost valence electrons overlap and the electronic configuration is altered. In fact, each discrete orbital energy of the free atom contributes to a continuous *band* of allowed energy levels in the solid. The greater the amount of overlap between the wavefunctions, the broader the band. So the valence electrons occupy rather broad bands, whereas the bands produced from the more tightly bound core electrons are narrow.

The band formation process is illustrated for sodium in Fig. 5.4. The atomic energy levels, corresponding to infinitely separated Na atoms, are shown on the left of the figure. A free Na atom has fully occupied 1s, 2s and 2p sub-shells, and a single electron in the 3s orbital. The 3p orbital is empty in the ground state. As the atoms are brought together the wavefunctions of the valence electrons overlap and band formation occurs. At the equilibrium bonding distance,

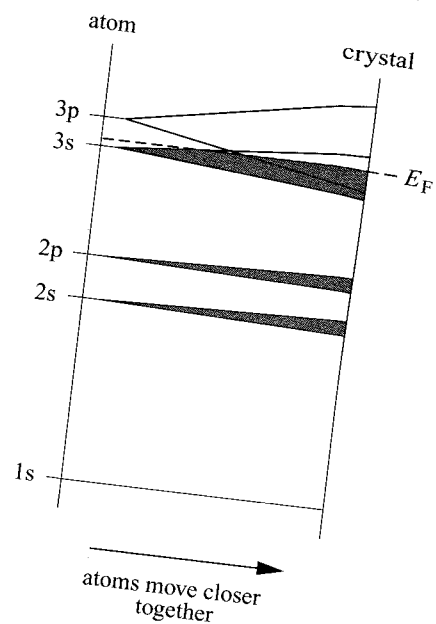


Figure 5.4 Energy band formation in sodium metal.

the bands derived from the 3s and 3p atomic orbitals are so wide that they overlap. The lower-lying core electrons have very little wavefunction overlap, and correspondingly narrow bands.

Just as in free atoms, the electrons in solids occupy the energy bands starting with those of the lowest energy and working up. The bands which derived from filled atomic orbitals are filled completely. In sodium, the electrons which occupied the 3s orbital in the atom now occupy the overlapping 3s–3p bands – a fraction are in 3s states and the remainder are in 3p states. (We'll see in the next chapter that this overlapping of energy bands has an important effect in determining the average atomic magnetic moments in ferromagnetic transition metals.)

The highest energy level which is filled with electrons at zero kelvin is called the Fermi energy,  $E_F$ . One characteristic of paramagnetic metals is that the energy states for up- and down-spin electrons are the same, and so the energy levels at the Fermi energy are identical for up- and down-spins. (We'll see later that this is not the case in ferromagnetic metals, where there are more electrons of one spin, giving rise to a net magnetic moment.) This is illustrated schematically in Fig. 5.5(a). (Remember that the energy levels really form a continuous band; we have drawn discrete levels for clarity). When a magnetic field is applied, however, those electrons with their magnetic moments aligned parallel to the field have a lower energy than those which are antiparallel. (If the field is applied in the up direction, then the down-spin electrons have lower energy than the up-spin electrons, since the negative electronic charge makes the magnetic moment point in the opposite direction to the spin.) So there is a tendency for the antiparallel electrons to try and reorient themselves parallel to the field. However, because of the Pauli exclusion principle, the only way that they can do this is by moving into one of the vacant parallel-moment states, and only those electrons close to the Fermi level have sufficient energy to

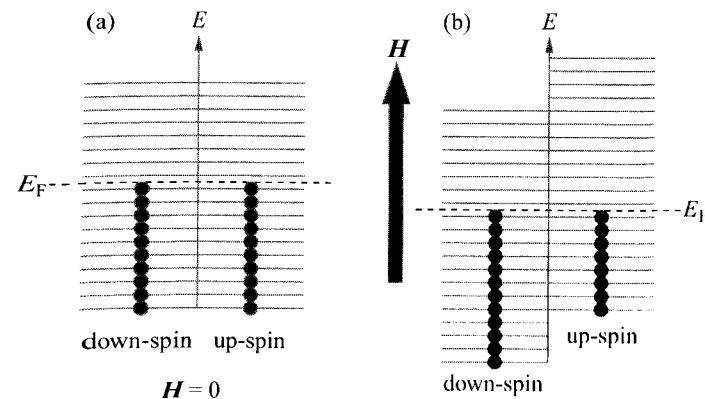


Figure 5.5 Adjustment of electronic energies in a paramagnetic metal when a magnetic field is applied.

do this. For the lower-lying electrons, the energy gained by realignment would be outweighed by that required to promote the electron to the vacant state. This is illustrated in Fig. 5.5(b). Figure 5.5 also shows that Pauli paramagnets develop an overall magnetization when a magnetic field is applied.

Before we can quantify this change in induced magnetization, and derive an expression for the susceptibility, we need to have a model for the electrons in a metal. In the next section we'll derive the so-called 'free electron theory' which describes the properties of many simple metals well.

### 5.4.2 Free electron theory of metals

The free electron theory assumes that the valence electrons in a solid are completely ionized from their parent atoms, and behave like a 'sea' of electrons wandering around in the solid. These electrons, the free electron gas, move in the average field created by all the other electrons and the ion cores, and, for each electron, the repulsive potential from the other electrons is assumed to exactly cancel out the attractive ion core potentials. Despite this huge approximation, the free electron theory yields surprisingly good results for simple metals. (The reasons for the success of the free electron model are rather subtle and confused condensed matter physicists for a long time. Unfortunately we don't have time to go into them here – there is an excellent discussion in the review by Cohen.<sup>17</sup>)

The Schrödinger equation for free electrons includes only a kinetic energy term, because by definition the potential energy is zero. So, in three dimensions it is

$$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_k(\mathbf{r}) = E_k \psi_k(\mathbf{r}). \quad (5.23)$$

The most straightforward method for solving this equation is to pretend that the electrons are confined to a cube of edge length  $L$ , and that they satisfy periodic boundary conditions. Then the solutions are traveling plane waves,

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \quad (5.24)$$

provided that the wavevector  $\mathbf{k}$  satisfies

$$k_x, k_y, k_z = \pm \frac{2n\pi}{L} \quad (5.25)$$

where  $n$  is any positive integer. In a macroscopic solid,  $L$  is very large and so the spectrum of allowed  $\mathbf{k}$  values is effectively continuous.

Substituting  $\psi_k(\mathbf{r})$  back into the Schrödinger equation gives us the energy eigenvalues

$$E_k = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2). \quad (5.26)$$

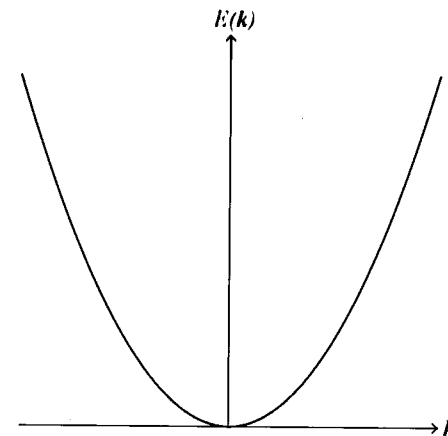


Figure 5.6 Energy versus wavevector for a free electron gas.

The energy is quadratic in the wavevector, as shown in Fig. 5.6.

Now as we saw in Section 5.4.1, the important quantity for determining the response of a Pauli paramagnet to a magnetic field is the *number* of electrons close to the Fermi energy level which are able to reverse their spin when a field is applied. So next let's derive an expression for the *density of states* (that is the number of electron energy levels per unit energy range) at the Fermi level.

We just showed that the energy of a particular  $\mathbf{k}$ -state is given by  $E = (\hbar^2/2m_e)k^2$ . In particular the Fermi energy is given by  $E = (\hbar^2/2m_e)k_F^2$ , where  $k_F$  is the *wavevector* of the highest filled state, and lies on a sphere of volume  $\frac{4}{3}\pi k_F^3$ , within which all states are filled. We also know that the components of the  $\mathbf{k}$ -vector,  $k_x$ ,  $k_y$  and  $k_z$ , are quantized in multiples of  $2\pi/L$ . So the volume occupied by a single quantum state in  $\mathbf{k}$ -space must be  $(2\pi/L)^3$ . Therefore the total number of electrons, which is equal to twice the number of occupied orbitals (one electron each of up- and down-spin), is given by

$$N = \frac{\text{volume of Fermi sphere}}{\text{volume per } \mathbf{k}\text{-state}} \times 2 \quad (5.27)$$

$$= \left( \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} \right) \times 2 \quad (5.28)$$

$$= \frac{V}{3\pi^2} k_F^3 \quad (5.29)$$

$$= \frac{V}{3\pi^2} \left( \frac{2m_e E_F}{\hbar^2} \right)^{3/2} \quad (5.30)$$

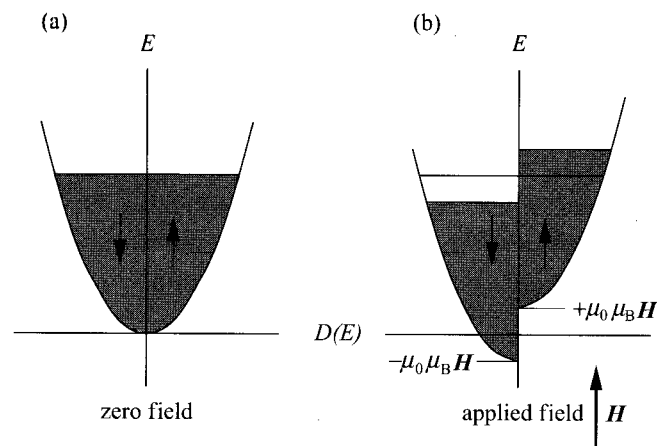


Figure 5.7 (a) Density of states in a free electron gas with no applied field. The up- and down-spin densities of states are equal and proportional to the square root of the energy. (b) Density of states in a free electron gas when a magnetic field is applied in the 'up' direction (i.e. parallel to the *down*-spin magnetic moments). The down-spin states (which have up magnetic moment) are lowered in energy, and the up-spin states are raised in energy, each by an amount  $\mu_B H$ .

where  $V$  is the volume of the crystal. Similarly, the number of electrons required to fill up the states to a general energy level  $E$  (below  $E_F$ ) is  $(V/3\pi^2)(2m_e E/\hbar^2)^{3/2}$ . The density of states,  $D(E)$ , is defined as the derivative of the number of electron states with respect to energy. So differentiating the above expression gives us the density of states at the Fermi level,

$$D(E_F) = \frac{V}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} E_F^{1/2}. \quad (5.31)$$

The number of electronic states per unit energy range is proportional to the square root of the energy, as shown in Fig. 5.7(a). We can simplify the expression by recognizing that  $(V/3\pi^2)(2m_e/\hbar^2)^{3/2} = N/E_F^{3/2}$ . Substituting gives

$$D(E_F) = \frac{3}{2} \frac{N}{E_F}. \quad (5.32)$$

Next let's use this expression for the density of states of a free electron gas to derive the susceptibility of our Pauli paramagnet.

### 5.4.3 Susceptibility of Pauli paramagnets

We saw in Chapter 3 that a single free electron, with spin angular momentum only, has a magnetic moment along the field direction of one Bohr magneton. (Remember, the moment along the field direction,  $m = -g_c \mu_B m_s = \pm \mu_B$  for a free electron.)

Also, the application of a magnetic field will change the energy of the electron by an amount  $\mu_0 \mu_B \cos \theta$  where  $\theta$  is the angle between the axis of the magnetic moment and the applied field. So an electron with its magnetic moment in the direction of the field will be lowered in energy by an amount  $\mu_0 \mu_B H$ , and one antiparallel to the field will be increased in energy by  $\mu_0 \mu_B H$ . Thus a magnetic field changes the density of states in a free electron gas as shown in Fig. 5.7(b).

If the field is applied in the up direction (so that it is parallel to the down-spin magnetic moment), there is a spill-over of electrons from up-spin to down-spin until the new Fermi levels for up- and down-spin are equal (and in fact very close to the original Fermi level,  $E_F$ .) The zero of energy for the down-spin density of states is at  $-\mu_0 \mu_B H$  and for the up-spin density of states at  $+\mu_0 \mu_B H$ . Therefore the total number of down-spin electrons is now given by

$$\frac{1}{2} \int_{-\mu_0 \mu_B H}^{E_F} D(E + \mu_0 \mu_B H) dE \quad (5.33)$$

and of up-spin electrons

$$\frac{1}{2} \int_{+\mu_0 \mu_B H}^{E_F} D(E - \mu_0 \mu_B H) dE. \quad (5.34)$$

(The factor of  $\frac{1}{2}$  occurs because only *one* electron occupies each up- or down-spin state, and the density of states was defined for two electrons per orbital).

The net magnetic moment,  $M$ , is the number of down-spin moments minus the number of up-spin moments, multiplied by the moment per spin,  $\mu_B$ :

$$M = \frac{\mu_B}{2} \left[ \int_{-\mu_0 \mu_B H}^{E_F} D(E + \mu_0 \mu_B H) dE - \int_{+\mu_0 \mu_B H}^{E_F} D(E - \mu_0 \mu_B H) dE \right]. \quad (5.35)$$

Changing variables gives

$$M = \frac{\mu_B}{2} \int_{E_F - \mu_0 \mu_B H}^{E_F + \mu_0 \mu_B H} D(E) dE. \quad (5.36)$$

The value of the integral is equal to the area of a strip of width  $2\mu_0 \mu_B H$  centered around  $E_F$ . This area is  $2\mu_0 \mu_B H D(E_F)$ , so the net magnetic moment in the direction of the field is given by

$$M = \mu_0 \mu_B^2 H D(E_F), \quad (5.37)$$

where  $D(E_F)$  is the density of states at the Fermi level, which we derived earlier:

$$D(E_F) = \frac{3}{2} \frac{N}{E_F}. \quad (5.38)$$

So the susceptibility,

$$\chi = \frac{M}{H} = \frac{3N\mu_0\mu_B^2}{2E_F} \quad (5.39)$$

which is independent of temperature! Remember that there is also a diamagnetic contribution to the susceptibility, which it turns out is one-third of the Pauli paramagnetism and of course in the opposite direction. Thus the expression for the total susceptibility of a metal which fits the free electron model is

$$\chi = \frac{\mu_0\mu_B^2 N}{E_F} \quad (5.40)$$

(in SI units). The values of susceptibility calculated using this formula are in good agreement with measured values for metals such as Na or Al which are well described by the free electron model.

### 5.5 Paramagnetic oxygen

When two oxygen atoms (each with electronic configuration  $1s^2, 2s^2, 2p^4$ ) join together to form an  $O_2$  molecule, their atomic orbitals combine to form molecular orbitals, as shown in Fig. 5.8. (For an explanation of why the orbitals are ordered as shown, see Ref. 6.) The 16 electrons fill up the molecular orbitals from the lowest energy up, and they occupy orbitals of equal energy individually before pairing up, just as they did in the atom. The consequence of this occupation scheme is that there are unpaired electrons in an  $O_2$  molecule, and therefore gaseous oxygen has a paramagnetic response to an applied magnetic field.

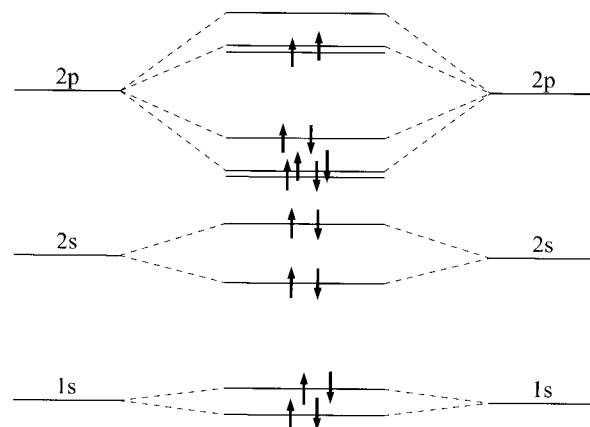


Figure 5.8 Molecular orbitals in oxygen.

### 5.6 Uses of paramagnets

Like the diamagnets, paramagnets do not find wide application because they have no permanent net magnetic moment. They are used, however, in the production of very low temperatures, by a process called adiabatic demagnetization. At a 'conventional' low temperature, such as that of liquid helium (a few degrees above absolute zero), the term  $\alpha$  in the Langevin function is actually quite large – certainly greater than unity. Therefore if a paramagnet is cooled to liquid helium temperature in the presence of a strong magnetic field, the magnetization is nearly saturated, so most of the spins are lined up parallel to the field. If the paramagnet is then thermally isolated (for example by removing the liquid helium and leaving a good vacuum) and the field is turned off slowly, then the temperature of the paramagnet drops even further. The reason for the temperature drop is that, when the spins randomize as a result of the field's being removed, they must do work against whatever field remains. The only energy which is available to them is their thermal energy, and when they use this to demagnetize they lower their temperature. It is possible to reach temperatures as low as a few thousandths of a degree using this technique.

In addition, paramagnets allow us to study the electronic properties of materials which have atomic magnetic moments, without the interference of strong cooperative effects.

In the next chapter we will extend the Langevin theory of paramagnetism to help us start to understand the properties of the most important class of magnetic materials – the ferromagnets – in which the cooperative effects between magnetic moments are indeed strong.

### Homework

#### Exercises

- 5.1 Show that the Brillouin function approaches the Langevin function as  $J \rightarrow \infty$ . What are the limits of the Brillouin function as  $J \rightarrow \frac{1}{2}$  and  $\alpha \rightarrow 0$ ?
- 5.2 Calculate the room temperature paramagnetic susceptibility of an ideal gas, in which each atom has  $J = 1$  and  $g = 2$ . (Remember the ideal gas law:  $PV = nRT$ ). These are in fact the values of  $J$  and  $g$  for molecular oxygen. Note that your answer is small and positive.
- 5.3 In this problem we will explore the properties of a model three-dimensional lattice of spins, each with spin,  $S = \frac{1}{2}$ .
  - (a) What is the magnetic moment of each spin? What are the allowed values of the projection of the magnetic moment,  $m_i$ , onto some chosen axis,  $z$  say?
  - (b) What are the possible values of the magnetic energy of each spin?
  - (c) Assuming that the spins are non-interacting, calculate the magnetization of the lattice of spins when a magnetic field,  $H$  is applied along the  $z$  axis. (HINT: Use the



result from statistical thermodynamics that the average magnetization of a spin is given by  $\langle \mathbf{M} \rangle = (1/Z) \sum_i \mathbf{m}_i e^{-E_i/k_B T}$  where  $\mathbf{m}_i$  is the magnetization of a spin along the field direction when it has energy  $E_i$ , and  $Z = \sum_i e^{-E_i/k_B T}$  is called the partition function.)

- (d) For a given value of field,  $\mathbf{H}$ , how does the magnetization,  $\mathbf{M}$ , depend on temperature? Explain the behavior of  $\mathbf{M}$ , for  $T \rightarrow 0$ . Taking the number of spins per unit volume to be  $3.7 \times 10^{28} \text{ m}^{-3}$ , calculate the numerical value of the saturation magnetization,  $\mathbf{M}_s$ , at  $T = 0$ . Explain the behavior of  $\mathbf{M}$  for  $T \rightarrow \infty$ .
- (e) What does the relationship between  $\mathbf{M}$  and  $\mathbf{H}$  reduce to for weak fields ( $\mathbf{H} \rightarrow 0$ )? What is the expression for the susceptibility,  $\chi$ , in this case, and how does it depend on temperature? Calculate the numerical value of  $\chi$  at room temperature.
- (f) Comment on the results which you have obtained for this spin system. What kind of magnetic behavior (antiferromagnetic, paramagnetic, diamagnetic, etc.) is displayed by this model system? Justify your conclusion. How would we need to modify the model in order to describe ferromagnetic behavior?

#### To think about

What mechanism might we use to lower the temperature below that obtained by the procedure described in Section 5.6?

#### Further reading

B.D. Cullity, *Introduction to magnetic materials*. Addison-Wesley, 1972, Chapter 3.

## 6

### Interactions in ferromagnetic materials

“Anyone who is not shocked by quantum theory has not understood it.”  
Niels Bohr, 1885–1962

In Chapter 2 we introduced the concept of ferromagnetism, and looked at the hysteresis loop which characterizes the response of a ferromagnetic material to an applied magnetic field. This response is really quite remarkable! Look at Figs. 2.3 and 2.4 again – we see that it is possible to change the magnetization of a ferromagnetic material from an initial value of *zero*, to a saturation value of around  $1000 \text{ emu/cm}^3$  by the application of a rather small magnetic field – around tens of oersteds.

The fact that the *initial* magnetization of a ferromagnet is zero is explained by the domain theory of ferromagnetism. The domain theory was postulated in 1907 by Weiss<sup>18</sup> and has been very successful. We will discuss the details of the domain theory, and the experimental evidence for the existence of domains, in the next chapter.

The subject of *this* chapter is: how can such a small external field cause such a large magnetization? In Exercise 6.2(b), you’ll see that a field of 50 Oe has almost no effect on a system of *weakly interacting* elementary magnetic moments. Thermal agitations act to oppose the ordering influence of the applied field, and when the atomic magnetic moments are independent, the thermal agitation wins. In ferromagnetic materials there must be a strong interaction between the magnetic moments, and we’ll see later that this interaction is quantum mechanical in nature. We’ll need to learn some more quantum mechanics as we go along, but hopefully we can make this as painless as possible.

But first let’s start with the phenomenological model of ferromagnetism, which was again proposed by Weiss in his classic 1907 paper.<sup>18</sup> We won’t worry about the *origin* of the strong interactions until Section 6.2 – instead we’ll look first at their effect on observables such as susceptibility.