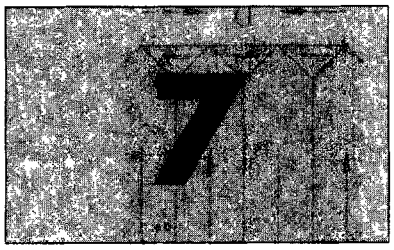

Magnetism in metals

In this chapter the magnetic properties of metals are considered. In previous chapters we have concentrated on interacting but localized magnetic moments. The conduction electrons in metals are delocalized and can wander freely through the sample; they are known as itinerant electrons. In some cases the magnetic moments in metals are associated with the conduction electrons, in other cases the magnetic moments remain localized. In both cases paramagnetic and diamagnetic behaviour can occur. Ferromagnetism is possible under certain conditions. Most of the discussion in this chapter will be centred around the free electron model, which is introduced in the following section. The free electron model is a crude approximation to most real situations, but it is simple to consider and will allow the discussion to proceed a long way. Subsequent sections contain derivations of the magnetic properties of the electron gas which include Pauli paramagnetism, Landau diamagnetism, the origin of RKKY interactions, instabilities of the electron gas such as spin-density wave formation, and the Kondo effect which occurs when localized moments interact with the electron gas.

7.1 The free electron model

We begin our discussion of the magnetism of itinerant electrons by reviewing the **free electron model**. In this model, the periodic potential due to the lattice is ignored, and the electrons fill states up to the **Fermi wave vector** k_F. Points in k-space are separated by $2\pi/L$ (see Fig. 7.1(a)) where $V = L^3$ is the volume of the sample, so that the number of states between k and $k + \mathrm{d}k$ is equal to $4\pi k^2\,\mathrm{d}k$, the volume of a spherical shell of radius k and width $\mathrm{d}k$ (see Fig. 7.1(b)) divided by $(2\pi/L)^3$, the volume occupied by one point in k-space. Each state is doubly occupied, by an electron with spin-up and an electron with spin-down, so there is an additional factor of two. Hence the density of states $g(k)\,\mathrm{d}k$ can be written as

$$g(k)\,\mathrm{d}k = \frac{2}{(2\pi/L)^3} \times 4\pi k^2\,\mathrm{d}k, \tag{7.1}$$

where the factor of 2 takes care of the two spin-states of the electrons. Hence

$$g(k)\,\mathrm{d}k = \frac{Vk^2\,\mathrm{d}k}{\pi^2}. \tag{7.2}$$

If the material has N electrons, then at absolute zero ($T = 0$) these electrons will fill up the states up to a maximum wave vector of k_F. Hence

$$N = \int_0^{k_F} g(k)\,\mathrm{d}k = \frac{Vk_F^3}{3\pi^2}, \tag{7.3}$$

so that

$$k_F^3 = 3\pi^2 n \tag{7.4}$$

where $n = N/V$ is the number of electrons per unit volume. The Fermi energy E_F is defined by

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}. \tag{7.5}$$

The density of states as a function of energy $E \propto k^2$ is proportional to $E^{1/2}$, i.e.

$$g(E) = \frac{dn}{dE} \propto E^{1/2} \tag{7.6}$$

so that

$$n = \int_0^{E_F} g(E)\,dE \propto E_F^{3/2} \tag{7.7}$$

and hence

$$\frac{dn}{n} = \frac{3}{2}\frac{dE_F}{E_F}. \tag{7.8}$$

The density of states at the Fermi energy is therefore given by[1]

$$g(E_F) = \left(\frac{dn}{dE}\right)_{E=E_F} = \frac{3}{2}\frac{n}{E_F}. \tag{7.9}$$

We note in passing that another useful expression for $g(E_F)$ can be obtained by combining eqn 7.4, eqn 7.5 and eqn 7.9 to yield

$$g(E_F) = \frac{m_e k_F}{(\pi\hbar)^2}, \tag{7.10}$$

which shows that $g(E_F) \propto m_e$. Many important properties depend on the density of states at the Fermi energy and therefore it is useful to know that it is proportional to the electron's mass. In many systems of interest, the electron's mass is enhanced above its free space value due to the effect of the band structure or interactions.

In the free electron model we ignore the periodic potential due to the lattice. However if it is included as a perturbation (the **nearly free electron model**) it turns out that it has very little effect *except* when the wave vector of the electron is close to a reciprocal lattice vector. At such points in k-space **energy gaps** appear in the dispersion relation (see Fig. 7.2).

So far, everything has been treated at $T = 0$. When $T > 0$, the density of states $g(E)$ is unchanged but the occupancy of each state is governed by the Fermi function $f(E)$ which is given by

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}, \tag{7.11}$$

where μ is the chemical potential which is temperature dependent. This function is plotted in Fig. 7.3. At $T = 0$, $f(E)$ is a step function, taking the value 1 for $E < \mu$ and 0 for $E > \mu$. The step is smoothed out as the temperature T increases. When the Fermi function is close to a step function, as is the usual case for most metals at pretty much all temperatures below their melting temperature, the electrons are said to be in the **degenerate limit**. The Fermi

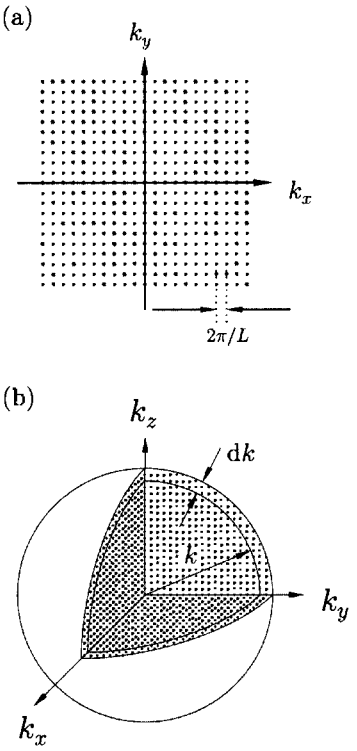

Fig. 7.1 (a) Electron states are separated by $2\pi/L$. Each state can be doubly occupied and occupies a volume $(2\pi/L)^3$. (b) The density of states can be calculated by considering the volume in k-space between states with wave vector k and states with wave vector $k + dk$, namely $4\pi k^2\,dk$.

[1] Equation 7.9 could also be derived using eqns 7.2, 7.4 and 7.5 directly.

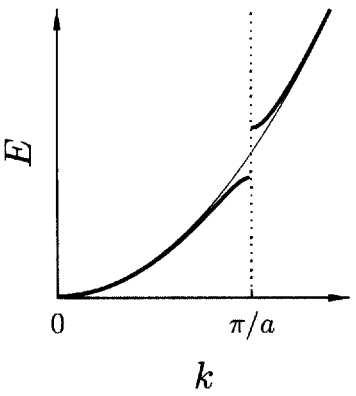

Fig. 7.2 The energy gap at the Brillouin zone boundary.

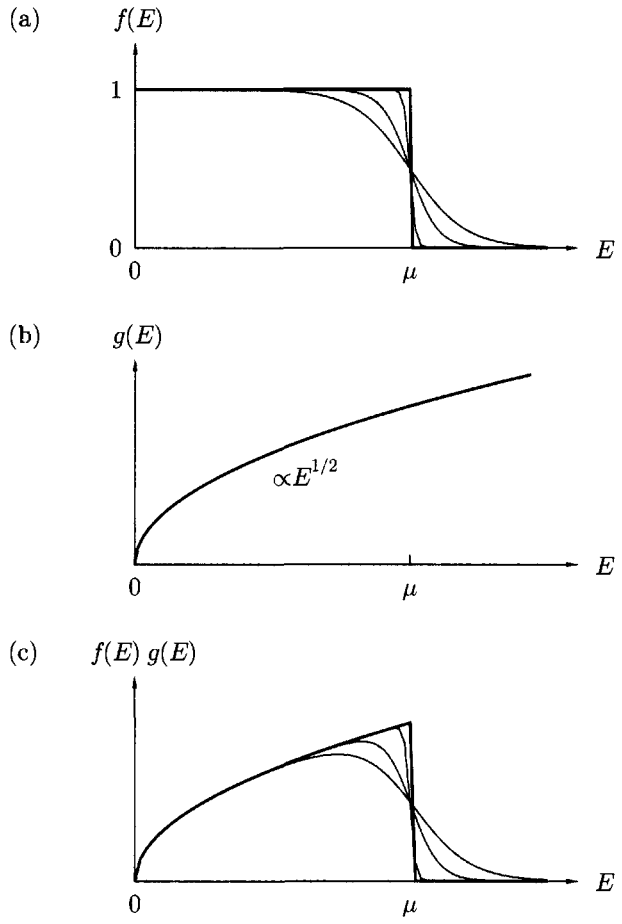

Fig. 7.3 (a) The Fermi function $f(E)$ defined by eqn 7.11. The thick line is for $T = 0$. The step function is smoothed out as the temperature increases. The temperatures shown are $T = 0$, $T = 0.01\mu/k_B$, $T = 0.05\mu/k_B$ and $T = 0.1\mu/k_B$. (b) The density of states $g(E)$ for a free electron gas is proportional to $E^{1/2}$. (c) $f(E)g(E)$ for the same temperatures as in (a).

function is a consequence of the Pauli exclusion principle, that each electron must have a unique set of quantum numbers and no two electrons can sit in the same state. For $(E - \mu) \gg k_B T$ the Fermi function approaches the Maxwell–Boltzmann form $e^{-(E-\mu)/k_B T}$ which is known as the **non-degenerate limit**.

The Fermi energy is the energy of the highest occupied level at $T = 0$ and is determined by the equation

$$\int_0^{E_F} f(E)g(E)\,dE = n. \tag{7.12}$$

The function $f(E)g(E)$ is shown in Fig. 7.3(c). At $T = 0$ we easily find that the Fermi energy precisely equals the chemical potential: $E_F = \mu$. For $T > 0$, a tedious calculation gives

$$\mu = E_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2 + O\left(\left(\frac{k_B T}{E_F}\right)^4\right)\right] \tag{7.13}$$

but this means that equating E_F and μ is good to 0.01% for typical metals even at room temperature, although it is worthwhile keeping in the back of one's mind that the two quantities are not the same. The **Fermi surface** is the

set of points in k-space whose energy is equal to the chemical potential. If the chemical potential lies in a gap, then the material is a semiconductor or an insulator and there will be no Fermi surface. Thus a metal is a material with a Fermi surface.

7.2 Pauli paramagnetism

Each k-state in a metal can be doubly occupied because of the two possible spin states of the electron. Each electron in a metal is therefore either spin-up or spin-down. When a magnetic field is applied, the energy of the electron is raised or lowered depending on its spin. This gives rise to a paramagnetic susceptibility of the electron gas and is known as Pauli paramagnetism.

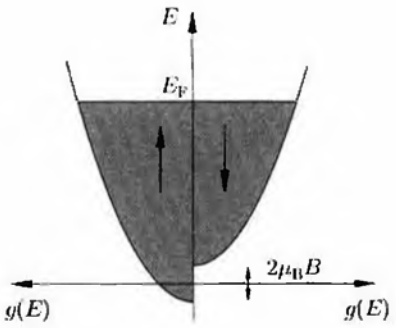

Fig. 7.4 Density of states showing splitting of energy bands in a field B. The splitting is shown greatly exaggerated.

7.2.1 Elementary derivation

Initially, we neglect the orbital contribution and take $g = 2$. We also neglect smearing of the Fermi surface due to finite temperature. As shown in Fig. 7.4, in an applied magnetic field, the electron band is spin-split into two spin subbands separated by $g\mu_B B = 2\mu_B B$. We will assume that $g\mu_B B$ is a very small energy so that the splitting of the energy bands is very small. The number of extra electrons per unit volume with spin-up is $n_\uparrow = \frac{1}{2}g(E_F)\mu_B B$. This is also the number per unit volume of the deficit of electrons with spin-down, $n_\downarrow = \frac{1}{2}g(E_F)\mu_B B$. Thus the magnetization is given by

$$M = \mu_B(n_\uparrow - n_\downarrow) = g(E_F)\mu_B^2 B \tag{7.14}$$

and the magnetic susceptibility χ_P (the subscript 'P' denoting the Pauli susceptibility) by

$$\chi_P = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \mu_0 \mu_B^2 g(E_F) \tag{7.15}$$

$$= \frac{3n\mu_0\mu_B^2}{2E_F} \tag{7.16}$$

where the final equality is obtained using eqn 7.9. Because $\chi_P \ll 1$ we are justified in writing $\chi_P \approx \mu_0 M/B$ (see Section 1.1.4).

Our expression for Pauli paramagnetism is temperature independent, although admittedly this is because we started out by ignoring the smearing of the Fermi surface due to finite temperature. However, if temperature is included, it makes only a rather small correction (see Exercise 7.1). Pauli paramagnetism is a weak effect, much smaller than the paramagnetism observed in insulators at most temperatures due to Curie's law. This is because in paramagnetic insulators at least one electron on every magnetic atom in the material contributes, but in a metal, it is only those electrons close to the Fermi surface which play a rôle. The small size of the paramagnetic susceptibility of most metals was something of a puzzle until Pauli pointed out that it was a consequence of the fact that electrons obeyed Fermi Dirac, rather than classical, statistics.