7.2.3   Experimental techniques

The expressions that we have derived for the Pauli paramagnetism of metals agree moderately well with experiment, but can be improved by correcting for the effect of electron–electron interactions. The spin susceptibility of a metal can be extracted from NMR measurements which are much more sensitive to the field due to the spin magnetic moment of the conduction electrons than to the fields which arise from the electron's orbital motion (which give rise to the diamagnetic effects considered in Section 7.6).

The effect of the contact interaction between the conduction electron spin and the nuclear spin leads to a small shift $\Delta\omega$, known as a **Knight shift**, in the nuclear resonance frequency ω. It can be understood by imagining that individual conduction electrons hop on and off a given nucleus; the net hyperfine coupling which the nucleus experiences is the result of averaging over all the electron spin orientations. This net hyperfine coupling will be zero without an applied field because the average of the electronic spin orientations will vanish; the net hyperfine coupling will be non-zero in a non-zero static field because this will polarize the electron spins. The Knight shift, $K = \Delta\omega/\omega$, is therefore proportional to the conduction electron density at the nucleus (which expresses the dependence on the coupling strength) and also to the Pauli spin susceptibility (which expresses the extent to which an applied field polarizes the electrons).

Walter D. Knight (1919–2000)

The static average of the hyperfine interactions causes the Knight shift. Fluctuations about this average provide a mechanism for T_1 relaxation (known as **Korringa relaxation**). The dominant T_1 processes are flip-flop transitions of the electron and nuclear (or muon) spins, in which the difference in electron and nuclear Zeeman energies is taken up by a change in kinetic energy of the conduction electron. The exchange in energy between the nucleus and the conduction electrons is very small, so only electrons within $k_B T$ of the Fermi surface are able to participate since only these have empty states nearby into which they can make a transition. Thus for simple metals the spin–lattice relaxation rate T_1^{-1} is proportional to temperature. The Knight shift, usually expressed in the dimensionless form $\Delta\omega/\omega$, and the Korringa relaxation rate T_1^{-1} are usually connected by the equation

$$\frac{1}{T_1} \propto T \left(\frac{\Delta\omega}{\omega}\right)^2 , \qquad (7.24)$$

which is known as the **Korringa relation**.

7.3   Spontaneously spin-split bands

The magnetic moment per atom in iron is about 2.2 μ_B (see Table 5.1). This non-integral value is not possible to understand on the basis of localized moments on atoms. It is therefore strong evidence for **band ferromagnetism** (also known as **itinerant ferromagnetism**) in which the magnetization is due to spontaneously spin-split bands. In this section we will explore some models which can be used to understand how bands in some materials can become spontaneously spin-split.
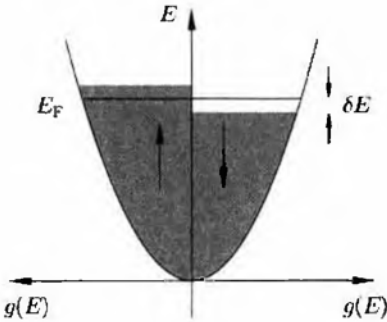
In molecular field theory we say that all spins 'feel' an identical average exchange field λM produced by all their neighbours. In a metal, the molecular field can magnetize the electron gas because of the Pauli paramagnetism χ_P. The resulting magnetization of the electron gas M would in turn be responsible for the molecular field. This is a chicken-and-egg scenario (also known as *bootstrapping*); can this positive feedback mechanism lead to spontaneous ferromagnetism? Presumably yes, if λ (expressing how much molecular field you get for a given M) and χ_P (expressing how much magnetization you get for a given molecular field) are both large enough.

It is desirable to make the above heuristic argument a little more rigorous! The question that we need to ask is: can the system as a whole save energy by becoming ferromagnetic?

Let us first imagine that in the absence of an applied magnetic field we take a small number of electrons at the Fermi surface from the spin-down band and place them in the spin-up band. Specifically we take spin-down electrons with energies from $E_F - \delta E$ up to E_F and flip their spins, placing them in the spin-up band where they sit with energies from E_F up to $E_F + \delta E$. This situation is illustrated in Fig. 7.5. The number of electrons moved is $g(E_F)\delta E/2$ and they increase in energy by δE. The total energy change is $g(E_F)\delta E/2 \times \delta E$. The total kinetic energy change $\Delta E_{K.E.}$ is therefore

$$\Delta E_{K.E.} = \frac{1}{2}g(E_F)(\delta E)^2. \tag{7.25}$$

Fig. 7.5 Density of states showing spontaneous splitting of energy bands without an applied magnetic field.

This is an energy cost so this process looks unfavourable. However, the interaction of the magnetization with the molecular field gives an energy reduction which can outweigh this cost. The number density of up-spins is $n_\uparrow = \frac{1}{2}(n + g(E_F)\delta E)$ and the number density of down-spins is $n_\downarrow = \frac{1}{2}(n - g(E_F)\delta E)$. Hence the magnetization is $M = \mu_B(n_\uparrow - n_\downarrow)$, assuming each electron has a magnetic moment of $1\,\mu_B$. The molecular field energy is

$$\Delta E_{P.E.} = -\int_0^M \mu_0(\lambda M')\,dM' = -\frac{1}{2}\mu_0\lambda M^2 = -\frac{1}{2}\mu_0\mu_B^2\lambda(n_\uparrow - n_\downarrow^2). \tag{7.26}$$

[2] The molecular field is due to exchange. Exchange is due to the Coulomb interaction. In more advanced treatments, the Coulomb energy is included directly as $Un_\uparrow n_\downarrow$ which yields the same result.

Writing $U = \mu_0\mu_B^2\lambda$, where U is a measure of the Coulomb energy,[2] we have

$$\Delta E_{P.E.} = -\frac{1}{2}U(g(E_F)\delta E)^2. \tag{7.27}$$

Hence the total change of energy ΔE is

$$\Delta E = \Delta E_{K.E.} + \Delta E_{P.E.} = \frac{1}{2}g(E_F)(\delta E)^2(1 - Ug(E_F)). \tag{7.28}$$

Thus spontaneous ferromagnetism is possible if $\Delta E < 0$ which implies that

$$Ug(E_F) \geq 1 \tag{7.29}$$

Edmund C. Stoner (1899–1968)

which is known as the **Stoner criterion**. This condition for the ferromagnetic instability requires that the Coulomb effects are strong and also that the density of states at the Fermi energy is large. If there is spontaneous ferromagnetism, the spin-up and spin-down bands will be split by an energy Δ, where Δ is the exchange splitting, in the absence of an applied magnetic field.

If the Stoner criterion is not satisfied, then spontaneous ferromagnetism will not occur. But the susceptibility may be altered. We can calculate this easily by including both the effects of an applied magnetic field and the interactions. The magnetization produced by an energy shift δE is simply $M = \mu_B(N_\uparrow - N_\downarrow) = 2\mu_B g(E_F)\delta E$. Thus

$$\Delta E = \frac{1}{2}g(E_F)(\delta E)^2(1 - Ug(E_F)) - MB \qquad (7.30)$$

$$= \frac{M^2}{2\mu_B^2 g(E_F)}(1 - Ug(E_F)) - MB \qquad (7.31)$$

This is minimized when

$$\frac{M}{\mu_B^2 g(E_F)}(1 - Ug(E_F)) - B = 0 \qquad (7.32)$$

so that the magnetic susceptibility χ is given by

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{\mu_0\mu_B^2 g(E_F)}{1 - Ug(E_F)} = \frac{\chi_P}{1 - Ug(E_F)}. \qquad (7.33)$$

This is larger than the value χ_P expected without the presence of Coulomb interactions by a factor $(1 - Ug(E_F))^{-1}$, a phenomenon known as **Stoner enhancement**. It is responsible for the enhanced Pauli susceptibility measured in the metals Pd and Pt which can both be thought of as systems on the verge of ferromagnetism; they have a large enough value of the parameter $Ug(E_F)$ to cause a significant enhancement of the magnetic susceptibility but not large enough (i.e. not sufficiently close to 1) to cause spontaneous ferromagnetism.

7.4 Spin-density functional theory

So far we have used free electron models or nearly free electron models in our discussion. It is possible to improve on this with more advanced methods, and one of these will be discussed in this section. In real systems one cannot ignore Coulomb interactions between electrons and the effect of exchange interactions on the motion of the electrons. The positions and motions of all the particles are correlated because the particles interact with each other and exert forces upon each other as they move. Thus the interactions lead to **correlations** appearing between particles. Such correlations can be very difficult to deal with theoretically, but a useful and successful approach is that of **density functional theory**.

In this theory it is recognized that the ground state energy of a many electron system can be written as a functional[3] of the electron density $n(\mathbf{r})$. The functional contains three contributions, a kinetic energy, a Coulomb energy due to the electrostatic interactions between the charged particles in the system, and a term called the **exchange-correlation energy** that captures all the many-body interactions. Rather than dealing with the wave function $\psi(\mathbf{r})$, in density functional theory one only has to consider the electron density $n(\mathbf{r}) = |\psi(\mathbf{r})|^2$, and this results in a considerable simplification. Minimizing the energy functional leads to an equation which can be used to find the ground state energy.

[3] A function is a rule which maps one number into another number. For example the function

$$f(x) = x^2$$

maps the number 2 into the number 4. A **functional** is a rule which maps an entire function into a number. For example, the functional

$$F[f] = \int_{-1}^{1} f(x)\,dx$$

maps the function $f(x) = x^2$ into the number 2/3.