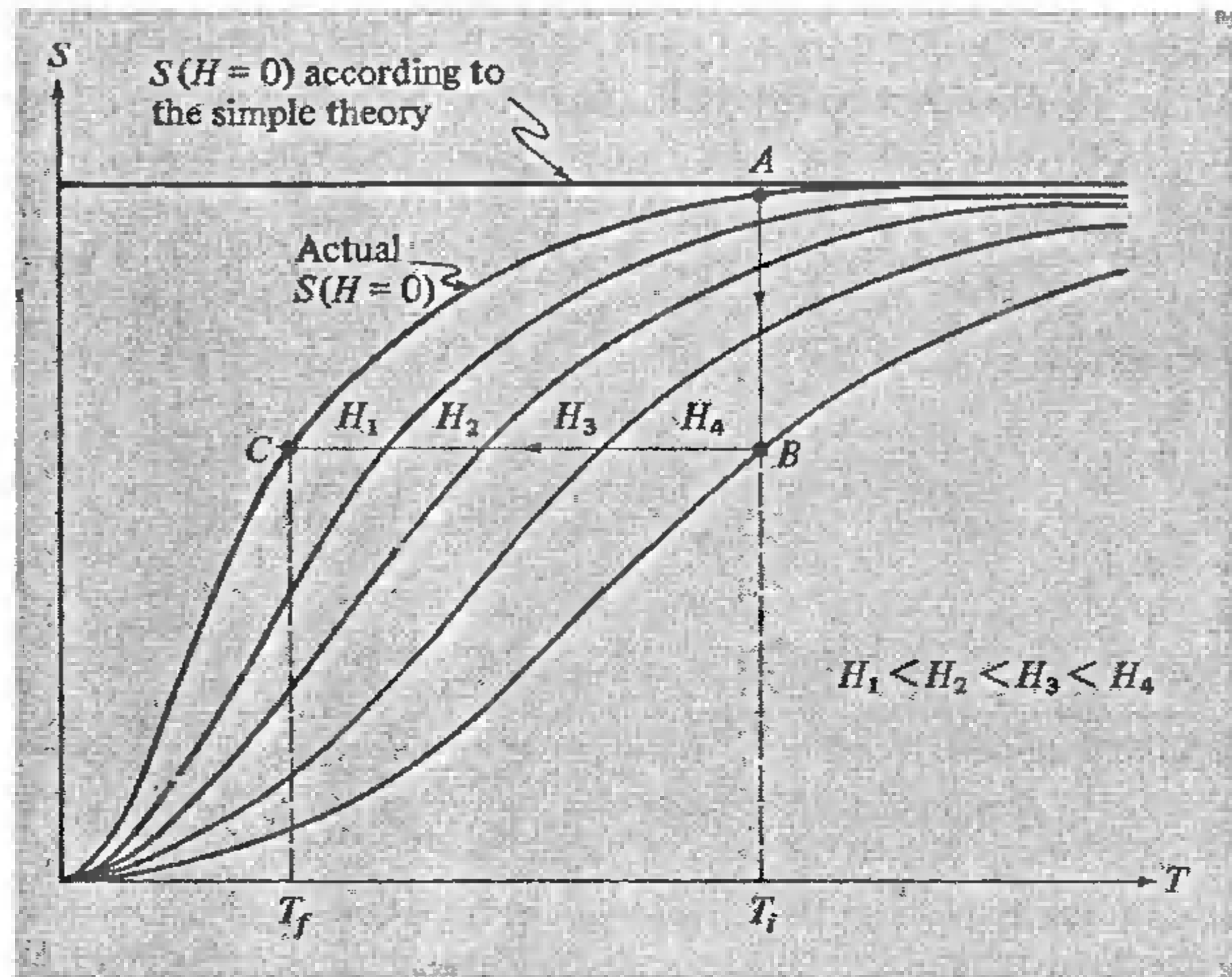


Figure 31.2

Plots of the entropy of a system of interacting spins for various values of external magnetic field,  $H$ . (The dashed line represents the constant  $Nk_B \ln(2J + 1)$  for independent spins in zero field.) The cooling cycle is this: Starting at  $A$  ( $T_i, H = 0$ ), we proceed isothermally to  $B$ , raising the field in the process from zero to  $H_4$ . The next step is to remove the field adiabatically (constant  $S$ ), thereby moving to  $C$  and achieving a temperature  $T_f$ .



## SUSCEPTIBILITY OF METALS: PAULI PARAMAGNETISM

None of the above discussions bear on the problem of the contribution of conduction electrons to the magnetic moment of a metal. The conduction electrons are not spatially localized like electrons in partially filled ionic shells, nor, because of the stringent constraints of the exclusion principle, do they respond independently like electrons localized on different ions.

However, within the independent electron approximation the problem of conduction electron magnetism can be solved. The solution is quite complicated, owing to the intricate way in which the electron orbital motion responds to the field. If we neglect the orbital response (i.e., consider the electron to have only a spin magnetic moment, but no charge), then we may proceed as follows:

Each electron will contribute  $-\mu_B/V$  (taking  $g_0 = 2$ ) to the magnetization density if its spin is parallel to the field  $H$ , and  $\mu_B/V$ , if antiparallel. Hence if  $n_{\pm}$  is the number of electrons per unit volume with spin parallel (+) or antiparallel (-) to  $H$ , the magnetization density will be

$$M = -\mu_B(n_+ - n_-). \quad (31.55)$$

If the electrons interact with the field only through their magnetic moments, then the only effect of the field is to shift the energy of each electronic level by  $\pm\mu_B H$ , according to whether the spin is parallel (+) or antiparallel (-) to  $H$ . We can express this simply in terms of the density of levels for a given spin. Let  $g_{\pm}(\varepsilon) d\varepsilon$  be the number of electrons of the specified spin per unit volume in the energy range  $\varepsilon$  to  $\varepsilon + d\varepsilon$ .<sup>27</sup> In the absence of the field we would have

$$g_{\pm}(\varepsilon) = \frac{1}{2}g(\varepsilon), \quad (H = 0), \quad (31.56)$$

<sup>27</sup> To avoid confusing the density of levels with the  $g$ -factor, we shall always make the energy argument of the level density explicit. A subscript distinguishes the Bohr magneton  $\mu_B$  from the chemical potential  $\mu$ .

where  $g(\varepsilon)$  is the ordinary density of levels. Since the energy of each electronic level with spin parallel to the field is shifted up from its zero field value by  $\mu_B H$ , the number of levels with energy  $\varepsilon$  in the presence of  $H$  is the same as the number with energy  $\varepsilon - \mu_B H$  in the absence of  $H$ :

$$g_+(\varepsilon) = \frac{1}{2}g(\varepsilon - \mu_B H). \quad (31.57)$$

Similarly,

$$g_-(\varepsilon) = \frac{1}{2}g(\varepsilon + \mu_B H). \quad (31.58)$$

The number of electrons per unit volume of each spin species is given by

$$n_{\pm} = \int d\varepsilon g_{\pm}(\varepsilon) f(\varepsilon), \quad (31.59)$$

where  $f$  is the Fermi function

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}. \quad (31.60)$$

The chemical potential  $\mu$  is determined by noting that the total electronic density is given by

$$n = n_+ + n_-. \quad (31.61)$$

Eliminating  $\mu$  through this relation we can use (31.59) and (31.55) to find the magnetization density as a function of the electronic density  $n$ . In the nondegenerate case ( $f \approx e^{-\beta(\varepsilon - \mu)}$ ) this leads back to our earlier theory of paramagnetism, giving precisely (31.44) with  $J = 1/2$ . (See Problem 8.)

However, in metals one is very much in the degenerate case. The important variation in the density of levels  $g(\varepsilon)$  is on the scale of  $\varepsilon_F$ , and since  $\mu_B H$  is only of order  $10^{-4}\varepsilon_F$  even at  $10^4$  gauss, we can, with negligible error, expand the density of levels:

$$g_{\pm}(\varepsilon) = \frac{1}{2}g(\varepsilon \pm \mu_B H) = \frac{1}{2}g(\varepsilon) \pm \frac{1}{2}\mu_B H g'(\varepsilon). \quad (31.62)$$

In conjunction with (31.59) this gives

$$n_{\pm} = \frac{1}{2} \int g(\varepsilon) f(\varepsilon) d\varepsilon \mp \frac{1}{2} \mu_B H \int d\varepsilon g'(\varepsilon) f(\varepsilon), \quad (31.63)$$

so that, from (31.61),

$$n = \int g(\varepsilon) f(\varepsilon) d\varepsilon. \quad (31.64)$$

This is precisely the formula for the electronic density in the absence of the field, and thus the chemical potential  $\mu$  can be taken to have its zero field value, Eq. (2.77):

$$\mu = \varepsilon_F \left[ 1 + O\left(\frac{k_B T}{\varepsilon_F}\right)^2 \right]. \quad (31.65)$$

In conjunction with Eq. (31.55), Eq. (31.63) gives a magnetization density

$$M = \mu_B^2 H \int g'(\varepsilon) f(\varepsilon) d\varepsilon, \quad (31.66)$$

or, integrating by parts,

$$M = \mu_B^2 H \int g(\varepsilon) \left( -\frac{\partial f}{\partial \varepsilon} \right) d\varepsilon. \quad (31.67)$$

At zero temperature,  $-\partial f/\partial \varepsilon = \delta(\varepsilon - \varepsilon_F)$ , so that

$$M = \mu_B^2 H g(\varepsilon_F). \quad (31.68)$$

Since (see Chapter 2) the  $T \neq 0$  corrections to  $-\partial f/\partial \varepsilon$  are of order  $(k_B T/\varepsilon_F)^2$ , Eq. (31.68) is also valid at all but the very highest temperatures ( $T \approx 10^4$  K).

It follows from (31.68) that the susceptibility is

$$\chi = \mu_B^2 g(\varepsilon_F). \quad (31.69)$$

This is known as the *Pauli paramagnetic susceptibility*. In contrast to the susceptibility of paramagnetic ions given by Curie's law, the Pauli susceptibility of conduction electrons is essentially independent of temperature. In the free electron case the density of levels has the form  $g(\varepsilon_F) = mk_F/\hbar^2\pi^2$ , and the Pauli susceptibility takes on the simple form

$$\chi_{\text{Pauli}} = \left( \frac{\alpha}{2\pi} \right)^2 (a_0 k_F), \quad (31.70)$$

where  $\alpha = e^2/\hbar c = 1/137$ . An alternative form is

$$\chi_{\text{Pauli}} = \left( \frac{2.59}{r_s/a_0} \right) \times 10^{-6}. \quad (31.71)$$

These expressions reveal that  $\chi_{\text{Pauli}}$  has the minute size characteristic of diamagnetic susceptibilities, in contrast to the strikingly larger paramagnetic susceptibilities of magnetic ions. This is because the exclusion principle is far more effective than thermal disorder in suppressing the tendency of the spin magnetic moments to align with the field. Another way of comparing Pauli paramagnetism with the paramagnetism of magnetic ions is to note that the Pauli susceptibility can be cast into the Curie's law form (Eq. (31.47)), but with a fixed temperature of order  $T_F$  playing the role of  $T$ . Thus the Pauli susceptibility is hundreds of times smaller, even at room temperatures.<sup>28</sup>

Values of the Pauli susceptibility, both measured and theoretical (from Eq. (31.71)) are given in Table 31.5 for the alkali metals. The rather significant discrepancy between the two sets of figures is mainly a result of the neglected electron-electron interactions (see Problem 12).<sup>29</sup>

<sup>28</sup> Until Pauli's theory, the absence of a strong Curie's law paramagnetism in metals was another of the outstanding anomalies in the free electron theory of metals; as in the case of the specific heat, the anomaly was removed by observing that electrons obey Fermi-Dirac, rather than classical, statistics.

<sup>29</sup> The reader who recalls the large correction to the electronic density of levels appearing in the electronic specific heat, which arises from the electron-phonon interaction, may be surprised to learn that a similarly large correction does not arise in the Pauli susceptibility. There is an important difference between the two cases. When the specific heat is computed, one calculates a fixed temperature-independent correction to the electronic density of levels, and then inserts that *fixed* density of levels into formulas (such as (2.79)) telling how the energy changes as the temperature varies. When a magnetic field is varied, however, the density of levels itself changes. We have already noted, for example (ignoring phonon

Table 31.5  
COMPARISON OF FREE ELECTRON AND MEASURED PAULI  
SUSCEPTIBILITIES

METAL	$r_s/a_0$	$10^6 \chi_{\text{Pauli}}$ (from Eq. (31.71))	$10^6 \chi_{\text{Pauli}}$ (measured) <sup>a</sup>
Li	3.25	0.80	2.0
Na	3.93	0.66	1.1
K	4.86	0.53	0.8 <sub>s</sub>
Rb	5.20	0.50	0.8
Cs	5.62	0.46	0.8

<sup>a</sup> The measured values are taken from the following sources: Li: R. T. Schumacher and C. P. Slichter, *Phys. Rev.* **101**, 58 (1956); Na: R. T. Schumacher and W. E. Vehse, *J. Phys. Chem. Solids* **24**, 297 (1965); K: S. Schultz and G. Dunifer, *Phys. Rev. Lett.* **18**, 283 (1967); Rb, Cs: J. A. Kaeck, *Phys. Rev.* **175**, 897 (1968).

## CONDUCTION ELECTRON DIAMAGNETISM

In the foregoing discussion of conduction electron magnetism we considered only the paramagnetic effects arising from the coupling of the intrinsic spin of the electrons with the applied field  $H$ . There are also diamagnetic effects arising from the coupling of the field to the orbital motion of the electrons. We discussed this at some length in Chapter 14, where we found that at very low temperatures, high fields, and high purities ( $\omega_c \tau = eH\tau/mc \gg 1$ ) there was a complicated oscillatory structure to the dependence of  $M$  on  $H$ . In ordinary specimens the condition of high  $\omega_c \tau$  is not met, and the oscillatory structure is not perceptible. However, the dependence of  $M$  on  $H$  does not average out to zero: There is a net nonvanishing magnetization antiparallel to  $H$ , known as the *Landau diamagnetism*, that is due to the orbital electronic motion induced by the field. For *free* electrons it can be shown<sup>30</sup> that

$$\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}}. \quad (31.72)$$

If the electrons move in a periodic potential but are otherwise independent, the analysis becomes quite complicated, but again results in a diamagnetic susceptibility of the same order of magnitude as the paramagnetic susceptibility. In practice, of

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corrections), that the density of levels for each spin population is shifted up or down in energy with changing field. The phonon correction to this result occurs in a neighborhood (of width  $\hbar\omega_D$ , which is large compared with the shift  $\hbar\omega_c$  due to the field) of the Fermi level. But the Fermi level does not shift with field, in contrast to the uncorrected density of levels. Consequently, one cannot simply substitute a phonon-corrected density of levels into (31.68) as one can in (2.79) because the corrected density of levels varies with field in an intrinsically different way from the uncorrected one. A careful analysis reveals that because the phonon correction is tied to the Fermi level, it has very little effect on the magnetization as the field varies, leading to a correction factor in the susceptibility that is only of order  $(m/M)^{1/2}$  (in contrast to the correction of order unity in the specific heat).

<sup>30</sup> See, for example, R. E. Peierls, *Quantum Theory of Solids*, Oxford, 1955, pp. 144–149. An analysis that takes band structure into account can be found in P. K. Misra and L. M. Roth, *Phys. Rev.* **177**, 1089 (1969) and references therein.