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Figure 9 Nuclear domagnetizations of copper nuclei in the metal, starting from 0.012 K and various fields. (After M. V. Hobden and N. Kurti.)

experiment. If we start at B = 50 kG and  $T_1 = 0.01$  K, then  $\mu B/k_B T_1 \approx 0.5$ , and the entropy decrease on magnetization is over 10 percent of the maximum spin entropy. This is sufficient to overwhelm the lattice and from (41) we estimate a final temperature  $T_2 \approx 10^{-7}$  K. The first nuclear cooling experiment was carried out on Cu nuclei in the metal, starting from a first stage at about 0.02 K as attained by electronic cooling. The lowest temperature reached was  $1.2 \times 10^{-6}$  K.

The results in Fig. 9 fit a line of the form of (41):  $T_2 = T_1(3.1/B)$  with B in gauss, so that  $B_{\Delta} = 3.1$  gauss. This is the effective interaction field of the magnetic moments of the Cu nuclei. The motivation for using nuclei in a metal is that conduction electrons help ensure rapid thermal contact of lattice and nuclei at the temperature of the first stage.

## PARAMAGNETIC SUSCEPTIBILITY OF CONDUCTION ELECTRONS

We are going to try to show how on the basis of these statistics the fact that many metals are diamagnetic, or only weakly paramagnetic, can be brought into agreement with the existence of a magnetic moment of the electrons.

W. Pauli, 1927

Classical free electron theory gives an unsatisfactory account of the paramagnetic susceptibility of the conduction electrons. An electron has associated with it a magnetic moment of one Bohr magneton,  $\mu_B$ . One might expect that the conduction electrons would make a Curie-type paramagnetic contribution (22) to the magnetization of the metal:  $M = N\mu_B^2 B/k_B T$ . Instead it is observed that the magnetization of most normal nonferromagnetic metals is independent of temperature.

Pauli showed that the application of the Fermi-Dirac distribution (Chapter 6) would correct the theory as required. We first give a qualitative explanation. The result (18) tells us that the probability an atom will be lined up parallel to the field *B* exceeds the probability of the antiparallel orientation by roughly  $\mu B/k_BT$ . For *N* atoms per unit volume, this gives a net magnetization  $\approx N\mu^2 B/k_BT$ , the standard result.

Most conduction electrons in a metal, however, have no possibility of turning over when a field is applied, because most orbitals in the Fermi sea with parallel spin are already occupied. Only the electrons within a range  $k_BT$  of the top of the Fermi distribution have a chance to turn over in the field; thus only the fraction  $T/T_F$  of the total number of electrons contribute to the susceptibility. Hence

$$M \approx \frac{N\mu^2 B}{k_B T} \cdot \frac{T}{T_F} = \frac{N\mu^2}{k_B T_F} B \quad , \tag{42}$$

which is independent of temperature and of the observed order of magnitude.

We now calculate the expression for the paramagnetic susceptibility of a free electron gas at  $T \ll T_F$ . We follow the method of calculation suggested by Fig. 10. An alternate derivation is the subject of Problem 5.



Figure 10 Pauli paramagnetism at absolute zero; the orbitals in the shaded regions in (a) are occupied. The numbers of electrons in the "up" and "down" band will adjust to make the energies equal at the Fermi level. The chemical potential (Fermi level) of the moment up electrons is equal to that of the moment down electrons. In (b) we show the excess of moment up electrons in the magnetic field.

The concentration of electrons with magnetic moments parallel to the magnetic field is

$$N_{+} = \frac{1}{2} \int_{-\mu B}^{\epsilon_{F}} d\epsilon \, D(\epsilon + \mu B) \cong \frac{1}{2} \int_{0}^{\epsilon_{F}} d\epsilon \, D(\epsilon) + \frac{1}{2} \, \mu B \, D(\epsilon_{F}) \quad , \tag{43}$$

written for absolute zero. Here  $\frac{1}{2}D(\epsilon + \mu B)$  is the density of orbitals of one spin orientation, with allowance for the downward shift of energy by  $-\mu B$ . The approximation is written for  $k_BT \ll \epsilon_F$ .

The concentration of electrons with magnetic moments antiparallel to the magnetic field is

$$N_{-} = \frac{1}{2} \int_{\mu B}^{\epsilon_{F}} d\epsilon \, D(\epsilon - \mu B) \cong \frac{1}{2} \int_{0}^{\epsilon_{F}} d\epsilon \, D(\epsilon) - \frac{1}{2} \, \mu B \, D(\epsilon_{F}) \quad . \tag{44}$$

The magnetization is given by  $M = \mu(N_+ - N_-)$ , so that

$$M = \mu^2 D(\epsilon_F) B = \frac{3N\mu^2}{2k_B T_F} B \quad , \tag{45}$$

with  $D(\epsilon_F) = 3N/2\epsilon_F = 3N/2k_BT_F$  from Chapter 6. The result (45) gives the **Pauli spin magnetization** of the conduction electrons, for  $k_BT \ll \epsilon_F$ .

In deriving the paramagnetic susceptibility, we have supposed that the spatial motion of the electrons is not affected by the magnetic field. But the wavefunctions are modified by the magnetic field; Landau has shown that for free electrons this causes a diamagnetic moment equal to  $-\frac{1}{3}$  of the paramagnetic moment. Thus the total magnetization of a free electron gas is

$$M = \frac{N\mu_B^2}{k_B T_F} B \quad . \tag{46}$$

Before comparing (46) with the experiment we must take account of the diamagnetism of the ionic cores, of band effects, and of electron-electron interactions. In sodium the interaction effects increase the spin susceptibility by perhaps 75 percent.

The magnetic susceptibility is considerably higher for most transition metals (with unfilled inner electron shells) than for the alkali metals. The high values suggest that the density of orbitals is unusually high for transition metals, in agreement with measurements of the electronic heat capacity. We saw in Chapter 9 how this arises from band theory.

## SUMMARY

## (In CGS Units)

- The diamagnetic susceptibility of N atoms of atomic number Z is  $\chi = -Ze^2N\langle r^2\rangle/6mc^2$ , where  $\langle r^2\rangle$  is the mean square atomic radius. (Langevin)
- Atoms with a permanent magnetic moment  $\boldsymbol{\mu}$  have a paramagnetic susceptibility  $\chi = N\mu^2/3k_BT$ , for  $\mu B \ll k_BT$ . (Curie-Langevin)