VII

MAGNETIC PROPERTIES OF METALS

7.1. Paramagnetism

In this and the next few sections we shall be concerned with the effect of magnetic fields on metals in thermal equilibrium, and only later with their effect on transport phenomena.

The simplest problem is that of paramagnetism, i.e. the orientation of the electron spins by an external magnetic field. In a field of strength H, the energy of an electron is

$$E_l(\mathbf{k}) \pm \mu H, \qquad (7.1)$$

where $\mu = e\hbar/2mc$ is the Bohr magneton, and the sign depends on whether the component of the electron spin in the field direction is $\frac{1}{2}$ or $-\frac{1}{2}$ units. The distribution of electrons over the states with energy (7.1) is now given again by the Fermi function, with a common value of η for electrons of both spin directions.

Since the Fermi function depends only on the difference $E - \eta$, this is equivalent to increasing the parameter η by μH for the electrons of one spin direction, and decreasing it for the other. If we therefore denote by $N(\eta)$ the total number of electrons without magnetic field, which is given by (4.54), then the number of electrons of the two spin directions is

$$\left. \begin{array}{l} N_+ = \frac{1}{2} N(\eta + \mu H) \\ N_- = \frac{1}{2} N(\eta - \mu H) \end{array} \right\} \qquad (7.2)$$

In practice, the field is always so weak that we may approximate (7.2) by

$$\left. \begin{array}{l} N_+ = \frac{1}{2} N(\eta) + \frac{1}{2} \mu H \dfrac{dN}{d\eta} \\[2mm] N_- = \frac{1}{2} N(\eta) - \frac{1}{2} \mu H \dfrac{dN}{d\eta} \end{array} \right\} \qquad (7.3)$$

Adding these equations, we see that the total number of electrons is $N(\eta)$, and since this must be the same number as for $H = 0$, it follows that to this order of approximation η is independent of H. (This could have been seen directly from the fact that η cannot depend on the sign of H and therefore cannot contain a first-order correction.)

If the temperature is low enough to make the electron gas degenerate, we may replace $N(\eta)$ by the leading term of (4.56), so that

$$\left. \begin{aligned} N_+ &= Z(\eta) + \mu H \left(\frac{dZ}{dE} \right)_\eta \\ N_- &= Z(\eta) - \mu H \left(\frac{dZ}{dE} \right)_\eta \end{aligned} \right\} . \tag{7.4}$$

The magnetic moment is therefore

$$M = \mu(N_+ - N_-) = 2\mu^2 H \left(\frac{dZ}{dE} \right)_\eta . \tag{7.5}$$

The paramagnetic susceptibility is therefore independent of temperature, and related to the coefficient of the linear term in the specific heat (cf. (4.57)). However, since we have neglected the interaction between the electrons, which probably affects the paramagnetism more than the specific heat, as we shall see in the next chapter, this relation should not be taken too literally.

Like the electronic specific heat, the paramagnetism is largest for a narrow band, and this also ceases to be degenerate at a lower temperature, so that we should use (7.3) rather than (7.4). Mott (cf. Mott and Jones, 1936, pp. 189 ff.) has applied this to the discussion of the transition elements, like Pd and Pt, in which there is an incomplete inner shell. The electronic states corresponding to those inner shells would, by themselves, give rise to narrow bands, since the overlap of the atomic wave functions between neighbouring atoms is small, and the approximation of § 4.2 therefore reasonable. The problem is complicated by the presence of the outer electron states, but the high value of dZ/dE due to the inner shell remains.

The result (7.5), showing the possibility of a large temperature-independent paramagnetism, was first derived by Pauli (1926) in a paper which started the development of the quantum theory of metals.

7.2. Diamagnetism of free electrons (Landau)

In the preceding section, I have dealt with the effect of a magnetic field on the electron spin. We must now consider its effect on the electron orbit. This is a much more difficult, but also much more interesting, problem. We shall first solve the case of free electrons, and discuss its relation to real metals later.

It is important to avoid a very natural error, which for a time gave rise to the impression that there is some fundamental difficulty about this problem.

In classical mechanics, the projection of the electron orbit on a plane at right angles to the magnetic field is a circle of radius

$$r = \frac{mcv}{eH} = \frac{v}{2\Omega},$$ (7.6)

where v is the velocity of the electron in the transverse plane, c that of light, and

$$\Omega = \frac{eH}{2mc}$$ (7.7)

is the Larmor frequency. Since a single circular orbit has, on the time average, a magnetic moment of

$$\frac{erv}{2c} = \frac{mv^2}{2H},$$

one is tempted to regard this as the magnetic moment per electron. The fact that this expression is independent of the charge, and inversely proportional to H, makes it obvious that the answer must be wrong. What has gone wrong is that we have assumed we are dealing with a number of complete circular orbits. In any finite volume, however, the electrons near the boundary cannot complete the circle. In addition to a number of complete circles, we must then consider also some circular arcs belonging to all those electrons whose orbits intersect the wall. These arcs amount together to a surface current which circles the volume in a sense opposite to that of the individual electron orbit, and which can easily be shown to cancel the effect of the complete orbits.

This argument might then give the impression that the answer to our problem is sensitive to the shape and nature of the surface. This, however, can be avoided if, instead of the moment due to each particle, we calculate the free energy F of the system, and then use the thermodynamic relation

$$M = -\frac{\partial F}{\partial H}.$$ (7.8)

In classical mechanics, and using classical statistics,

$$F = -NkT \log \iint d^3p\, d^3v\; e^{-E(p,r)/kT},$$ (7.9)

where $E(\mathbf{p}, \mathbf{r})$ is the Hamiltonian function, expressing the energy of a particle as a function of momentum and coordinates. In a magnetic field

$$E(\mathbf{p}, \mathbf{r}) = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r}).$$ (7.10)

If we substitute as integration variable

$$\mathbf{\Pi} = \mathbf{p} - \frac{e}{c}\mathbf{A}$$ (7.11)

in place of $\mathbf{p}$ (Π is actually $m\mathbf{v}$, where $\mathbf{v}$ is the electron velocity) and perform the integration over Π first, it is at once evident that the vector potential $\mathbf{A}$, and with it the magnetic field, has disappeared from the equation. The free energy therefore does not depend on H, and by (7.8) there is no magnetic moment. The same argument can be used if we employ Fermi statistics for the classical energy function, and it is therefore clear that any magnetic moment in thermal equilibrium must be due to the quantum effects in the motion of the particles.

We require, therefore, the energy levels of an electron in a magnetic field. It turns out to be convenient to work with the vector potential

$$A_x = 0, \qquad A_y = Hx, \qquad A_z = 0, \tag{7.12}$$

which gives a uniform field of strength H in the z-direction. The Schrödinger equation is then

$$\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial}{\partial y} - \frac{ieHx}{\hbar c}\right)^2 \psi + \frac{\partial^2\psi}{\partial z^2} + \frac{2mE}{\hbar^2}\psi = 0. \tag{7.13}$$

Since this equation contains neither y nor z explicitly, we may assume

$$\psi(x,y,z) = e^{i(k_y y + k_z z)}u(x) \tag{7.14}$$

and obtain for the function u the equation

$$u'' + \left\{\frac{2mE_1}{\hbar^2} - \left(k_y - \frac{eH}{\hbar c}x\right)^2\right\}u = 0, \tag{7.15}$$

where

$$E_1 = E - \frac{\hbar^2}{2m}k_z^2 \tag{7.16}$$

is the energy of the motion in the transverse plane.

(7.15) is the wave equation of an harmonic oscillator with frequency (cf. (7.7))

$$\frac{eH}{mc} = 2\Omega \tag{7.17}$$

and centre

$$x_0 = \frac{\hbar c}{eH}k_y. \tag{7.18}$$

Its energy eigenvalues are therefore

$$E_1 = (2n+1)\hbar\Omega = (2n+1)\mu H. \tag{7.19}$$

This is thus independent of k_y. To find the number of states belonging to each eigenvalue, we have to specify boundary conditions. In the y- and z-directions we shall assume the cyclic condition, as before, which allows values for k_y and k_z which are multiples of $2\pi/L_2$ and of $2\pi/L_3$ respectively. It is not convenient to enforce a cyclic condition in the x-direction, since (7.13) and (7.15) depend on x and therefore have no periodic solutions. We assume, instead, that the metal is bounded by

two walls, a distance L_1 apart, in the x-direction. If, then, L_1 is large compared to the extension of the oscillator function $u_n(x-x_0)$, which is of the order of the orbital radius (7.6), the functions for which the centre x_0 lies well inside the volume will not be affected by the presence of the walls. No solutions exist if x_0 lies well outside the volume; for a small range of x_0 near the wall, the presence of the wall modifies the oscillator eigenfunction and the energy value (7.19). Since in a field of 1,000 gauss, and an electron energy of 2 eV, the radius is about $5 . 10^{-3}$ cm., this border region may usually be neglected.

Then the permissible interval of k_y is $(eH/\hbar c)L_1$. Hence we may write altogether

$$E(n, k_z) = (2n+1)\mu H + \frac{\hbar^2}{2m} k_z^2, \tag{7.20}$$

there being

$$\frac{L_1 L_2 eH}{2\pi\hbar c} \tag{7.21}$$

states for each energy. One easily verifies that the number of states in an interval large compared to $2\mu H$ is the same as for free electrons, so that the only new feature is their spacing.

It follows that, if we regard k_z as practically continuous, the number of states of energy below E is (apart from spin)

$$Z(E) = \frac{2(2m)^{\frac{3}{2}}L_1 L_2 L_3 eH}{(2\pi\hbar)^2 c} \sum_n \{E-(2n+1)\mu H\}^{\frac{1}{2}}, \tag{7.22}$$

where the sum is understood to extend over all those non-negative integers n for which the radicand is positive.

The free energy is (cf. (4.46))

$$F = N\eta - 2kT \int \frac{dZ}{dE} \log(1+e^{(\eta-E)/kT}) \, dE, \tag{7.23}$$

or, on integrating by parts,

$$F = N\eta - 2 \int Z(E)f(E) \, dE, \tag{7.24}$$

where $f(E)$ is the Fermi function. Substituting from (7.22) we find, after a further integration by parts,

$$F = N\eta - A \int_{-\infty}^{\infty} \phi(\epsilon) \frac{d}{d\epsilon}\left(\frac{1}{1+e^{(\epsilon-\epsilon_0)/\theta}}\right) d\epsilon \tag{7.25}$$

with

$$\phi(\epsilon) = \sum_n (\epsilon-n-\tfrac{1}{2})^{\frac{3}{2}}, \tag{7.26}$$

the sum being again limited to those integers n for which the bracket is positive, and

$$\epsilon_0 = \eta/2\mu H, \qquad \theta = kT/2\mu H$$
$$A = \frac{16m^{\frac{3}{2}}(\mu H)^{\frac{1}{2}} L_1 L_2 L_3}{3\pi^2 \hbar^3} \Biggr\} \, . \qquad (7.27)$$

We evaluate ϕ by means of Poisson's summation formula,† and find

$$\phi(\epsilon) = \sum_{l=-\infty}^{\infty} (-1)^l \int_0^\epsilon (\epsilon-x)^{\frac{3}{2}} e^{2\pi i l x} \, dx. \qquad (7.28)$$

For an evaluation of $\phi(\epsilon)$ this sum would converge rather slowly. However, the further integration required in (7.25) reduces the higher terms, provided θ is not too small. (7.25) shows also that ϕ is required only in the neighbourhood of ϵ_0, which is a large number provided

$$2\mu H \ll \eta. \qquad (7.29)$$

For $l \neq 0$, the integral in (7.28) can be reduced to

$$- \frac{3}{8\pi^2 l^2} e^{\pi i l \epsilon} \int_0^{\sqrt{\epsilon}} dy \, e^{-2\pi i l y^2} + \frac{3\epsilon^{\frac{1}{2}}}{8\pi^2 l^2} - \frac{\epsilon^{\frac{3}{2}}}{2\pi i l}. \qquad (7.30)$$

The first term is a rapidly oscillating function of ϵ which, for moderate temperatures,

$$kT \gg 2\mu H, \qquad (7.31)$$

gives a negligible contribution to (7.25). We therefore omit this term for the present. We then obtain

$$F = N\eta + A \int^{\cdot} \left(\tfrac{2}{5}\epsilon^{\frac{5}{2}} - \frac{\sqrt{\epsilon}}{16} \right) \frac{d}{d\epsilon} \left(\frac{1}{1+e^{(\epsilon-\epsilon_0)/\theta}} \right) d\epsilon. \qquad (7.32)$$

The last factor has, as always, a steep maximum near ϵ_0 and, provided $\epsilon_0 \gg \theta$, i.e.

$$\eta \gg kT, \qquad (7.33)$$

we may take the value of the other factor at ϵ_0 outside the integral. This leaves

$$F = N\eta - \tfrac{2}{5}A\epsilon_0^{\frac{5}{2}} + \frac{A}{16}\epsilon_0^{\frac{1}{2}}. \qquad (7.34)$$

Remembering the definitions (7.27), we see that the first two terms are independent of H, and they should therefore represent the free energy in the absence of the field. The third term gives

$$F_1 = \frac{m^{\frac{3}{2}}(\mu H)^2 L_1 L_2 L_3 \sqrt{\eta}}{3\pi^2 \hbar^3 \sqrt{2}}, \qquad (7.35)$$

† Cf. Titchmarsh (1937), § 2.8.

and, according to (7.8), a susceptibility

$$\chi_1 = \frac{M_1}{H} = -\frac{\sqrt{2}m^{\frac{1}{2}}\eta^{\frac{1}{2}}\mu^2}{3\pi^2\hbar^3} = -\frac{e^2}{12\pi^2\hbar c^2}\left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \tag{7.36}$$

per unit volume.

In terms of the wave number k_0 of the electrons in the border region, $\eta = (\hbar k_0)^2/2m$, so that

$$\chi_1 = -\frac{e^2 k_0}{12\pi^2 m c^2}. \tag{7.37}$$

Strictly speaking, in the first two terms of (7.34), η should be allowed to depend on H, since in the equation

$$\frac{\partial F}{\partial \eta} = 0, \tag{7.38}$$

which gives the correct defining equation for η, we should also include the field-dependent term. However, the change in η is then proportional to H^2, and since by (7.38) the variation of F with η is small, of the second order, this gives in F only a correction proportional to H^4, which is in general negligible.

The constant susceptibility which we have found can be seen to arise qualitatively from the fact that the energy levels (7.20) are bunched together. While their mean density is independent of H, the number of electrons that can be accommodated below any given level depends on whether this level coincides with one of the eigenvalues or falls between them. On the average we lose, since near $E = 0$ we always start with an empty interval. Hence on the average the energy of the electrons in the field is higher than without it.

It is easy to see that the diamagnetic moment M_1 is numerically equal to one-third of the paramagnetic moment (7.5) if the latter is also evaluated for free electrons. This relation is true not merely for high degeneracy of the Fermi gas, but also in the intermediate case and in the limit of Boltzmann statistics.

If we had required to know only the part of the moment which is proportional to H, somewhat simpler mathematical techniques would have sufficed. We shall now, however, evaluate the remaining term of (7.30) which is of interest at low temperatures. We therefore now assume that, instead of (7.31), $2\mu H$ is of the same order as kT. We retain, however, the assumption (7.29) so that we may take the integral in (7.30) to infinity. The first term then becomes

$$\frac{1-i}{4}\frac{3}{8\pi^2}\frac{1}{l^{\frac{3}{2}}}\,e^{2\pi i l\epsilon},$$

and this gives a further term in the free energy

$$F_2 = -A \sum_{l=1}^{\infty} (-1)^l \frac{3}{8\sqrt{2}\pi^2 l^{\frac{5}{2}}} \mathrm{re}\left[\int e^{i(2\pi l\epsilon - (\pi/4))} \times \frac{d}{d\epsilon}\left\{\frac{1}{1+e^{(\epsilon-\epsilon_0)/\theta}}\right\} d\epsilon \right],$$
(7.39)

where re means 'real part of'.

The integral is easily evaluated in the complex plane, by displacing the path of integration towards infinitely large positive imaginary values, and allowing for the poles at $(2n+1)\pi i$. The result is

$$-e^{i(2\pi l\epsilon_0 - (\pi/4))} \frac{2\pi^2 l\theta}{\sinh 2\pi^2 l\theta}.$$

This gives, to the free energy per unit volume, the contribution

$$F_2 = \frac{\sqrt{2}m^{\frac{3}{2}}(\mu H)^{\frac{3}{2}}kT}{\pi^2\hbar^3} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{\frac{3}{2}}} \frac{\cos\{(\pi l\eta/\mu H) - (\pi/4)\}}{\sinh(\pi^2 lkT/\mu H)}.$$
(7.40)

The oscillatory behaviour of this expression is evidently related to the fact that, as the field varies, the border region of the Fermi distribution will sometimes be near one of the discrete levels and at other times between two levels. The denominator becomes large rapidly as soon as $kT/2\mu H$ is appreciable. In calculating the magnetic moment by (7.8), it is now essential to allow for the variation of η with H, since F_2 is very sensitive to small changes in η.

It would appear that this anomalous part of the diamagnetism is very hard to observe, since to make the denominator of the first term even as small as sinh 3, one has to use 80,000 gauss at 2° K. In addition, with $\eta \sim 2$ eV, the argument of the first cos in (7.40) would be about 10^4 at that field, so that the field would have to be kept constant to rather better than one part in 10^4 to observe any effect. We shall see later that for electrons in a lattice the position may in some cases be much easier.

7.3. Effect of a periodic field

It is now of interest to see how the diamagnetism is changed, if, instead of free electrons, we are concerned with electrons in a periodic potential. In this case we must include a potential energy term in the Schrödinger equation (7.13). Now since the force due to the magnetic field is always small compared to the force exerted by the lattice potential $V(\mathbf{r})$, one might be tempted to start from the solution without magnetic field and treat the magnetic terms as a small perturbation. This would not, however, be permissible, as is evident from the fact that even in the periodic field the particle orbits will be closed, and hence the energy levels presumably

discrete. No disturbance that changes a continuous spectrum into a discrete one can be treated as a small perturbation. Indeed, the fact that H occurs in (7.13) multiplied by x means that far from the origin this term is very large.

We can choose any arbitrary point, say the centre of the nth lattice cell, as origin, if we modify the vector potential (7.12) accordingly. We must then change the wave function $\psi(\mathbf{r})$ to

$$\psi(\mathbf{r})e^{(ieH/\hbar c)x_\mathbf{n}v}, \tag{7.41}$$

where $x_\mathbf{n}$ means the x component of $\mathbf{a_n}$. The function (7.41) satisfies, near $\mathbf{a_n}$, an equation which differs very little from that without magnetic field and it will therefore in that neighbourhood be similar to a combination of eigenfunctions without field.

This is the spirit of the approximation that may be applied to this equation in a number of ways. The first step then consists in taking the function (7.41) in the nth cell as a combination of electron states all belonging to the same band. The distortion of the wave by the magnetic field will then bring in also other bands just as, in expanding the wave function of an atom in a magnetic field, it will be found to contain small contributions from different atomic states. These terms will be referred to as non-diagonal terms.

As long as non-diagonal terms are neglected, one can show that the energy levels of the electron are given by changing the argument of the function $E_l(\mathbf{k})$ to a vector $\varkappa$ whose components are now operators, satisfying the commutation law

$$\varkappa_x \varkappa_y - \varkappa_y \varkappa_x = \frac{ie}{\hbar c} H_z \tag{7.42}$$

(and corresponding equations for the other components), while $E_l(\mathbf{k})$ is the energy function of the periodic field as used previously. This is an extension of the free-particle case, in which we may regard (7.13) as expressing the energy in terms of the wave vector, and substituting for the wave vector

$$\varkappa = \text{grad} - \frac{ie}{\hbar c} \mathbf{A}, \tag{7.43}$$

where $\mathbf{A}$ is the vector potential. The components of (7.43) satisfy (7.42).

The proof of this statement is somewhat too long to be set out here. It was given by Peierls (1933) for the particular case of tight binding (§ 4.2), and a more elegant and general proof is contained in a thesis by Harper (1954).

If in the normal energy function of the conduction band we regard the wave vector components as non-commuting, we are left with an operator

of which the exact eigenvalues are not easily found. It is, however, possible to calculate the high-temperature susceptibility (i.e. apart from any oscillating parts) without knowing the energy levels exactly. For this I must again refer to the original derivation by Peierls (1933) or a number of alternative forms, e.g. Wilson (1936). The result is that the constant part of the susceptibility is proportional to the integral over the border region of

$$R = \frac{\partial^2 E}{\partial k_x^2} \frac{\partial^2 E}{\partial k_y^2} - \left(\frac{\partial^2 E}{\partial k_x \partial k_y} \right)^2, \qquad (7.44)$$

where the axis of the magnetic field has been taken as z-axis, and $E(\mathbf{k})$ is the energy function in the absence of a magnetic field. Since the volume of the border region is proportional to dZ/dE, the susceptibility is proportional to

$$\frac{dZ}{dE} \bar{R}. \qquad (7.45)$$

For free electrons, this quantity is equal to

$$\frac{\hbar^2 k_0}{\pi^2 m}, \qquad (7.46)$$

and for the general case the susceptibility is obtained by inserting (7.45) in place of (7.46) in (7.37). This may be carried out by defining an 'effective mass' from the equality of (7.45) and (7.46), choosing k_0 for this purpose as some average of the wave vector in the border region.

In particular, near the bottom of a symmetric zone, where the energy may be assumed proportional to k^2, and where we have already defined an effective mass in (4.44), we merely have to substitute m^* for m in (7.37). It is of interest that the diamagnetic effect increases for small effective mass, whereas the paramagnetic susceptibility (7.5) decreases in that case. Metals like bismuth, in which the total susceptibility is strongly diamagnetic, are therefore likely to have a small effective mass, or, from (7.44), an energy function whose gradient varies very rapidly with $\mathbf{k}$.

This explanation links up well with Jones's theory of the structure of Bi, § 5.4, since we have seen there that the structure arises from a near coincidence of the border of the Fermi distribution with a zone boundary created by the distortion of the structure from a simple cubic one. Now a glance at Fig. 13 shows that near a zone boundary created by a small distortion the second derivative of the energy with respect to the wave vector, and hence the effective mass, is particularly large. The same applies to certain types of alloy structure mentioned in § 5.4, which are also diamagnetic.

According to Jones, there is at least one band which is almost completely filled, containing only a few 'holes', and only a few electrons are overflowing into the next band. We are therefore here concerned with the neighbourhood of the energy maximum and minimum, respectively, and it seems reasonable to regard the energy as a quadratic function of **k**. At first sight, one would again be inclined to take a nearly isotropic function, since the Bi structure differs little from cubic symmetry. However, the energy maximum is likely to lie on the corners of the polyhedron defining the zone boundary, and the minimum of the next band near the middle of the faces. There are therefore several points with the same energy, which do not differ by a reciprocal lattice vector and therefore correspond to different electron states, but which are transformed into each other by a rotation of the crystal to an equivalent position. In this situation, as I pointed out in § 4.5, the energy surfaces near each minimum need not have any particular symmetry.

In spite of this we do not expect the susceptibility to be strongly dependent on direction, since the different portions of the energy surface will give contributions to (7.44) which will combine to a fairly isotropic overall result.

Turning now to the case of low temperatures, where the oscillating parts of the type (7.40) might be of importance, we require a knowledge of the actual grouping of the energy levels. For a general function of the non-commuting variables κ referred to in (7.42) this is not easy, but the problem is simple for the case of a quadratic function, i.e. near the maximum and minimum energy of a band. If this quadratic function is, in fact, isotropic, we can take over the whole theory of the preceding section, except for the value of the mass, which has to be replaced by the effective mass; this substitution has to be made also in μ where it occurs in (7.40), which is then replaced by

$$\mu^* = \frac{e\hbar}{2m^*c}.$$

For small effective mass the oscillating term will not only come in at higher temperatures, since the denominator of (7.40) is reduced, but will oscillate less rapidly, and be therefore more easily detectable.

If the energy is quadratic, but no longer isotropic, so that the energy surfaces are ellipsoids rather than spheres, one can reduce the eigenvalue problem to that solved previously, by a transformation which changes the scale of the different components of **k** by different factors. One may then show that the energy values near each minimum are still given by (7.20) provided μ, H, and m are changed by factors which depend on the

direction of the magnetic field (Blackman (1938)). One therefore obtains a combination of terms like (7.40), containing different scale factors, one for each of the energy minima or maxima. Since now a change in orientation of the crystal will shift the different oscillatory turns relatively to each other in frequency, as well as altering their amplitudes, the overall result is far from isotropy.

Such an oscillatory behaviour of the susceptibility of bismuth had indeed been discovered by de Haas and van Alphen (1930) at low temperatures and in strong fields, and in fact this discovery led to the development of the theory of this and the preceding section. Further work by Shoenberg (1939) showed that the results, which are of fascinating complexity, can be used to provide a good deal of detailed information about the nature of the energy function near the maximum or minimum, and the number of electrons in each group. Later work (Shoenberg, 1952) has shown the existence of similar effects in other metals.

This raises the question whether one should also expect a de Haas–van Alphen effect if the conduction band is not nearly empty or nearly full. The characteristic features of the energy levels (7.20), (7.21) which we have used were that they were discrete (except for the motion in the field direction), equidistant, and of a very high multiplicity (7.21) proportional to H. Unpublished work by Harper has shown that going from the top or bottom of a band towards its centre, the energy levels cease to be equidistant; at the same time the sharp and degenerate levels are drawn out into narrow bands, whose width increases until, somewhere in the middle of the conduction band, they almost join together. The variability of the spacing will not affect the de Haas–van Alphen effect qualitatively, and the broadening will not affect it until the width becomes comparable with their spacing or with kT. Further work has to be done to decide whether there is a region in which the oscillatory behaviour becomes completely negligible. It would seem, at any rate, that, for sufficiently low temperatures, and with a very accurately uniform field, the effect should be found in most metals.

I stressed at the beginning that the non-diagonal terms have been omitted in this discussion. These must, in the limit of very strong binding, contain the susceptibility of the single atom as far as it is due to the electron orbits. They contain, however, also a cross term depending both on the function $E(\mathbf{k})$ and on transitions to different bands, which has no analogue either in the single atom or for free electrons. It has generally been assumed that these non-diagonal terms would contribute

a constant susceptibility of the order of magnitude of that of single atoms, and would therefore be negligible both in cases of exceptionally high diamagnetism, as in Bi, and in the discussion of the de Haas–van Alphen effect.

In a recent paper Adams (1953) has, however, pointed out that when a small effective mass is due to a small gap between two energy bands as in Jones's theory of Bi, the non-diagonal terms may also be exceptionally large because the transitions to other bands are then associated only with small energy changes. It is not yet possible to estimate the total contribution from these terms, or to say whether they may also affect the oscillatory parts.

A further apparent difficulty is that the discrete nature of the energy levels, which we have used in the calculations of § 7.2, is connected with the fact that the classical electron orbits are periodic. Now if the electrons are subject to collisions, their orbits will not be periodic unless the collision time is longer. This might throw suspicion on all our results except when $\tau \gg 1/\Omega$, i.e.

$$\frac{\hbar}{\tau} \ll \mu H. \tag{7.47}$$

However, it was shown by Peierls (1933) that the collisions do not affect the constant susceptibility provided

$$\frac{\hbar}{\tau} \ll kT. \tag{7.48}$$

This condition is, in general, weaker than (7.47) and is satisfied, except at high temperatures, cf. § 6.8. It is, in fact, almost certain that (7.48) is not a necessary condition for the validity of the formula for the constant susceptibility, but that it is sufficient to have

$$\frac{\hbar}{\tau} \ll \eta. \tag{7.49}$$

This does not seem to have been proved. If true, it would make the collisions unimportant at all temperatures, except possibly for very poor conductors with a small number of conduction electrons.

For the de Haas–van Alphen effect, condition (7.48) is probably essential, since the level broadening due to the collisions is equivalent to an increase in temperature, as pointed out by Dingle (1952).

7.4. Hall effect and magneto-resistance

In discussing the effect of a magnetic field on transport phenomena, we again omit non-diagonal terms. If we then introduce again the

non-commuting components of $\varkappa$, it follows from the commutator (7.42) that

$$\begin{aligned}
\frac{d\kappa_x}{dt} &= -\frac{i}{\hbar}(E\kappa_x - \kappa_x E) = -\frac{eH}{\hbar^2 c}\frac{\partial E}{\partial \kappa_y} = -\frac{eH}{\hbar c}v_y \\
\frac{d\kappa_y}{dt} &= -\frac{i}{\hbar}(E\kappa_y - \kappa_y E) = \frac{eH}{\hbar^2 c}\frac{\partial E}{\partial \kappa_x} = \frac{eH}{\hbar c}v_x
\end{aligned} \right\} \tag{7.50}$$

if the magnetic field is in the z-direction. Here v is again the function defined by (4.41) with $\varkappa$ as argument. Now we may describe the electrons by wave packets in which the values of both κ_x and κ_y are approximately fixed, and this will be adequate for a statistical description provided the extent in k space of these wave packets is small compared to the border region, which amounts in order of magnitude to the condition

$$\mu H \ll kT. \tag{7.51}$$

Subject to this condition we may from now on replace $\varkappa$ by its mean over the wave packet, whose components commute, and revert to the notation k. (7.50) then confirms the equation for acceleration by a field, which we surmised in (4.43).

To obtain the effect of the field on the current, we must add in the Boltzmann equation besides (6.9) a term

$$\frac{eH}{\hbar c}\left(v_y\frac{\partial n}{\partial k_x} - v_x\frac{\partial n}{\partial k_y}\right). \tag{7.52}$$

We shall again start with the assumption of a definite collision time, which may still be a function of the energy. Then we have in place of (6.13), omitting again $\bar{n}_1$ for the same reason as before,

$$\frac{1}{\tau}n_1 + \frac{eH}{\hbar c}\left(v_y\frac{\partial n_1}{\partial k_x} - v_x\frac{\partial n_1}{\partial k_y}\right) = -e(F_x v_x + F_y v_y)\frac{df}{dE}. \tag{7.53}$$

For free electrons, this simplifies to

$$\frac{1}{\tau}n_1 + \frac{eH}{mc}\left(v_y\frac{\partial n_1}{\partial v_x} - v_x\frac{\partial n_1}{\partial v_y}\right) = -e(F_x v_x + F_y v_y)\frac{df}{dE}. \tag{7.54}$$

The bracket on the left-hand side represents an operation which gives zero when applied to any function of the energy, and which turns a linear function of the velocities into another such linear function. It follows therefore that the equation can be solved by putting

$$n_1 = g_x v_x + g_y v_y, \tag{7.55}$$

where g_x, g_y are functions of the energy. Inserting this and comparing the angular dependence of the terms on either side,

$$\left.\begin{aligned}
\frac{1}{\tau}g_x - 2\Omega g_y &= -eF_x\frac{df}{dE} \\
\frac{1}{\tau}g_y + 2\Omega g_x &= -eF_y\frac{df}{dE}
\end{aligned}\right\}, \qquad (7.56)$$

where Ω is the Larmor frequency, defined in (7.7). Hence

$$\left.\begin{aligned}
g_x &= \frac{-e\tau(F_x + 2\Omega\tau F_y)}{1+4\Omega^2\tau^2}\frac{df}{dE} \\
g_y &= \frac{-e\tau(F_y - 2\Omega\tau F_x)}{1+4\Omega^2\tau^2}\frac{df}{dE}
\end{aligned}\right\}. \qquad (7.57)$$

If we have current flowing along a wire, the direction of the current is given. If we take this as the x-direction, J_y must vanish. Now since (cf. (6.14))

$$\left.\begin{aligned}
J_x &= 2e\int \overline{v_x^2}\frac{dZ}{dE}g_x\,dE \\
J_y &= 2e\int \overline{v_y^2}\frac{dZ}{dE}g_y\,dE
\end{aligned}\right\}, \qquad (7.58)$$

and since the factor df/dE vanishes except near $E = \eta$, this means that the other factor in g_y must vanish at η,

$$F_y = 2\Omega F_x\tau(\eta). \qquad (7.59)$$

It is customary to express the transverse potential gradient in terms of the longitudinal current and the magnetic field, thus defining the Hall coefficient R:

$$R = \frac{F_y}{HJ_x} = \frac{e\tau(\eta)}{mc\sigma}, \qquad (7.60)$$

or, inserting for the conductivity σ from (6.16),

$$R = \frac{1}{ecN}. \qquad (7.61)$$

This well-known result would seem to indicate that the Hall coefficient is a measure of the number of conduction electrons per unit volume.

Under the same assumptions we see that, for energies near η, the first equation (7.56) is independent of the magnetic field. Since only these energies are of importance for (7.58), it therefore follows also that the magneto-resistance effect is negligible.

These results hold good for isotropic conditions, even if the scattering probability is a function of the scattering angle, as in (6.17). This follows because the distribution (7.56) is a spherical harmonic of first

order, so that, as in the case of electric conductivity, the collision time τ_1 from (6.21) replaces τ in our equations.

The reason for the absence of magneto-resistance has been particularly simply expressed by Wilson (1939): In the isotropic case each electron will have the same mean velocity. The transverse electric field will adjust itself so as to cancel the transverse force due to the magnetic field of an electron of that velocity. Hence the electrons are subject only to the longitudinal field and to collisions.

If, however, the mean velocity is different for different groups of electrons, then the transverse force balances only on the average, and each electron is still travelling on a curved path. This can be illustrated simply if we assume there are electrons in two different bands, each isotropic, and each with its own collision time. We assume that the exchange of electrons between the bands is slow. Then for each band

$$F_x = \frac{1}{\sigma} J_x - RHJ_y,$$

$$F_y = \frac{1}{\sigma} J_y + RHJ_x,$$

or, solving for the current,

$$J_x = \frac{\sigma F_x + RH\sigma^2 F_y}{1 + R^2 H^2 \sigma^2}, \qquad J_y = \frac{\sigma F_y - RH\sigma^2 F_x}{1 + R^2 H^2 \sigma^2}. \tag{7.62}$$

The resultant current is the sum of the currents in the two bands. Adding two expressions like (7.62), and again requiring $J_y = 0$, we find, after some tedious algebra,

$$F_y = \frac{R_1 \sigma_1^2 + R_2 \sigma_2^2 + R_1 R_2 \sigma_1^2 \sigma_2^2 H^2 (R_1 + R_2)}{\sigma_1 + \sigma_2 + \sigma_1 \sigma_2 (R_1^2 \sigma_1 + R_2^2 \sigma_2) H^2} HF_x, \tag{7.63}$$

and for the relative increase in resistivity

$$\frac{\Delta\rho}{\rho_0} = \frac{\sigma_1 \sigma_2 (\sigma_1 R_1 - \sigma_2 R_2)^2 H^2}{(\sigma_1 + \sigma_2) + H^2 \sigma_1^2 \sigma_2^2 (R_1 + R_2)^2}. \tag{7.64}$$

The first of these equations gives the Hall coefficient if we express F_x in terms of J_x. Usually the Hall effect is measured in moderately weak fields, and then we may neglect the terms in H^2 in (7.63), and also put $F_x = J_x/(\sigma_1 + \sigma_2)$. Then

$$R = \frac{R_1 \sigma_1^2 + R_2 \sigma_2^2}{(\sigma_1 + \sigma_2)^2}. \tag{7.65}$$

As regards the change in resistance, we notice that it vanishes again when the product of Hall coefficient and conductivity is the same in the two bands. From (7.61) and (6.16) this means that the 'mobility'

e_T/m must be the same for both bands, in accordance with the qualitative argument given above.

Otherwise, there is an increase in resistance which is initially proportional to H^2 but saturates at fields for which $H\sigma R$ is larger than unity for both bands. This amounts dimensionally to the condition that the collision time for each band be larger than the Larmor frequency, or again to (7.47). While for the constant susceptibility the relative magnitude of collision time and Larmor period was unimportant, we see that in the magneto-resistance it plays an important part.

If we are dealing with a nearly full band, so that there are only a few places near an isotropic energy maximum, the theory goes through as before, but, as there are now positive 'holes' carrying the current, the sign of the Hall effect is reversed, as is indicated by the occurrence of the first power of the charge in (7.61).

If a metal contains some positive holes in one band and a few electrons in another, the Hall coefficient is given by (7.65) and it is clear that the sign now depends on the numbers and mobilities of electrons and holes.

All this discussion applies to the isotropic case. For a more general case we would have to return to equation (7.53). Its solution can no longer be given in closed form, though it can be given in the form of a power series in either ascending or descending powers of H, the limits of validity of either being given again by the ratio between collision time and Larmor period. The magneto-resistance again does not vanish, and we may interpret this as due to the fact that, although we have assumed the collision time constant, the effective mass is different for electrons moving in different directions. One can also show that for very high fields the resistance again tends to a constant limit.

However, there is little point in putting much effort into a discussion of this equation, since the assumption of a constant collision time is certainly not justified in the anisotropic case. We may no longer argue, as we did in the case of the Wiedemann–Franz law, that we are dealing with a deviation from equilibrium which varies over the Fermi zone as a component of the electron velocity, so that we may use the same average of the collision time as in the electric conductivity. This is true in the isotropic case, where we found a solution of the form (7.55), but it is easily seen by inserting (7.55) in the general anisotropic equation (7.53) that this does not give a solution.

One interesting application of the arguments of this section is to demonstrate the anisotropy of metals like the alkalis. Here it is almost certain that all electrons are in the same band, and if their energy

surfaces and their collisions with lattice waves were isotropic, one should expect zero magneto-resistance. In fact, their magneto-resistance coefficients are rather smaller than those of other metals, but not in order of magnitude.

In this discussion we have neglected effects arising from the quantum character of the electron motion. At not too low temperatures this can be allowed for by a perturbation treatment. A calculation of this kind was carried out by Titeica (1935) who showed that there are effects of the order of $\mu H/\eta$, but not, as one might have expected, of the order of $\mu H/kT$. Titeica's method is valid only when the field is strong enough for the Larmor period to be less than the collision time. This has been extended to the general case in unpublished calculations by van Wieringen. The magneto-resistance due to this cause is always much less than the 'detour' effect considered before.

These quantum effects become particularly interesting at very low temperatures, where Schubnikow and de Haas (1930) found anomalies in the magneto-resistance of Bi in parallel with the de Haas–van Alphen effect. No theory of this case is as yet available, and it represents a most fascinating problem in quantum statistics, since the conditions for the validity of a Boltzmann equation, which we discussed in § 6.8, are probably not satisfied.

Note added January 1956

The work by Harper referred to at the bottom of page 151 has been published. *Proc. Phys. Soc.* A, **68,** 874, 1955 and **68,** 879, 1955.