4. DIAMAGNETISM OF METALS

It is shown that in quantum theory even free electrons, besides spin-paramagnetism, have a non-vanishing diamagnetism originating from their orbits, which is due to the limitation of the electron orbits in the magnetic field. A few further possible inferences concerning this orbit limitation are indicated.

1. Up to now, it has been more or less quietly assumed that the magnetic properties of electrons, other than spin, are due exclusively to the binding of electrons in atoms. For free electrons, the classical zero-result is assumed for the orbital effect, on the basis that the Fermi integral of the corresponding Hamiltonian, just as the Boltzmann function, is independent of the magnetic field. However, a quantum phenomenon is thereby allowed to be neglected. In the presence of a magnetic field, the motion of the electron is obviously finite in the plane perpendicular to the field. This leads, of necessity, to a partial discreteness (corresponding to the motion in this plane) of the eigenvalues of the system, which gives rise, as will be shown, to a non-vanishing orbital magnetism.

The Hamiltonian of a free electron in a magnetic field can be written in the familiar form:

$$E = \frac{m\,v_1^2}{2} + \frac{m\,v_2^2}{2} + \frac{m\,v_3^2}{2} \tag{1}$$

where

$$v_1 = \frac{1}{m}\left(p_1 - \frac{eH}{2c}y\right), \quad v_2 = \frac{1}{m}\left(p_2 + \frac{eH}{2c}x\right), \quad v_3 = \frac{1}{m}p_3 \tag{2}$$

are the velocities of the systems (H is the absolute value of the magnetic field in the direction of the z-axis). The motion in the direction of the field is independent of the field and of other components of motion, and can be split off by putting p_3 simply equal to a constant, which corresponds to the Schrödinger function

$$\psi(x,\,y,\,z) = f(x,\,y)\,e^{ip_3z/\hbar}. \tag{3}$$

The energy value of the system will then be represented as the sum of two independent terms. Now, instead of having to solve the two corresponding Schrödinger equations for the xy-motion, we can use an artificial method for deriving the energy values by writing down the commutation relationships of the component velocities v_1 and v_2. From equation (2) it follows directly

$$[v_1,\,v_2] \equiv v_1v_2 - v_2v_1 = \frac{\hbar}{i}\frac{eH}{cm^2}, \tag{4}$$

L. Landau, Diamagnetismus der Metalle, Z. Phys. 64, 629 (1930).

since, as is well known $[x, y] = [p_1, p_2] = 0$, $[p_1, x] = [p_2, y] = \hbar/i$. The constant on the right-hand side of equation (4) is reminiscent of the usual p, q-commutation relation. In order to come back to that case, we can now temporarily introduce the co-ordinates P and Q by means of

$$v_1 = \frac{P}{\sqrt{m}}, \quad v_2 = \frac{eH}{c\,m\sqrt{m}}Q.$$ (5)

The commutation relation reduces into the usual form $[P, Q] = \hbar/i$. The equation referring to the energy can now be written in the form:

$$E = \frac{P^2 + \left(\dfrac{eH}{mc}\right)^2 Q^2}{2}.$$ (6)

This, however, is none other than the Hamiltonian of a linear oscillator with mass m and frequency $\omega = eH/m\,c$. The eigenvalues of such a system are, as is well-known, equal to

$$E = \left(n + \frac{1}{2}\right)\hbar\,\omega = \left(n + \frac{1}{2}\right)\frac{e\hbar}{mc}H,$$ (7)

where n can assume all positive integral values. Together with the z-motion this gives

$$E = \left(n + \frac{1}{2}\right)\frac{e\hbar}{mc}H + \frac{p_3^2}{2m},$$ (8)

for the eigenvalue of the translational motion of the electron.

The eigenfunctions can also be determined in a simple manner. For this purpose we eliminate one of the co-ordinates, for example x, from the velocity operators (and thus also from the energy operator), by putting

$$\psi = e^{-\frac{ieHxy}{2\hbar c}}\chi.$$ (9)

This gives

$$v_1\,\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x} - \frac{eH}{2c}y\,\psi = e^{-\frac{ieH}{2\hbar c}xy}\left(\frac{\hbar}{i}\frac{\partial\chi}{\partial x} - \frac{eH}{c}y\chi\right),$$

$$v_2\,\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial y} + \frac{eH}{2c}x\psi = e^{-\frac{ieH}{2\hbar c}xy}\frac{\hbar}{i}\frac{\partial\chi}{\partial y}.$$ (10)

The Schrödinger equation corresponding to this is written

$$\left\{\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{eH}{\hbar c}y\right)^2 - 2mE\right\}\chi = 0.$$ (11)

This equation does not contain x explicitly; thus, its solutions can be written in the exponential form

$$\chi = e^{\frac{i}{\hbar}\sigma x}\varphi(y),$$ (12)

where σ is a constant and φ is no longer dependent on x. If we substitute equation (12) in equation (11), we obtain immediately for φ an oscillator equation

$$\frac{d^2\varphi}{dy^2} + \frac{2m}{\hbar^2}\left[E - \frac{m}{2}\left(\frac{eH}{mc}\right)^2\left(y - \frac{c}{eH}\sigma\right)^2\right]\varphi = 0,\qquad(13)$$

which is just as we should expect from what has previously been said. The "equilibrium point" of this oscillator is at the point $\eta = c\,\sigma/e\,H$. Thus, we obtain finally for the complete eigenfunction of the system

$$\psi = e^{\frac{i}{\hbar}\left(p_3z + \sigma x - \frac{eH}{2c}xy\right)}\varphi_n\left[\sqrt{\frac{eH}{\hbar c}}\left(y - \frac{c}{eH}\sigma\right)\right],\qquad(14)$$

where φ_n denotes the eigenfunction of the equation

$$\frac{d^2\varphi_n}{d\,u^2} + (2n + 1 - u^2)\,\varphi_n = 0.\qquad(15)$$

The quantity σ does not enter into the eigenvalue. Since it can assume an arbitrary value, then our problem is still degenerate in a continuous way. In order to determine the density of the eigenvalues we replace, as usual, the infinite space by a finite container with the linear dimensions A, B and C in the x-, y- and z-directions. In the z-direction the number of possible p_3-values in the interval Δp is well known, and is equal to

$$R_{\Delta p} = \frac{C}{2\pi\hbar}\Delta p.\qquad(16)$$

In a quite similar manner, we obtain for the x-direction

$$R_{\Delta\lambda} = \frac{A}{2\pi\hbar}\Delta\sigma.\qquad(17)$$

In the y-direction we require that the trajectory always lies in the container at a sufficient distance from the walls. Then we need not consider the influence of the "y"-walls, because of the rapid damping of φ_n with range. Since the number of trajectories colliding at the walls can be considered as small, with an adequately large container, then we can assume that this requirement gives us practically all the existing trajectories. On account of the large container dimensions, we can thus neglect also the radius of the trajectory and we can simply write

$$0 < \frac{c}{eH}\sigma < B$$

or

$$0 < \sigma < \frac{eB}{c}H.\qquad(18)$$

If, now, we wish to obtain the total number of eigenvalues corresponding to the given non-degenerate quantum number n, then we have to substitute $\varDelta \sigma = (e\,B/c)\,H$ in equation (17). This gives

$$R_n = \frac{e\,H}{2\pi\,\hbar\,c}\,A\,B = \frac{e\,H}{2\pi\,\hbar\,c}\,S,$$

where S is the area of the container sides. Altogether we have

$$R_{\varDelta p,\,n} = R_{\varDelta p}\,R_n = \frac{e\,H}{4\pi^2\,\hbar^2\,c}\,V\varDelta\,p,\tag{19}$$

thus, as was to be expected, proportional to the volume. It can be easily checked that equation (19), as a result of the limiting transition $H \to 0$, converts into the usual eigenvalue distribution of free motion. Together with the spin, we have

$$E' = E \pm \frac{e\,\hbar}{2\,m\,c}\,H,\tag{20}$$

that is to say

$$E = \frac{e\,\hbar\,H}{m\,c}\,n + \frac{p_3^2}{2\,m},\tag{21}$$

so that to every $n > 0$, the double degeneracy

$$R_{n,\,\varDelta p} = \frac{e\,H}{2\pi^2\,\hbar^2\,c}\,V\varDelta p\tag{22a}$$

corresponds, and with $n = 0$, we have

$$R_{0,\,\varDelta p} = \frac{e\,H}{4\pi^2\,\hbar^2\,c}\,V\varDelta p.\tag{22b}$$

2. In order to obtain the magnetic properties of the system, we require, as is well known, only to evaluate the summation

$$\varOmega = -kT\sum \ln\left(1 + e^{\frac{\omega - E}{kT}}\right)\tag{23}$$

over all eigenvalues; ω denotes the so-called chemical potential. The number of particles N is linked with ω through the expression

$$N = -\frac{\partial\varOmega}{\partial\omega},\tag{24}$$

and the magnetic moment through

$$M = -\frac{\partial\varOmega}{\partial H}.\tag{25}$$

In our case, we have a continuous and a discrete parameter, so that the summation in equation (23) can be represented by a sum of integrals. Thus, in

order to resolve the effect more clearly, we shall start from the orbital energies of equation (8) and consider to begin with the spin only in the multiplicity. If we put

$$\frac{e\,\hbar}{m\,c} = \mu, \tag{26}$$

then we have

$$\Omega = -\,k\,T \sum_{n=0}^{\infty} \int \ln\left[1 + e^{\frac{\omega-(n+1/2)\mu H}{kT} - \frac{p^2_3}{2mkT}}\right] \frac{e\,H}{2\pi^2\,\hbar^2\,c}\,V\,dp_3. \tag{27}$$

If, now, for the sake of brevity we write

$$-\,k\,T \int \ln\left(1 + e^{\frac{\omega}{kT} - \frac{p^2_3}{2mkT}}\right) \frac{m\,V}{2\pi^2\,\hbar^3}\,d\,p_3 = f(\omega), \tag{28}$$

then Ω assumes the form

$$\Omega = \mu\,H \sum_{0}^{\infty} f\left[\omega - \left(n + \frac{1}{2}\right)\mu\,H\right]. \tag{29}$$

In order to determine this sum, we can use the familiar series expansion

$$\sum_{a}^{b} f\left(x + \frac{1}{2}\right) = \int_{a}^{b} f(x)\,dx - \frac{1}{24}\left|f'(x)\right|_{b}^{a}. \tag{30}$$

Its admissibility requires, in general, that

$$\frac{f_{x+1} - f_x}{f_x} \ll 1. \tag{31}$$

It can easily be seen in our case that this corresponds to

$$\mu\,H \ll k\,T. \tag{32}$$

This condition is no longer fulfilled at very low temperatures and in strong fields. On account of this, the latter case should lead to a complicated, no longer linear dependence of the magnetic moment on H, which should have a very strong periodicity in the field. Because of this periodicity, it should be hardly possible to observe this phenomenon experimentally, since on account of the inhomogeneity of the existing field, an averaging will occur. If, however, we average the series in equation (29) over an interval ΔH, the condition for equation (31) will again be fulfilled, if in the "dangerous" part near $\omega - [n + (1/2)]\,\mu\,H = 0$, the change of argument is considerably larger than the difference between the two successive arguments, i. e.

$$n\,\mu\,\Delta H \gg \mu\,H, \qquad \omega\,\frac{\Delta H}{H} \gg \mu\,H,$$

or

$$\frac{\Delta H}{H} \gg \frac{\mu\,H}{\omega}. \tag{33}$$

2*

Even with the strongest possible fields ($H = 3 \times 10^5$ gauss), the right-hand side gives only 0·1 per cent with $\omega = 3$ eV.

If we now use the summation formula (30) explicitly, we obtain

$$\Omega = \mu H \int_0^\infty f(\omega - n\,\mu\,H)\,\mathrm{d}n + \frac{1}{24}\,\mu^2 H^2 \left|\frac{\partial f(\omega - n\,\mu\,H)}{\partial \omega}\right|_0^\infty$$

$$= \int_{-\infty}^\omega f(x)\,\mathrm{d}x - \frac{\mu^2 H^2}{24}\,\frac{\partial}{\partial \omega} f(\omega) \tag{34}$$

$[f(\infty) = 0]$. The first term of this summation is independent of the magnetic field. It represents the summation in the field-free state, so that in place of equation (34) we can write

$$\Omega = \Omega_0 - \frac{\mu^2 H^2}{24}\,\frac{\partial^2 \Omega_0}{\partial \omega^2}.$$

From this, we obtain

$$M = -\frac{\partial \Omega}{\partial H} = \frac{\mu^2}{12}\,\frac{\partial^2 \Omega_0}{\partial \omega^2}\,H. \tag{35}$$

If we now put

$$\frac{\partial \Omega}{\partial \omega} = -N, \qquad \omega = \frac{\partial F}{\partial N},$$

where $F = \Omega - \omega(\partial\Omega/\partial\omega)$ is the free energy of the system, then equation (35) becomes

$$M = -\frac{\mu^2 H}{12\,\dfrac{\partial \omega}{\partial N}} = -\frac{\mu^2 H}{12\,\dfrac{\partial^2 F}{N^2}}. \tag{36}$$

We have thus in reality a diamagnetism, which is exactly equal to one third of the Pauli spin paramagnetism[1], for which we have, in the familiar form

$$\Omega = \frac{1}{2}\,\Omega_0\!\left(\omega + \frac{\mu H}{2}\right) + \frac{1}{2}\,\Omega_0\!\left(\omega - \frac{\mu H}{2}\right) = \Omega_0 + \frac{\mu^2 H^2}{8}\,\frac{\partial^2 \Omega_0}{\partial \omega^2} + \cdots \tag{37}$$

Thus, free electrons are altogether still paramagnetic.

. If the electrons are found in the periodic field of a lattice, then it is well known[2] that their motion can still be considered as free, in a certain sense. The principal characteristic of the effect of the magnetic field therefore remains unchanged, although the above calculation is, of course, no longer quantitatively applicable. In particular, the ratio of para- and diamagnetism changes, and it is quite possible that in actual cases the latter can also exceed the former, so that we obtain a diamagnetic substance like bismuth. However, this is only possible with a relatively powerful lattice effect, so that a quantitative theory of this phenomenon should scarcely be possible. Another effect of the

interaction consists in the fact that the diamagnetism loses its symmetry and now depends on direction, a property in which this type of diamagnetism differs from the normal atomic diamagnetism as well as from the necessarily symmetrical spin-paramagnetism.

A similar phenomenon can also take place in non-conducting substances and indeed with paramagnetic substances, where we also have a continuous eigenvalue spectrum. Here, we also get discrete eigenvalues in the magnetic field and, as a result of this—diamagnetism. This diamagnetism is quite small compared with the paramagnetism which is present, but differs from it by its asymmetry, so that perhaps it forms the main basis of the observed asymmetry in paramagnetic crystals (another reason is the so-called magnetic or relativistic interaction between spins). On this account, it is of interest to estimate the order of magnitude of the effect. This is done in the simplest manner dimensionally. The susceptibility is first of all proportional to $(e/c)^2$, since the action of the magnetic field is always introduced by $e H/c$. The mass of the electron m does not occur explicitly in the calculation, in this case. It plays its role in the exchange-integral, which characterises the exchange phenomena in the lattice. Moreover, only $\hbar$ and the density N/V can still make their appearance. Clearly this leads to the expression

$$\chi \sim \frac{e^2}{\hbar^2 c^2} \left(\frac{V}{N}\right)^{1/3} J.$$ (38)

The exchange integral J determines as is well-known, the Curie temperature Θ, and $k\,\Theta$ is of the order of magnitude of J, so that in place of equation (38) we can write

$$\chi \sim \frac{e^2}{\hbar^2 c^2} \left(\frac{V}{N}\right)^{1/3} k\,\Theta.$$ (39)

The phenomena turn out to be quite different if the external effects are of a non-periodic nature. Such effects destroy the direction-degeneracy of the motion and consequently, if they cannot be assumed to be small, the possibility that the field produces an effect of the type investigated here. This requires that the "mean free path" corresponding to this effect is small compared with the diameter of the electron orbits in the magnetic field. Since this diameter in normal fields is of the order of magnitude of a tenth of a millimetre, then even very small impurities or even powdering of the substance can suffice. Such changes of susceptibility have been detected in bismuth, and for the first case in a whole range of substances. It would be of great interest to be able to observe in these cases a change of susceptibility with field, which ought to take place according to the present theory, when $r_H \gg \lambda$ (r_H is the radius of the orbit in the magnetic field, λ is the mean free path or the dimensions of the crystal) changes to $r_H \ll \lambda$.

In conclusion, I should like to make the supposition that the phenomena which have been investigated might explain also the Kapitza effect of linear resistance changes in a magnetic field. For the admissibility of the presumed approximation of free electrons in a magnetic field, it is not necessary that r_H

be smaller than the mean free path corresponding to the lattice (which would be impossible at normal temperatures), because the interaction with the lattice oscillations involves, apart from momentum transfer, also energy transfer. However, according to the foregoing remarks, it is probably essential that r_H be considerably smaller than the mean free path of the lattice distortions, which leads, after short calculations, to the expression

$$H \gg e\, c \frac{N}{V} R, \tag{40}$$

where R is the specific resistance (in electrostatic units) of the crystal. If inequality (40) is not fulfilled, then the method considered here is not applicable and it can be seen quite easily that all the effects of the field must be necessarily quadratic. The field in expression (40) is in good agreement with the critical field of the Kapitza experiments, which should lend support to the theory. I have not yet succeeded in presenting a quantitative development of the theory.

At this stage, I should like to thank sincerely Mr P. Kapitza for discussions of the experimental results and for the communication of certain unpublished data.

REFERENCES

1. W. PAULI, Z. Phys. 41, 81 (1927).
2. F. BLOCH, Z. Phys. 52, 555 (1928).