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ON THE DIAMAGNETISM OF ELECTRONS IN METALS

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In the following, it is proposed to calculate the induced diamagnetic moment due to the free electrons in a metal, using, instead of the classical assumptions of elastic collisions, the recently developed wave-nature of the electron and the Fermi statistics. The problem resolves itself into three parts: to find (1) the ψ functions for an electron in a lattice for the case of small perturbations by the atoms of the lattice, (2) the induced magnetic moment derived from the ψ functions and its dependence on the energy, (3) the total induced magnetic moment, which will then be obtained by applying the statistics for a degenerate system.

The form of the ψ functions is most easily obtained by solving the wave equation by the ordinary perturbation methods, with the potential due to the lattice playing the part of a perturbation.

$$\Delta^2\psi + \frac{8\pi^2\mu}{h^2} E\psi = \frac{8\pi^2\mu}{h^2} \epsilon V\psi. \qquad (1)$$

In (1), ϵ is a numerical constant which, for free electrons, is small. Following the usual procedure, put

$$\psi = \psi_0 + \epsilon\psi_1 \quad E = E_0 + \epsilon E_1$$

and the condition that (1) have a solution is that

$$\int (\mathrm{V} - E_1)\psi_0(l)\psi_0(k)dxdydz = 0 \qquad (2)$$

for all values of k satisfying the relation that

$$E_0(l) = E_0(k).$$

In order to proceed, it is necessary to find the form of V. For a simple cubic lattice with an elementary cell having the linear dimensions $2a$ and the origin of coördinates at the center of the cell, the following symmetry conditions must hold,

$$V(-x, y, z) = V(x, y, z)$$
$$\vdots \qquad\qquad \vdots$$
$$V(x + 2a, y, z) = V(x, y, z).$$
$$\vdots \qquad\qquad \vdots$$

We may therefore write

$$V = \sum_{pqr} B_{pqr} \cos \frac{p\pi x}{a} \cos \frac{q\pi y}{a} \cos \frac{r\pi z}{a}.$$

Any other cubic lattice may then be obtained by putting

$$V = \sum_s V_s$$

$$V_s = \sum_{pqr} {}_sB_{pqr} \cos \frac{p\pi(x + {}_s\delta_x a)}{a} \cos \frac{q\pi(y + {}_s\delta_y a)}{a} \cos \frac{r\pi(z + {}_s\delta_z a)}{a}.$$

The cases that will interest us particularly will be face-centered and body-centered cubic lattices. For these we may write,

Face-centered cubic	*Body-centered cubic*
${}_1\delta_x = {}_1\delta_y = {}_1\delta_z = 0$	${}_1\delta_x = {}_1\delta_y = {}_1\delta_z = 0$
${}_2\delta_x = {}_2\delta_y = 1\ {}_2\delta_z = 0$	${}_2\delta_x = {}_2\delta_y = {}_2\delta_z = 1$
${}_3\delta_x = {}_3\delta_z = 1\ {}_3\delta_y = 0$	
${}_4\delta_y = {}_4\delta_z = 1\ {}_4\delta_x = 0$	

and

$$V = \sum_{pqr} C_{pqr} \cos \frac{p\pi x}{a} \cos \frac{q\pi y}{a} \cos \frac{r\pi z}{a}. \tag{3}$$

With this form for V, it is easily shown that (2) is satisfied by

$$\psi_0(l,m,n) = A \cos \frac{l\pi x}{a} \cos \frac{m\pi y}{a} \cos \frac{n\pi z}{a}. \tag{4}$$

The inclusion of terms involving $\sin \frac{l\pi x}{a}$, etc., adds nothing to the result, so they are omitted here. The above value of ψ_0 is the "zeroth" approximation to the solution of (1), and for free electrons, where ϵ is very small, it is proposed to proceed with this approximation. The constant A is so determined that

$$\int_{-a}^{a} dx \int_{-a}^{a} dy \int_{-a}^{a} \psi_0^2 dz = 1$$
$$A^2 = \left(\frac{1}{a}\right)^3$$

The calculation of the induced moment now becomes a matter of sub-

stituting (4) into the proper formulae. It can easily be shown that in the cases under discussion the induced moment is independent of the orientation of the crystal in the magnetic field. It is sufficient, therefore, to apply the formula for the susceptibility[1,2]

$$\chi(l, m, n) = \frac{2}{3} \sum'_{l'm'n'} \frac{|M^{lmn}_{l'm'n'}|^2}{E(l', m', n') - E(l, m, n)} - \frac{e^2}{6mc^2} \bar{r}^2(l, m, n) \quad (5)$$

$$|M^{lmn}_{l'm'n'}|^2 = \text{const } [\int \psi_0(l', m', n') \vec{r} \times \nabla \psi_0(l, m, n) dxdydz]^2$$

$$\bar{r}^2(l_1, m, n) = \int r^2 \psi_0^2(l, m, n) dxdydz$$

$\chi(l, m, n)$ is the susceptibility per cell $8a^3$ with one electron per cell if the limits of integration in the above expression are taken as $+a$ and $-a$. The first term in (5) vanishes because it contains factors of the form

$$\int_{-\pi}^{\pi} \cos mx \cos nx \, dx = 0, \text{ etc.}$$

The second term is easily evaluated and the expression for χ becomes

$$\chi(l, m, n) = -\frac{e^2}{3mc^2} \left(\frac{\alpha}{4}\right)^2 + f(l, m, n)$$

where $f(l, m, n)$ is small compared to the constant term, and for simplicity the linear dimension of the elementary cell is taken as α instead of $2a$.

The fact that $\chi(l, m, n)$ is essentially independent of the quantum numbers, and therefore of the energy, shows that the statistics will have no influence on the total susceptibility. All electrons have the same susceptibility, and the total susceptibility is the susceptibility per electron times the number of electrons. The more rigorous procedure of evaluating $f(l, m, n)$ and applying the Fermi statistics has been carried out, and of course gives the result

$$K = -\frac{e^2}{3mc^2} \left(\frac{\alpha}{4}\right)^2 n, \quad (6)$$

where K is the volume susceptibility and n is the number of electrons per unit volume. The classical expression is identical except that instead of $\frac{\alpha}{4}$ there appears λ, the mean free path.

It is now possible to compare the formula found by Pauli[3] for the paramagnetic susceptibility K_p of the electron gas, with the above expression, henceforth called K_d. The expression found by Pauli may be written in the following form

$$K_p = \frac{1}{4\pi} \left(\frac{3}{\pi}\right)^{1/3} \frac{e^2}{mc^2} n^{1/3} \quad (7)$$

where n is the number of atoms per cc., each atom contributing one free electron. In the corresponding case, if ν is the number of atoms per cell α^3, we may write

$$\alpha^3 n = \nu$$

$$K_d = -\frac{\nu^{2/3}}{48}\frac{e^2}{mc^2}n^{1/3}. \qquad (8)$$

For body-centered lattices $\nu = 2$ and for face-centered lattices $\nu = 4$. The interesting result found is that

$$K_p/K_d = -2.4 \text{ for body-centered lattices}$$
$$= -1.5 \text{ for face-centered lattices.}$$

The results of the investigation may therefore be stated as follows. By taking into account the wave structure of the electron, a formula for the diamagnetic susceptibility of free electrons is obtained having the same form as the classical formula, but instead of the mean free path λ there appears $\frac{\alpha}{4}$ where α is the grating constant of the cubic lattice under consideration. Whereas the classical formula gave values in general much too large,[4] the new derivation gives for those substances to which it may properly be applied a value less than the paramagnetism of the free electrons. For the heavy elements K, Rb, Cs, Cu, Ag, Au, a quantitative check with experiment cannot be undertaken because K_p and K_d are both small compared to the diamagnetism of the atoms of the lattice themselves. Accurate measurements on lithium would, however, offer a reliable check on the above theory. Let K_a be the diamagnetism of the closed inner shell of the atom. K_a has been calculated by Pauling,[5] and the situation is the following:

For Lithium

K_p	K_d	K_a	
0.79	−0.33	−0.05	$\times 10^{-6}$

Here K_a is certainly small, and comparison with experiment would really check K_p and K_d rather than K_a. If this theory is correct, the volume susceptibility of lithium should be nearer to 0.4×10^{-6} than to 0.8×10^{-6}.

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