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THE ELECTRIC AND MAGNETIC PROPERTIES OF GRAPHITE

R. R. HAERING and P. R. WALLACE

Department of Mathematics, McGill University, Montreal, Quebec, Canada

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Abstract—The conduction electron magnetic susceptibility has been calculated taking into account band-to-band transitions. The calculation is an extension to three dimensions of a calculation by McClure. It is shown that agreement with experiment can only be retained if the inter-layer interaction is much weaker than was previously supposed. If the Fermi energy at zero temperature is $\sim 0{\cdot}06$ eV and if the shift of the Fermi surface with temperature is taken into account, excellent agreement with experiment is obtained for all temperatures. The average value of the susceptibility at low temperatures and the average period of the de Haas-Van Alphen effect fluctuations independently determine the position of the Fermi level at low temperatures. The de Haas–Van Alphen effect fluctuations turn out to be far too large, both in a two and in a three-dimensional calculation. In order to test the values of the various parameters, the ratio of the electrical conductivities, the Hall coefficient and the transverse magneto-resistance have also been calculated.

INTRODUCTION

Several attempts have been made to explain the diamagnetic susceptibility of graphite.(1,2,3) Most of these calculations are based on the Peierls formula(4,5) which neglects band-to-band transitions.(6) McClure, however, has extended these investigations by taking the previously neglected transition terms into account. Using the equations of Luttinger and Kohn(7) and the two-dimensional band structure of Wallace,(8)* he has succeeded in solving the equations for the energy relation in the presence of a magnetic field. McClure's work presents a very satisfactory explanation of the high temperature susceptibility. It will, in fact, be seen that the same model is also capable of explaining the average value of the susceptibility at low temperatures, and the average period of the fluctuations in the de Haas–Van Alphen effect.

Agreement with the experimentally observed average low-temperature susceptibility of -30×10^{-6} e.m.u./g(1) is obtained if the Fermi surface is taken to be about 0·06 eV from the degeneracy corner. Similarly, the experimental average period of the de Haas–Van Alphen effect fluctuations(9,10) can be accounted for by choosing $\zeta_0 \simeq 0{\cdot}065$ eV. We shall see that this rather large value of ζ_0 does not imply that the high temperature susceptibility becomes vanishingly small, as McClure supposed. The apparent discrepancy is reconciled by taking account of the shift of the Fermi level with temperature.

In calculating the high temperature susceptibility from a three-dimensional model, we will be led to the conclusion that the inter-layer interactions are much smaller than was previously supposed.(11) If we are going to retain any susceptibility at all, we require $\gamma_1 \lesssim 0{\cdot}01$ eV, where γ_1 is the exchange integral between nearest neighbours in adjacent planes. Thus, we shall find that graphite is essentially two-dimensional.

An independent rough estimate of γ_1 can be obtained from the de Haas–Van Alphen effect if one uses the semi-classical (Bohr-Sommerfeld) approximation.(12) The two periods of the de Haas–Van Alphen effect(9,10) determine in this approximation both ζ_0 and γ_1. A simple calculation gives $\zeta_0 \simeq 0{\cdot}065$ eV; $\gamma_1 \simeq 0{\cdot}005$ eV.

The origin of the excess electrons implied by this value of ζ_0 is not clear. A possible source might

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* This paper will hereafter be referred to as *A*.

be the incomplete valence bonds on the carbon atoms near the surface of the graphite crystal, as suggested by MROZOWSKI.(13) There are, however, objections to this interpretation, e.g. the prediction of a size effect which is not experimentally established.

Our choice of the Fermi level ζ_0 implies about 10^{-4} excess electrons per carbon atom. This value is in fair agreement with estimates based on additive compound and radiation damage studies.(2,14,15) In particular, bromination experiments seem to indicate a variation of the susceptibility with ζ which is consistent with our model. This point will be further discussed in Section 5.

In order to test our explanation of the susceptibility and the de Haas–Van Alphen effect, it is desirable to investigate the consequences of our small value of γ_1 and large value of ζ_0 on other properties of graphite. Unfortunately, the usual difficulties with the relaxation time prevent one from doing this satisfactorily. However, it should still be possible to decide whether a compatible explanation is possible, or whether a completely different choice of parameters is required. Using standard formulae for the electrical conductivities, the Hall coefficient and the transverse magneto-resistance, we will show, using the three-dimensional band structure of A, that satisfactory agreement is obtained with the following choice of parameters:

γ_0 = nearest "in-plane" neighbour exchange integral $\simeq -2{\cdot}5$ to $-2{\cdot}6$ eV.
γ_1 = nearest "out-of-plane" neighbour exchange integral $\simeq 0{\cdot}005$ eV.
ζ_0 = Fermi level at low temperatures $\simeq 0{\cdot}06$ eV.

We shall see that if the relaxation time τ is assumed constant or a function of energy only, the ratio of the two principal conductivities of graphite $\sigma_{\parallel}/\sigma_{\perp}$ becomes 10^5 with our choice of parameters, in fair agreement with the experimental results of KRISHNAN and GANGULI(16) and DUTTA.(17) Lower values of this ratio have also been reported, for example, by PRIMAK and FUCHS.(18) We feel, however, that the largest reported experimental value should be chosen for comparison with theory, since any slight misalignment during an experiment would greatly reduce the ratio.

The zero field Hall coefficient will also be calculated. At low temperatures, where the difficulties due to the relaxation time are least severe, the calculated Hall coefficient agrees with the measurement of KINCHIN.(30) At higher temperatures, our calculation becomes doubtful, due to the simplifying assumptions about the relaxation time, and the experiments become difficult to interpret.

At low temperatures, the mean free path cancels out in the expressions for the ratio of the conductivities and for the Hall effect, if one assumes that the relaxation time τ depends on $\boldsymbol{k}$ only through the energy. This is not true in the expression for the transverse magneto-resistance. In fact, $\Delta\rho/\rho$ is just proportional to τ^2. Comparison with experiment then yields a value for the relaxation time τ, which can be compared with the results of cyclotron resonance. Agreement with experiment is again satisfactory.

Summarizing, we shall find that a model of graphite based on excess electrons and a small interplanar interaction is in good agreement with experiment.

The position of the Fermi surface at low temperatures may be determined independently by each of the following effects:

(1) The mean period of the de Haas–Van Alphen effect.
(2) The average steady susceptibility at low temperatures.
(3) The low temperature, zero field Hall effect.
(4) The transverse magneto-resistance (only indirectly).

On the other hand, the smallness of the interplane exchange integral follows independently from:

(1) The high temperature susceptibility.
(2) The two periods of the de Haas–Van Alphen effect.
(3) The ratio of the electrical conductivities.
(4) The transverse magneto-resistance (only indirectly).

1. CALCULATION OF THE ENERGY SPECTRUM IN THE PRESENCE OF A MAGNETIC FIELD

LUTTINGER and KOHN(7) have developed a general theory of the motion of electrons and holes in perturbed periodic fields. These equations form the basis of MCCLURE's calculation of the diamagnetism of graphite.(3) MCCLURE's coupled equations (2.7a and 2.7b) are a special case of LUTTINGER and KOHN's equations after certain terms are neglected. Since we are primarily interested in a calculation of the susceptibility, we shall make use of the fact that in graphite the susceptibility with the magnetic field parallel to the crystal c-axis is about forty times larger than the ionic susceptibility. The terms that McClure has omitted from the equations of Luttinger and Kohn are terms which would lead to contributions to the susceptibility which are of the order of the ionic susceptibility.

In the extension of the work done by McClure, we shall also make use of the fact that the diamagnetic susceptibility of graphite is large. In such a case, it is possible to derive an approximate set of equations which, upon solution, yield the energy spectrum in the presence of a magnetic field. The derivation of these equations is based on Löwdin functions(19) and is carried out in the tight binding formalism, although one could generalize this approach. The proof is based on Luttinger's(20) derivation of the "perturbed lattice equation" and is given elsewhere.(21) In particular, the derivation shows that the neglected terms are of the order of the ion core susceptibility.

A simple prescription can be given for obtaining the set of coupled equations which determine the energy spectrum in the presence of the magnetic field. One simply takes the secular determinant which determines the $E(\boldsymbol{k})$ relation in the absence of the magnetic field, and makes the elements of this determinant operators by replacing k_x by $k_x+is(\partial/\partial ky)$, $(s = eH/\hbar c)$. The elements of the resulting matrix operator are to be taken in the sense of an expansion, and the operator acts on a column vector $B_i(\boldsymbol{k})$ whose dimensionality is the multiplicity of the degeneracy in question. Let us illustrate the procedure by re-deriving McClure's equations (2.7a and 2.7b) in this manner.

The secular equation in the two dimensional approximation is given in A as:

$$\begin{vmatrix} H_{11}'-E & H_{12}' \\ H_{12}^{*\prime} & -E+H_{22}' \end{vmatrix} = 0$$

where:

$$H'_{12} = H'_{21}{}^{*} = -\gamma_0\left[\exp\left(\frac{-ik'_x a}{\sqrt{3}}\right)+ + 2\cos\left(\frac{k'_y a}{2}\right)\exp\left(\frac{ik'_x a}{2\sqrt{3}}\right)\right]$$

$$H'_{11} = H'_{22} = E_0-2\gamma'_0\left[\cos(k'_y a)+ + 2\cos\left(\frac{k'_x a\sqrt{3}}{2}\right)\cos\left(\frac{k'_y a}{2}\right)\right]$$

The notation here is the same as that used in A except that our k's are defined differently by a factor of 2π.

We now expand these elements to lowest order about the degeneracy corner. Introducing:

$$k'_x = k_x^c+k_x \qquad k_x^c = \frac{2\pi}{\sqrt{3}a}$$

$$k'_y = k_y^c+k_y \qquad k_y^c = \frac{2\pi}{3a}$$

we find:

$$H'_{11} = H'_{22} \simeq E_0+3\gamma'_0$$

$$H'_{12} = \frac{\sqrt{3}}{2}\gamma_0 a e^{i\pi/3}(k_y-ik_x)$$
$$= \hbar v e^{i\pi/3}(k_y-ik_x).$$

The notation $\hbar v = (\sqrt{3}/2)\gamma_0 a$ was introduced by McClure(3) and will be used throughout this paper. Furthermore, we shall from here on measure energy from the degeneracy corner; we shall put $H_{11}' = H_{22}' = 0$.

Thus, in the absence of a field H, the energy spectrum in the vicinity of the corner of the zone is:

$$E(\boldsymbol{k}) = \pm\hbar v(k_x^2+k_y^2)^{\frac{1}{2}} = \pm\hbar v K.$$

Let us now apply a magnetic field H along the z direction. Following our prescription, our set of coupled equations is:

$$\begin{bmatrix} -E & \hbar v e^{i\pi/3}\left(k_y-ik_x+s\dfrac{\partial}{\partial k_y}\right) \\ \hbar v e^{-i\pi/3}\left(k_y+ik_x-s\dfrac{\partial}{\partial k_y}\right) & -E \end{bmatrix}\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = 0$$

or:

$$\hbar v e^{i\pi/3}\left[k_y - ik_x + s\frac{\partial}{\partial k_y}\right]B_2 = EB_1$$

$$\hbar v e^{-i\pi/3}\left[k_y + ik_x - s\frac{\partial}{\partial k_y}\right]B_1 = EB_2.$$

These equations are completely equivalent to McCLURE's equations (2.7a and 2.7b) (the sign of s is unimportant) and predict the following energy spectrum:

$$E = \pm\hbar v(2ns)^{\frac{1}{2}} = \pm\nu(ns)^{\frac{1}{2}}.$$

It should be pointed out that the secular determinant used here neglects overlap. COULSON and TAYLOR(11) have estimated the various overlap integrals, and have shown that only nearest neighbour overlap is important. If this overlap, which we shall call σ is considered, it can be easily shown that the above energy spectrum is replaced by:

$$\frac{E}{1-\dfrac{E\sigma}{\gamma_0}} = \pm\nu(ns)^{\frac{1}{2}}.$$

Now $\sigma \simeq 0{\cdot}25$. Since we are interested in energies near the degeneracy corner $0 \leqslant E \leqslant \zeta_0$ and since $\gamma_0 \simeq 2{\cdot}6$ eV, it is clear that overlap contributions are completely unimportant.

It may be similarly verified that inclusion of exchange integrals with second nearest neighbours in the graphite plane, as investigated by HOVE,(22) has no appreciable effect in the region of k-space which is of interest in our model.

Let us now extend this treatment to three dimensions. We shall consider only nearest neighbour exchanges within the plane and nearest out-of-plane exchange integrals. Second nearest-neighbour interactions in the plane are again unimportant. The introduction of the out-of-plane interaction on the other hand, changes the spectrum completely, since it is this term which introduces the k_z-dependence through which the two-dimensional levels are spread.

In view of the small value of γ_1 required by our model, the neglect of exchange integrals between more remote neighbours in different planes seems justified.

Finally, as pointed out by CARTER and KRUMHANSL,(23) there is a small difference in the energy of two neighbouring atoms in a plane. This primarily produces a slight splitting of the $n = 0$ level, which is however too small to affect our conclusions.

In this approximation, the secular equation is:(8)

$$\begin{vmatrix} H_0-E & -\gamma_0 S & \gamma_1\Gamma & 0 \\ -\gamma_0 S^* & H_0-E & 0 & 0 \\ \gamma_1\Gamma & 0 & H_0-E & -\gamma_0 S^* \\ 0 & 0 & -\gamma_0 S & H_0-E \end{vmatrix} = 0. \quad (1.1)$$

The notation used is the same as that used in A except for the slightly different definition of $\boldsymbol{k}$. We shall measure energy from the points at which both S and Γ are zero; that is, from the corner of the Brillouin zone at the points $k_z = \pm\pi/c$. Again, we shall expand S about the corner of the zone and then replace k_x by $k_x + is(\partial/\partial k_y)$. (We are using the vector potential $A_x = -yH$, $A_y = A_z = 0$.) The resulting set of coupled equations is:

$$\beta D^- B_2 + \alpha B_3 = \epsilon B_1 \quad (1.2a)$$

$$\beta^{-1} D^+ B_1 = \epsilon B_2 \quad (1.2b)$$

$$\alpha B_1 + \beta^{-1} D^+ B_4 = \epsilon B_3 \quad (1.2c)$$

$$\beta D^- B_3 = \epsilon B_4 \quad (1.2d)$$

where:

$$\alpha = \frac{\gamma_1\Gamma}{\hbar v} = \frac{2\gamma_1}{\hbar v}\cos\left(\frac{k_z c}{2}\right)$$

$$\epsilon = \frac{E}{\hbar v}; \qquad \beta = e^{i\pi/3}$$

$$D^+ = k_y + i\left(k_x + is\frac{\partial}{\partial k_y}\right)$$

$$D^- = k_y - i\left(k_x + is\frac{\partial}{\partial k_y}\right).$$

The substitution $B_m = e^{ik_x k_y/s} b_m$ $(m = 1, 2, 3, 4)$ results in a considerable simplification. Eliminating b_2, b_3, and b_4, the equation for b_1 becomes:

$$[(\Omega^-\Omega^+ - \epsilon^2)(\Omega^+\Omega^- - \epsilon^2) - \epsilon^2\alpha^2]b_1 = 0 \quad (1.3)$$

where:

$$\Omega^{+} = k_y + s\frac{\partial}{\partial k_y}$$

$$\Omega^{-} = k_y - s\frac{\partial}{\partial k_y}$$

But

$$\Omega^{-}\Omega^{+} = -s^2\frac{\partial^2}{\partial k_y^2} + k_y^2 - s$$

and

$$\Omega^{+}\Omega^{-} = -s^2\frac{\partial^2}{\partial k_y^2} + k_y^2 + s.$$

Hence, putting

$$L = -s^2\frac{\partial^2}{\partial k_y^2} + k_y^2 - \epsilon^2,$$

(1.3) becomes:

$$(L^2 - \lambda^2)b_1 = 0 \tag{1.4}$$

where:

$$\lambda^2 = s^2 + \epsilon^2\alpha^2.$$

It is easily seen that the only solutions of (1.4) which satisfy the regularity boundary conditions are φ and χ, which satisfy

$$(L-\lambda)\varphi = 0 \quad \text{and} \quad (L+\lambda)\chi = 0.$$

Now, $(L-\lambda)\varphi = 0$ leads to:

$$\epsilon^2 + (s^2+\alpha^2\epsilon^2)^{\frac{1}{2}} = (2p+1)s$$

(because of regularity of φ, $p = 0, 1, 2, \ldots$)

while $(L+\lambda)\chi = 0$ leads to:

$$\epsilon^2 - (s^2+\alpha^2\epsilon^2)^{\frac{1}{2}} = (2m+1)s$$

(because of regularity of χ, $m = 0, 1, 2, \ldots$).

It is easily checked that these two energy spectra are mutually exclusive when $\alpha \neq 0$. Solving each of these for the energy ϵ we find:

$$b_1 = \chi: \quad \epsilon^2 = \frac{\alpha^2}{2} + s(2m+1) + \left[\left(\frac{\alpha^2}{2}\right)^2 + \alpha^2 s(2m+1) + s^2\right]^{\frac{1}{2}}$$

$$b_1 = \varphi: \quad \epsilon^2 = \frac{\alpha^2}{2} + s(2p+1) - \left[\left(\frac{\alpha^2}{2}\right)^2 + \alpha^2 s(2p+1) + s^2\right]^{\frac{1}{2}}.$$

Thus, we find that the general, regular, non-trivial B_1 can be written

$$B_1 \sim \exp\left(\frac{ik_xk_y}{s}\right)\exp\left(-\frac{k_y^2}{2s}\right)H_n\left(\frac{k_y}{\sqrt{s}}\right) \times \times\delta(k_x-k'_x)\delta(k_z-k'_z).$$

The corresponding energy is:

$$\frac{E}{\hbar v} = \pm\left[\frac{\alpha^2}{2} + s(2n+1) \pm \left(\frac{\alpha^4}{4} + \alpha^2 s(2n+1) + s^2\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}.$$

$$n = 0, 1, \ldots \tag{1.5}$$

In order to determine whether or not we have missed any solutions, we have to go back to the original set of equations (1.2a, 1.2b, 1.2c, 1.2d). Making use of the fact that the various operators involved are the raising and lowering operators for oscillator functions, we find that the general solution is:

$$B_1 \sim H_n; \quad B_2 \sim H_{n-1}; \quad B_3 \sim H_n; \quad B_4 \sim H_{n+1}$$

(with the convention that $H_{-1} \equiv 0$).

The solution with $E = 0$ is:

$$B_1 \sim H_0; \quad B_2 = 0; \quad B_3 = 0; \quad B_4 \sim H_1.$$

It is, however, also possible to find another solution with energy zero, not included in the above set because in this case, $B_1 = 0$. The solution is:

$$B_1 = 0; \quad B_2 = 0; \quad B_3 = 0; \quad B_4 \sim H_0.$$

Let us now consider the limiting case of $\alpha = 0$. In this case, equation (1.5) becomes:

$$\frac{E}{\hbar v} = \pm(2ns)^{\frac{1}{2}} \tag{1.6a}$$

or:

$$\frac{E}{\hbar v} = \pm(2(n+1)s)^{\frac{1}{2}}. \tag{1.6b}$$

In addition to the $E = 0$ coming from $n = 0$ above, we have seen that there is also another $E = 0$ solution not included in the above relations.

We shall see that the degeneracy of each level (characterized by n and ± 1) is $2Vs/\pi c = qs/2$. Clearly, the energies arising from (1.6a) with $n \geqslant 1$ can be grouped with those from (1.6b) with $n \geqslant 0$. The result can then be written:

$$E = \pm \hbar v (2ns)^{1/2}. \tag{1.6c}$$

If the extra $E = 0$ level is included in (1.6c), the degeneracy of each level is just qs, in agreement with McClure's result.

We shall see later that we must choose a very small value of the interlayer exchange integral γ_1 if we wish to explain the experimentally observed susceptibility. The energy relation (1.5) is much too complicated for the calculation of the susceptibility, so that we want to expand equation (1.5) for small γ_1. Unfortunately, this cannot be done for an arbitrary s, since the condition for the validity of the expansion is:

$$\alpha^2 \ll s/(2n+1).$$

Our results will be meaningful only if we restrict ourselves to fields which satisfy this condition. We shall never be interested in high n values. Such an expansion can never be extrapolated to very small fields, but since susceptibility measurements usually involve a torsional technique, fields of several thousand gauss are generally employed. In this region, our expansion will be valid over the entire range of k_z.

The result for small γ_1 may be expressed in the following form:

$$E = \pm \hbar v (2ns)^{1/2} \left\{ 1 \pm \frac{\alpha^2}{4s} \right\}. \tag{1.7}$$

We have again grouped the levels, so that the degeneracy of each level (characterized by n and the external $\pm$ sign) is qs.

Note that the introduction of interplanar interaction has spread each level out into a narrow band of width $(\hbar v \alpha^2/2s)(2ns)^{1/2}$. Thus the levels become wider with increasing n values. The $n = 0$ level, however, has remained sharp. This result is independent of our approximation, and follows directly from equation (1.5). Note also, that the level width depends on the magnetic field and that all levels become sharp as the magnetic field becomes very large. This fact has an interesting consequence in the de Haas–Van Alphen effect. Eventually, for the higher n values, the levels will overlap each other. However, the levels near the degeneracy point are discrete. For example, in a field of 10^4 gauss with $\gamma_1 \simeq 0{\cdot}005$ eV, the levels do not overlap until one reaches an energy of $0{\cdot}07$ eV. This occurs between the $n = 5$ and $n = 6$ levels.

2. APPROXIMATE CALCULATION OF THE SUSCEPTIBILITY AT HIGH TEMPERATURES

Let us now estimate the susceptibility in a manner analogous to McClure's estimate in the two-dimensional case. We shall simply calculate the energy gain of our system as the magnetic field is turned on. For this purpose we need only the general features of our energy spectrum as predicted by equation (1.5). In particular we note that the $n = 0$ level is sharp and that the spacing between this level and the two $n = 1$ levels is larger than the spacing between any other two adjacent levels. Furthermore, it will be shown that at high temperatures the Fermi level is very near the $n = 0$ level. It follows that most of the energy gain of the system is due to the electrons, which in the presence of the field, occupy the $n = 0$ level.

When the field is applied, there is room for qs electrons in the $n = 0$ level. The number of electrons in the $n = 0$ level is then $qsf(0)$ and the total energy of these electrons is zero. Before the field was applied, these electrons had energies between $-\Delta$ and $+\Delta$, the negative energy states being preferentially occupied. The total energy of these electrons was thus:

$$E = \int_{-\Delta}^{+\Delta} N(E) f(E) E \, dE \tag{2.1}$$

where $N(E)$ is the density of states in the absence of a magnetic field and is given by:

$$N(E) = \frac{2V}{\pi^2 c (\hbar v)^2} \left[(4\gamma_1^2 - E^2)^{1/2} + \pi |E| + 2E \sin^{-1}\left(\frac{E}{2\gamma_1}\right) \right] \qquad E < 2\gamma_1 \tag{2.2a}$$

$$= \frac{4V}{\pi c (\hbar v)^2} |E|. \qquad E > 2\gamma_1 \tag{2.2b}$$

Furthermore, Δ is determined by the condition:

$$\int_{-\Delta}^{+\Delta} N(E)f(E)\,dE = qsf(0). \tag{2.3a}$$

At high temperatures, this condition simply becomes:

$$\int_{-\Delta}^{+\Delta} N(E)\,dE = qs. \tag{2.3b}$$

We now consider two separate cases. First, let us choose a high value for γ_1, say $\gamma_1 \simeq 0{\cdot}1$ eV. Since the integrations in equations (2.1) and (2.3b) extend over an energy range of the order of the magnetic level spacing, all energies involved in the integrands will then satisfy the condition $E/\gamma_1 \ll 1$. Hence the $N(E)$ in question is given by (2.2a). In fact, we only require this relation for small E and hence we may expand in powers of E/γ_1. We find:

$$N(E) \simeq \frac{4V\gamma_1}{\pi^2 c(\hbar v)^2} + \frac{2V}{\pi c(\hbar v)^2}\cdot|E|. \tag{2.4}$$

It is easily checked that under these circumstances

$$\Delta \simeq \frac{\pi(\hbar v)^2 s}{\gamma_1}. \tag{2.5}$$

and that the increase in energy contains no term proportional to s^2. This result has a simple physical interpretation. We note that in the three-dimensional case the density of states in the absence of a field does not approach zero when the energy approaches zero. Instead, it approaches a value proportional to γ_1. Hence there are already some electrons whose energies are zero before the field is applied. In fact, there are too many of them. The result is that the energy of the system cannot be raised much through the application of the field since Δ becomes very small and advantage cannot be taken of the preferential occupation of the lower energy states.

It is clear what one has to do in order to retain a susceptibility in the three-dimensional case. We need to reduce the number of electrons whose energies are zero before the field is applied; that is, we need to reduce γ_1. It is easily shown that if $\gamma_1 < \hbar v\sqrt{(\pi s/2)}$, the susceptibility is just equal to that predicted by McClure for the two-dimensional case.

This simple argument does not depend on the detailed structure of the energy spectrum and is independent of any approximations. We are thus led to the conclusion that graphite is essentially two-dimensional in structure. We shall see that $\gamma_1 \simeq 0{\cdot}005$ eV is consistent with all the observed properties of graphite. An upper limit for $\gamma_1 \simeq 0{\cdot}01$ eV can be established in this way. This value is about twenty times smaller than that used in A. A theoretical estimate of γ_1 was made by Godin.(24) His value for γ_1 is $0{\cdot}007$ eV, but no other estimate of this order of magnitude seems to have appeared in the literature.

3. CALCULATION OF THE FREE ENERGY

In order to calculate the free energy of our system, we need to obtain the density of states in the presence of a magnetic field. We shall write:

$$g(E) = \sum_n g(E_n) \tag{3.1}$$

where $g(E_n)$ is the density of states in the nth level and the sum extends over all levels which contribute at the energy E. For a general n, $g(E_n)$ is simply:

$$g(E_n) = \frac{8Vs}{4\pi^2}\cdot\frac{dk_z}{dE_n}. \tag{3.2}$$

The factor of 8 accounts for the various degeneracies in graphite: spin degeneracy (a factor of 2) and site degeneracy (a factor of 4). The total number of states for each value of n and choice of sign is just:

$$\frac{8Vs}{4\pi^2}\times\frac{2\pi}{c} = \frac{4Vs}{\pi c} = qs. \tag{3.3}$$

For the $n = 0$ level, which we have seen is always sharp, (3.2) is replaced simply by a δ-function. This level also contains qs states, exactly as in the two-dimensional case.

The above arguments are completely analogous to those made in the counting of states in the free electron case. This is a direct consequence of the form of our solutions $B_m(k)$. We note that k_x and k_z enter these solutions only parametrically. Thus the $\delta(k_x-k_x')$ and $\delta(k_z-k_z')$ factors lead to $e^{ik_x'x}$ and $e^{ik_z'z}$ in the spatial wave functions. Furthermore, the complex factor $e^{ik_xk_y/s}$ centres the spatial wave function at $y = k_x'/s$. Thus we can apply cyclic boundary conditions in the x and z directions. Limiting y to lie within the crystal then limits k_x and hence equation (3.2) follows.

We shall now take for E_n:

$$E_n = \nu(ns)^{\frac{1}{2}}\left[1 \pm \frac{2\gamma_1^2 \cos^2(k_z c)/2}{\nu^2 s}\right]. \qquad (3.4)$$

(cf. eqn. (1.7)

Evaluating dk_z/dE_n, it becomes convenient to introduce three new symbols. Let:

Minimum energy of nth level

$$= A_n = \nu(ns)^{\frac{1}{2}}[1-(2\gamma_1^2/\nu^2 s)]$$

Average energy of nth level

$$= C_n = \nu(ns)^{\frac{1}{2}}$$

Maximum energy of nth level

$$= B_n = \nu(ns)^{\frac{1}{2}}[1+(2\gamma_1^2/\nu^2 s)].$$

The resulting $g(E_n)$ may then be written:

$$g(E_n) = \frac{qs}{2\pi}[(E-A_n)(C_n-E)]^{-\frac{1}{2}} \qquad A_n \leqslant E \leqslant C_n \qquad (3.5a)$$

$$= \frac{qs}{2\pi}[(B_n-E)(E-C_n)]^{\frac{1}{2}} \qquad C_n \leqslant E \leqslant B_n. \qquad (3.5b)$$

We are now ready to evaluate the free energy. Following McClure, we write:

$$F = N\zeta + E_0 + \int_{-\infty}^{+\infty} dE\phi(E)\left[\frac{-\partial f}{\partial E}\right] \qquad (3.6)$$

where:

$$N = N_{\text{total}} - \int_{E(0)}^{0} dx g(x) \qquad (3.7)$$

$$E_0 = \int_{E(0)}^{0} dx \, . \, xg(x) \qquad (3.8)$$

$$\phi(E) = \int_{0}^{E} dx(x-E)g(x). \qquad (3.9)$$

Here $E(0)$ is the energy of the lowest state in the valence band and it is assumed that $\zeta - E(0) \gg kT$. We shall be primarily interested in $\phi(E)$ for $E \leqslant \zeta_0 \sim 0{\cdot}06$ eV. Since (3.4) involves the assumption that $2\gamma_1^2/\nu^2 s < 1$ it is easy to see that the magnetic energy levels corresponding to the first few n values do not overlap at all. Thus for $E < \zeta_0$ the integration in (3.9) never involves a sum over various n. Carrying out the integrals in $\phi(E)$, we find:

$$\phi(E) = qs\{-(m+\tfrac{1}{2})E + {} + \tfrac{1}{4}\sum_{n=1}^{m}(A_n+B_n+2C_n)+\delta\}$$

$$= qs\{-(m+\tfrac{1}{2})E + \tfrac{1}{4}\sum_{n=1}^{m} 4C_n + \delta\}$$

$$= qs\{-(m+\tfrac{1}{2})E + \sum_{n=1}^{m} \nu(ns)^{\frac{1}{2}} + \delta\} \qquad (3.10)$$

where: $m = \langle r^2 \rangle =$ maximum integer $\leqslant r^2 = E^2/\nu^2 s$. The term δ indicates the departure from the two-dimensional model. In general this term involves fractional contributions from several levels, but as long as the levels do not overlap ($E \lesssim 0{\cdot}07$ eV in fields $\gtrsim$ 10,000 gauss) δ will involve at most a fractional contribution from one level. In this case:

$$\delta = \frac{-1}{2\pi}\left\{[(B_m-E)(E-C_m)]^{\frac{1}{2}} + \frac{B_m+C_m-2E}{2}\left[\frac{\pi}{2}+\sin^{-1}\left(\frac{B_m+C_m-2E}{B_m-C_m}\right)\right]\right\} \qquad C_m \leqslant E \leqslant B_m \quad (3.11a)$$

$$= 0 \qquad B_m \leqslant E \leqslant A_{m+1} \quad (3.11b)$$

$$= \frac{-1}{2\pi}\left\{[(C_{m+1}-E)(E-A_{m+1})]^{\frac{1}{2}} + \frac{A_{m+1}+C_{m+1}-2E}{2}\left[\frac{\pi}{2}+\sin^{-1}\left(\frac{A_{m+1}+C_{m+1}-2E}{A_{m+1}-C_{m+1}}\right)\right]\right\}. \qquad A_{m+1} \leqslant E \leqslant C_{m+1} \quad (3.11c)$$

Our expression (3.10) is in agreement with McClure's result when $\delta = 0$. We shall see that δ is an unimportant correction for the high temperature susceptibility and for the average low temperature susceptibility. However, this term does play a role in the fluctuations of the susceptibility at low temperatures, where it serves to reduce the amplitudes of the oscillations and introduces an aperiodicity when plotted against the reciprocal of the magnetic field.

4. THE SHIFT OF THE FERMI LEVEL WITH TEMPERATURE

Before we go on to calculate the susceptibility at various temperatures, we will need to know the position of the Fermi surface at these temperatures. We shall now calculate this shift with temperature on the basis of a two-dimensional model. The error made in such a calculation is very small, since it is caused solely by the use of an approximate $N(E)$ relation in the region $0 \leqslant E \leqslant 2\gamma_1$. In general, we can have confidence in our result provided $\zeta(T) > 2\gamma_1$. As we shall see, this condition is satisfied up to a temperature of about 800°K.

The total number of electrons is given by:

$$N_0 = \int_{-\infty}^{+\infty} N(E) f(E)\, dE = \int_{-\infty}^{\zeta_0} N(E)\, dE \quad (4.1)$$

where

$$N(E) = \frac{4V|E|}{\pi c(\hbar v)^2}.$$

With the above density of states equation (4.1) can be re-written:

$$\int_{-\infty}^{0} E[1-f(E)]\, dE + \int_{0}^{\infty} Ef(E)\, dE = \frac{\zeta_0^2}{2}.$$

Writing $\theta = \frac{\zeta}{kT}$; $\theta_0 = \frac{\zeta_0}{kT}$, one finds:

$$\theta_0^2 = 2\theta \log\left[\frac{1+e^{\theta}}{1+e^{-\theta}}\right] - 3\theta^2 + 4\int_0^{\theta} \log(1+e^x)\, dx. \quad (4.2)$$

This expression can be approximated for large and small θ.

$$\theta_0^2 \simeq \theta \log 16 \qquad \theta \ll 1 \quad (4.2a)$$

$$\theta_0^2 \simeq \theta^2 + \frac{\pi^2}{3}. \qquad \theta \gg 1 \quad (4.2b)$$

Choosing a value for ζ_0, one can plot ζ as a function of temperature using equation (4.2). This is done by giving θ a value and solving the equation for θ_0. If ζ_0 is assumed known, one thus finds ζ and T.

The results are plotted in Fig. 1 for two values of ζ_0. The shift of the Fermi level plays in our model an important role in the susceptibility of graphite. Without this variation with temperature one could not reconcile the high and the low temperature results.

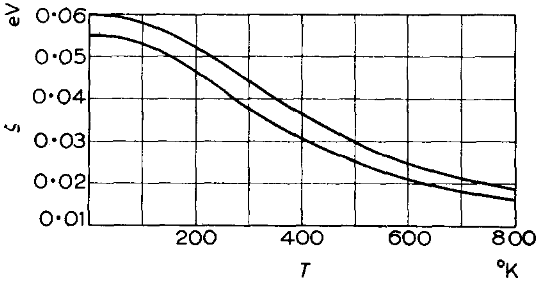

FIG. 1. The variation of the fermi level with temperature. The upper and lower curve corresponds to $\zeta_0 = 0{\cdot}06$ eV and $\zeta_0 = 0{\cdot}055$ eV respectively.

5. CALCULATION OF THE SUSCEPTIBILITY AND THE DE HAAS–VAN ALPHEN EFFECT

The magnetic moment and the susceptibility are defined in terms of the free energy by the following relations:

$$M = -\frac{\partial F}{\partial H} \quad (5.1)$$

$$\chi = -\frac{1}{H}\frac{\partial F}{\partial H} = \frac{M}{H}. \quad (5.2)$$

Our calculation of these quantities will thus be based on equation (3.6) and the additional relation (3.10). The correction term δ, which is a measure of the departure from the two-dimensional model is given by (3.11). However, this relation is far too complicated to be treated exactly.

At high temperatures this term need not be considered at all, since it does not contribute appreciably to the susceptibility. This can be seen as follows: At high temperatures the Fermi level is very near the $n = 0$ level (see Fig. 1). In this region the energy levels are very nearly sharp and the spacing between these levels is large. It follows that the correction term δ is primarily defined by (3.11b) and can be ignored completely. Thus at high temperatures the susceptibility is just equal to that calculated by McClure and is given by:

$$\chi = -0{\cdot}044qv^2\left(\frac{e}{\hbar c}\right)^2\frac{1}{kT}\cdot\text{sech}^2\left(\frac{\zeta}{2kT}\right). \quad (5.3)$$

Converted to e.m.u./g, (5.3) becomes ($\gamma_0 = 2.6$ eV):

$$\chi = \frac{-0{\cdot}010}{T}\,\text{sech}^2\left(\frac{\zeta}{2kT}\right)\text{ e.m.u./g.} \quad (5.4)$$

The condition of the validity of this result is that the level splitting be small compared to the thermal energy, that is $kT > vs^{\frac{1}{2}}$. In a field of 10,000 gauss $vs^{\frac{1}{2}} \simeq 0{\cdot}03$ eV so that the relation (5.4) is valid at temperatures higher than about 400°K. McClure did not consider the variation of the Fermi level with temperature and simply replaced the $\text{sech}^2(\zeta/2kT)$ factor by 1. Using the results of Section 4, we can now obtain the deviation of the high temperature susceptibility from a $1/T$ law. The results, together with the experimental curve are illustrated in Fig. 2.

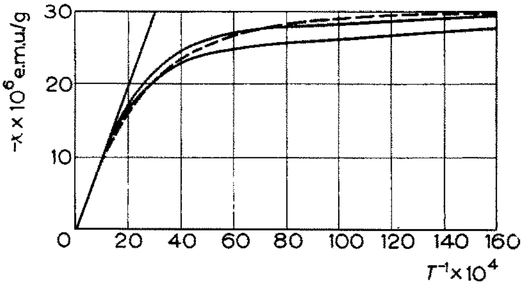

Fig. 2. The variation of the susceptibility with temperature. The dashed curve is taken from Ganguli and Krishnan. The two solid curves represent the theoretical variation of the susceptibility corresponding to $\zeta_0 = 0{\cdot}06$ eV and $\zeta_0 = 0{\cdot}055$ eV. The latter value results in slightly better agreement with experiment.

The dependence of the high temperature susceptibility on the Fermi level has been investigated by bromination of graphite.(15) These investigations show that as the bromine to carbon ratio is increased, the susceptibility first increases slightly and then decreases. This trend is in agreement with equation (5.4). The Br/C ratio which results in the maximum susceptibility is determined by the number of excess electrons originally in the conduction band. The number of these electrons implied by our model agrees well with the value of $1{\cdot}1 \times 10^{-4}$ per atom, estimated from the above experiment.(15)

At low temperatures there is no *a priori* reason why one can neglect the correction term δ. It will, however, be seen that even at low temperatures the average value of the susceptibility is not affected by this term. On the other hand, the fluctuations of the susceptibility are affected. Let us for the present deal with the two-dimensional model and consider the correction later. We thus choose for $\phi(E)$:

$$\phi(E) = qs\{\sum_{n=0}^{m} v(ns)^{\frac{1}{2}} - (m+\tfrac{1}{2})E\}. \quad (5.5)$$

Here m is the maximum integer $\leqslant E^2/v^2s$. The notation

$$\frac{E^2}{v^2s} = r^2 \qquad m = \langle r^2 \rangle$$

will be convenient. We shall now evaluate the sum involved in (5.5) by the Poisson summation formula.(25)

One form of this formula is:

$$\sum_{n=0}^{\infty} f(n) = \sum_{m=-\infty}^{+\infty} \int_0^{\infty} f(x)e^{2\pi imx}\,dx$$

where: (1) $f(x)$ is of bounded variation in the interval $(0, \infty)$ and $f(x) = 0 \qquad x < 0$

$$(2)\int_0^{\infty} f(x)\,dx \text{ exists}$$

(3) $f(x)$ is continuous at least near the points where x is an integer,
i.e.

$$\tfrac{1}{2}[f(n_+)+f(n_-)] = f(n).$$

We see how we have to define $f(x)$ in our case. Let us introduce the stepfunction $P(x)$ defined by:

$$P(x) = 1 \qquad x \leqslant 0$$

$$P(x) = 0 \qquad x > 0.$$

Then we may define $f(x)$ to be:

$$f(x) = x^{\frac{1}{2}}P(-x)P(x-r^2). \tag{5.6}$$

With this definition, one clearly has:

$$\sum_{n=0}^{m} n^{\frac{1}{2}} = \sum_{n=0}^{\infty} f(n). \tag{5.7}$$

Just exactly where we "chop" the function between $\langle r^2 \rangle$ and $\langle r^2 \rangle + 1$ is immaterial. By choosing the point to be r^2 we know that our result is exact provided r^2 is not an integer. In that case the continuity condition is not satisfied, but this clearly does not matter since these points coincide with the points of discontinuity of our original sum.

In this way we find:

$$\sum_{n=0}^{m} n^{\frac{1}{2}} = \sum_{m=-\infty}^{+\infty} \int_0^{r^2} x^{\frac{1}{2}} e^{2\pi imx}\, dx$$

$$= \tfrac{2}{3}r^3 + r\sum_{m=1}^{\infty} \frac{\sin(2\pi mr^2)}{\pi m} -$$

$$\frac{1}{2\pi}\sum_{m=1}^{\infty} m^{-3/2} S(2rm^{\frac{1}{2}}) \tag{5.8}$$

where:

$$S(\varphi) = \int_0^{\phi} \sin\left(\frac{\pi}{2}t^2\right) dt.$$

We can now substitute (5.8) into (5.5). The result is:

$$\phi(E) = q\nu s^{3/2}\left\{-\tfrac{1}{3}r^3 - \frac{1}{2\pi}\sum_{m=1}^{\infty} m^{-3/2} S(2rm^{\frac{1}{2}})\right\}. \tag{5.9}$$

We have made use of the relation

$$\sum_{m=1}^{\infty} \frac{\sin(2\pi mr^2)}{\pi m} = \langle r^2 \rangle + \tfrac{1}{2} - r^2;$$

$$\langle r^2 \rangle < r^2 < \langle r^2 \rangle + 1.$$

Equation (5.9) is exact. For large energies $r \to \infty$, and

$$S(2rm^{\frac{1}{2}}) \to S(\infty) = \tfrac{1}{2}.$$

Thus in the limit of large energies, (5.9) becomes:

$$\begin{aligned}\phi(E) &\simeq q\nu s^{3/2}\left[-\frac{1}{3}r^3 - \frac{1}{4\pi}\zeta\left(\frac{3}{2}\right)\right] \\ &\simeq q\nu s^{3/2}\left[-\frac{1}{3}r^3 - 0{\cdot}208\right].\end{aligned} \tag{5.10}$$

Here ζ is the Riemann Zeta-function.

The above result agrees with McClure's equation (3.9). We note that of these two terms, the first is independent of the magnetic field and the second is independent of the energy. Hence the first term does not contribute to the susceptibility. One can easily verify that the term independent of the energy just cancels the part of E_0 which depends upon the magnetic field when integrated in (3.6). Again following McClure, we write

$$\psi(E) = \phi(E) + \tfrac{1}{3}q\frac{E^3}{\nu^2} + 0{\cdot}208 q\nu s^{3/2}. \tag{5.11}$$

Neglecting the field dependence of ζ, the susceptibility is then given by:

$$\chi = -\frac{1}{H}\frac{\partial F}{\partial H} = -\frac{1}{H}\frac{\partial}{\partial H}(F - N\zeta)$$

$$= -\frac{1}{H}\frac{\partial}{\partial H}\int_{-\infty}^{+\infty} dE\psi(E)\left[-\frac{\partial f}{\partial E}\right]. \tag{5.12}$$

Since we are interested only in very low temperatures for the present, (5.12) simply becomes:

$$\chi = -\frac{1}{H}\frac{\partial}{\partial H}\psi(\zeta_0). \tag{5.13}$$

Here $\psi(E)$ is given by equation (5.11). We now anticipate where the Fermi surface will be at low temperatures. Thus our Hall effect results will show that $\zeta_0 \simeq 0{\cdot}06$ eV. Another estimate can be obtained from the period of the de Haas–Van Alphen effect fluctuations (cf. McClure). Thus in fields of the order of 10,000 gauss $r \sim 2$. We shall now expand $\psi(E)$ asymptotically for large r. This asymptotic form of $\psi(E)$ will be completely adequate at $E = \zeta_0$. Thus

$$S(2rm^{\frac{1}{2}}) = \int_0^{2rm^{\frac{1}{2}}} \sin\left(\frac{\pi}{2}z^2\right) dz$$

$$= \frac{1}{2} - \int_{2rm^{\frac{1}{2}}}^{\infty} \sin\left(\frac{\pi}{2}z^2\right) dz$$

$$\simeq \frac{1}{2} - \frac{1}{2\pi}\frac{\cos(2\pi mr^2)}{(2\pi mr^2)^{\frac{1}{2}}}.$$

When this result is substituted into (5.11) one finds:

$$\psi(E) \simeq qvs^{3/2}\left[\frac{1}{4\pi^2 r}\sum_{n=1}^{\infty}\frac{\cos(2\pi mr^2)}{m^2}\right]. \tag{5.14}$$

It may be verified that $\psi(E)$ as given by (5.14) differs from the exact $\psi(E)$ defined by (5.11) and (5.5) by less than 1 per cent when $r \gtrsim 1/2$. Hence we are completely justified in using (5.14) at low temperatures even in large magnetic fields.

The magnetic moment and the susceptibility are now easily evaluated at low temperatures. Making use of the relation

$$\sum_{m=1}^{\infty}\frac{\cos(2\pi mr^2)}{\pi^2 m^2}$$

$$= \tfrac{1}{6}+[r^2-\langle r^2\rangle]\cdot[r^2-\langle r^2\rangle-1]$$

$$\langle r^2\rangle < r^2 < \langle r^2\rangle+1.$$

we find:

$$M = -\frac{q\zeta_0}{12}\left(\frac{e}{\hbar c}\right)r_0^{-2}-\frac{q\zeta_0}{2}\left(\frac{e}{\hbar c}\right)\times$$

$$\times\left\{\frac{\langle r_0^2\rangle}{r_0^2}\left[1+\langle r_0^2\rangle\right]-\langle r_0^2\rangle-\tfrac{1}{2}\right\}. \tag{5.15}$$

The first factor in this relation is proportional to the magnetic field and yields the average value of the magnetic moment. The second factor, when plotted against the magnetic field, oscillates about zero. The oscillatory part of the magnetic moment is plotted against $r_0^{-2} = v^2 s/\zeta_0^2$ in Fig. 3. The observed behaviour is characteristic of a two-dimensional model and should be compared with the results of SEITZ[(26)] for free electrons. The susceptibility resulting from (5.15) is thus:

$$\chi = -\frac{qv^2}{12\zeta_0}\left(\frac{e}{\hbar c}\right)^2-\frac{qv^2}{2\zeta_0}\left(\frac{e}{\hbar c}\right)^2\times$$

$$\{\langle r_0^2\rangle[1+\langle r_0^2\rangle]-r_0^2[\tfrac{1}{2}+\langle r_0^2\rangle]\}. \tag{5.16}$$

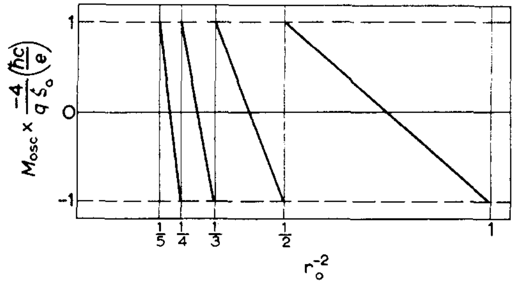

FIG. 3. Plot of the oscillatory part of the magnetic moment as a function of the magnetic field. The curve is based on a two-dimensional model.

The first factor in (5.16) is independent of the magnetic field and yields the average value of the low temperature susceptibility. The second factor is "periodic" in $1/H$ with period $(e/\hbar c)\,.\,(v^2/\zeta_0^2)$. A plot of the oscillatory part of (5.16) is given in Fig 4. Converting these quantities to e.m.u./g, we find:

$$\chi_{\text{av}} = -\frac{qv^2}{12\zeta_0}\left(\frac{e}{\hbar c}\right)^2$$

$$\simeq -27{\cdot}2\times 10^{-6}\ \text{e.m.u./g}. \tag{5.17}$$

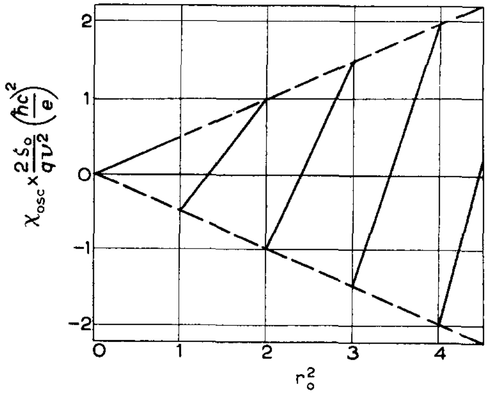

FIG. 4. The De Haas–Van Alphen effect in two-dimensional graphite.

We have chosen $\zeta_0 = 0{\cdot}06$ eV. χ_{av} would approach zero as suggested by McClure in the limit $r_0 \to \infty$; i.e. $\zeta_0 \to \infty$.

In order that the period of our oscillations agree with the average experimental period of $2{\cdot}15 \times 10^{-5}$ gauss^{-1}, we require $\zeta_0 \simeq 0{\cdot}065$ eV. On the other hand the theoretical amplitude of the oscillations is approximately 300×10^{-6} e.m.u./g in a field of 10^4 gauss. The experimentally observed amplitude is only $2\text{–}3 \times 10^{-6}$ e.m.u./g. (9,10) This discrepancy between theory and experiment will be discussed later.

The average value of the low temperature susceptibility is in good agreement with the reported experimental values, which range from -28×10^{-6} e.m.u./g to -34×10^{-6} e.m.u./g.(1,9,10)

Lifshitz and Kosevich(12) have developed a semi-classical theory of susceptibility. If their results are applied to two-dimensional graphite, one finds a period for the susceptibility fluctuations which is in agreement with our result. The oscillation amplitudes, however, are infinite in their approximation. We shall return to their results when we consider the introduction of the third dimension.

Before we go on to consider these three-dimensional effects, we shall calculate the temperature variation of the average susceptibility at low temperatures. We have already seen that at high temperatures the susceptibility is given by (5.4). In calculating the temperature dependence of the susceptibility at low temperatures we shall not be interested in the oscillatory part of the susceptibility. Hence we retain only that part of $\psi(E)$ which gives rise to the part of the magnetic moment which is proportional to H. In this case $\psi(E)$ simply becomes

$$\psi(E) = \frac{1}{24}\frac{qv^2s^2}{E}. \tag{5.18}$$

Actually $\psi(E)$ is a symmetric function of E, so that E should be replaced by $|E|$. (cf. McClure). However at low temperatures the contributions to χ from the $E < 0$ region are completely negligible because of the position of the Fermi level. Using (5.18), the expression (5.12) for the susceptibility becomes:

$$\chi \simeq -\frac{1}{48}\frac{qv^2}{kT}\left(\frac{e}{\hbar c}\right)^2 \int \frac{dE}{E}\operatorname{sech}^2\left(\frac{\zeta - E}{2kT}\right) \tag{5.19}$$

where the integral is taken over a range of the order of $3kT$ about $E = \zeta$.

Upon evaluation this yields:

$$\chi \simeq -\frac{1}{12}qv^2\left(\frac{e}{\hbar c}\right)^2 \frac{1}{\zeta}\left[1 - \frac{kT}{\zeta}\log 2\right]. \tag{5.20}$$

Or, converting to e.m.u./g,

$$\chi \simeq -\frac{1{\cdot}63}{\zeta} \times 10^{-6}\left[1 - \frac{kT}{\zeta}\log 2\right]\text{e.m.u./g} \tag{5.21}$$

where ζ, kT are measured in eV. The result, together with the variation at high temperatures, is plotted in Fig. 2. Expressions (5.20) and (5.21) are valid provided $kT < \zeta$. In Fig. 2, these expressions have been used between $T = 0$°K and $T = 200$°K.

We have seen that a two-dimensional model of graphite explains all the features of the susceptibility except the amplitude of the oscillations at low temperatures, which turn out to be 100–150 times too large. There are three main factors which serve to reduce this amplitude. These are:

(1) Introduction of k_z-dependence by a three-dimensional model. This clearly has the effect of broadening the energy levels in the presence of a magnetic field and hence reduces the amplitudes of the susceptibility fluctuations.

(2) Temperature damping of the oscillations at temperatures for which the thermal energy becomes greater than the level spacing.

(3) Collision damping of the levels. The effect of collisions is also to broaden the energy levels by an amount $\sim \hbar/\tau$ where τ is the relaxation time for electrons whose energies are near the Fermi energy.

The last two of these factors are unimportant at very low temperatures. We shall see later that the relaxation time in graphite at such temperatures is of the order of 10^{-11} seconds. If one uses this value for τ, and estimates the collision damping factor in the manner of Dingle,(27) one finds that the amplitudes are only reduced by about 5 per cent by the collision process. Similarly, temperature damping can be made arbitrarily unimportant by going to sufficiently low temperatures. We will now study the three-dimensional model in order to attempt an explanation of this discrepancy.

The experiments on graphite show that the low temperature susceptibility does not display a strict periodicity in $1/H$.(9,10) The pattern may be approximately resolved into two different periodicities, one with about 3/4 the period of the other. The period of $2{\cdot}15\times 10^{-5}$ gauss^{-1} which was used in the two-dimensional model, is then interpreted as an average period.

It is interesting to apply the theory of ONSAGER(28) and of LIFSHITZ and KOSEVICH(12) to graphite. As we shall see, their theory, together with the usually assumed band structure, affords a very nice picture for the origin of the two periodicities found in graphite. Unfortunately, since this approach is based on Bohr–Sommerfeld quantization, one cannot have faith in the results when the theory is applied to graphite. We shall find important differences between such a semi-classical treatment and a treatment based on the results of Section 1 of this paper. Let us first outline the semi-classical approach.

The $E(\boldsymbol{k})$ relation near a corner of the Brillouin zone is given in A as:

$$E(\boldsymbol{k}) = -\gamma_1 \cos\left(\frac{k_z c}{2}\right) \pm \left[\gamma_1^2 \cos^2\left(\frac{k_z c}{2}\right) + (\hbar v K)^2\right]^{\frac{1}{2}}. \qquad (5.22)$$

As before, $K = (k_x^2 + k_y^2)^{\frac{1}{2}}$ is measured from the corner of the zone, while k_z is measured from the half-way point on the vertical edge. The constant energy surfaces described by (5.22) are illustrated in Fig. 5. When $E < 2\gamma_1$ the surfaces are closed and capsule-shaped with the long axis parallel to the vertical edge of the zone. However, for $E > 2\gamma_1$ the surfaces become endless tubes of variable cross-section.

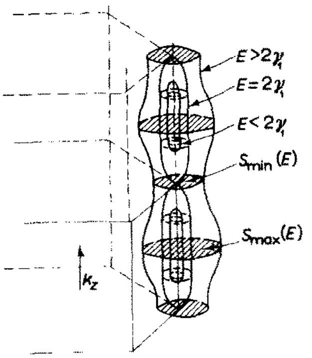

FIG. 5. The nature of the energy surfaces in graphite. Two Brillouin zones are shown. Actually 1/3 of the surfaces shown lies at each corner of the zone, resulting in a two-fold degeneracy of the illustrated surfaces, which have been pieced together for clarity.

Now consider a magnetic field to be applied along the c-axis in graphite. In the theory of LIFSHITZ and KOSEVICH(12) the periods of the susceptibility oscillations are then determined by the extreme cross-sectional areas of the planes k_z = constant with the surface of constant energy for $E = \zeta$. It is clear that two different periods can only result if $\zeta > 2\gamma_1$, since otherwise the minimum cross-sectional area is zero and gives no periodicity. Applying (5.22) to the theory of LIFSHITZ and KOSEVICH we find:

$$S(E, k_z) = \frac{\pi E[E + 2\gamma_1 \cos(k_z c/2)]}{(\hbar v)^2} = 2\pi(n+\gamma)s.$$

$$E \geqslant 2\gamma_1 \qquad (5.23)$$

The maximum and minimum areas in question are thus:

$$S_{\text{ext}}(\zeta) = \frac{\pi\zeta[\zeta \pm 2\gamma_1]}{(\hbar v)^2}.$$

$$\zeta \geq 2\gamma_1 \qquad (5.24)$$

It is interesting to note what (5.23) predicts for the energy spectrum in the presence of a magnetic field. Solving for $E(n,H,k_z)$ we find:

$$E(n, H, k_z) = -\gamma_1 \cos\left(\frac{k_z c}{2}\right) \pm \left[\gamma_1^2 \cos^2\left(\frac{k_z c}{2}\right) + v^2 s(n+\gamma)\right]^{\frac{1}{2}}. \qquad (5.25)$$

When $\gamma_1 = 0$ this relation gives the two-dimensional spectrum provided the parameter γ is chosen to be zero. However, if $\gamma_1 \neq 0$, this energy spectrum is radically different from that found in Section 1. When γ_1 is small, (5.25) predicts a width of $\sim 2\gamma_1$ for the higher n levels, independently of the magnetic field, while in our treatment the level width increases with n and depends on the magnetic field. We shall see later how this difference affects the de Haas–Van Alphen effect.

Since in the semi-classical treatment the periods of the low temperature susceptibility oscillations are completely determined by $S_{\text{ext}}(\zeta)$ a knowledge of the two periods completely determines ζ_0 and γ_1. In this way we find:

$$\zeta_0 \simeq 0{\cdot}065 \text{ eV}. \qquad \frac{\zeta_0}{\gamma_1} \simeq 14.$$

The amplitudes of the oscillations may also be determined by an application of the formulae of LIFSHITZ and KOSEVICH. At $T = 1{\cdot}37°\text{K}$ an evaluation yields approximately 20×10^{-6} e.m.u./g for the amplitudes in a field of 10,000 gauss. This is a factor of about 10 larger than the observed amplitude.(9,10)

An exact calculation of the three-dimensional de Haas–Van Alphen effect is impractical because of the complex nature of the correction term δ in equation (3.10). We can however construct a simplified model by noting how the density of states varies within the nth level. We shall replace $g(E_n)$ defined by (3.5a) and (3.5b) by:

$$g(E_n) = qs[\tfrac{1}{4}\delta(E-A_n)+\tfrac{1}{4}\delta(E-B_n)+ \\ +\tfrac{1}{2}\delta(E-C_n)]. \tag{5.26}$$

It is easily checked that this expression gives the correct degeneracy for the nth level, namely qs.

If (5.26) is used instead of (3.5a) and (3.5b), the correction term δ can be shown to be:

$$\delta = \frac{qs}{4}\Big[(2m-m'-m'')+ \\ + \sum_{m}^{m'} A_n + \sum_{m''}^{m} B_n\Big] \tag{5.27}$$

where:

$$m = \langle r^2 \rangle$$
$$m' = \langle r^2(1-\Delta)^{-2} \rangle \qquad \Delta = \frac{2\gamma_1^2}{\nu^2 s}$$
$$m'' = \langle r^2(1+\Delta)^{-2} \rangle.$$

It is a straightforward matter tó calculate the contribution of (5.27) to the low temperature susceptibility. The calculation is analogous to the two-dimensional model calculation carried out earlier. In calculating the derivative with respect to H, it is not necessary to differentiate the various $(1 \pm \Delta)$ factors, since these vary very slowly with H. The result is that to the oscillatory part of χ in (5.16) one must add the following term:

$$-\frac{q\nu^2}{8\zeta_0}\left(\frac{e}{\hbar c}\right)^2 \left\{ r_0^2\left[2\langle r_0^2\rangle - \left\langle\frac{r_0^2}{(1+\Delta)^2}\right\rangle - \left\langle\frac{r_0^2}{(1-\Delta)^2}\right\rangle\right] - 2\langle r_0^2\rangle^2 + (1+\Delta)^2\left\langle\frac{r_0^2}{(1+\Delta)^2}\right\rangle^2 + \right. \\ \left. +(1-\Delta)^2\left\langle\frac{r_0^2}{(1-\Delta)^2}\right\rangle^2 - 2\langle r_0^2\rangle + (1+\Delta)^2\left\langle\frac{r_0^2}{(1+\Delta)^2}\right\rangle + (1-\Delta)^2\left\langle\frac{r_0^2}{(1-\Delta)^2}\right\rangle \right\}. \tag{5.28}$$

Fig. 6 shows the de Haas–Van Alphen effect as calculated from this simplified three-dimensional model. In plotting the result Δ has been chosen to be $0{\cdot}014 r_0^2$, which corresponds to $\gamma_1 \simeq 0{\cdot}005$ eV and $\zeta_0 \simeq 0{\cdot}06$ eV. It can be seen that the simple periodicity in $1/H$ has been destroyed. Semi-classically this pattern was interpreted in terms of two slightly different periods, both however, strictly periodic in $1/H$. The amplitudes of the oscillations have been reduced by a factor of two or so at 10,000 gauss. They are however still far too large to be in agreement with experiment.

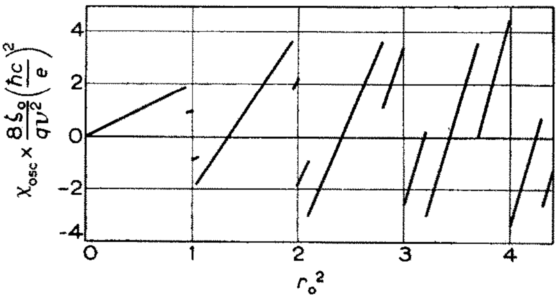

FIG. 6. The De Haas–Van Alphen effect in three-dimensional graphite.

Perhaps the most significant feature of the three-dimensional calculation is the behaviour in very large magnetic fields ($r_0^2 < 1$). Our calculation indicates that in these fields graphite will not display what looks like two periods. Instead, the oscillations will be strictly periodic in $1/H$, the period being just that predicted by the two-dimensional model. The semi-classical treatment on the other hand, predicts two periods regardless of the magnetic field. This result is independent of our simplifying assumptions and follows directly from the fact that the energy levels become sharp in very large magnetic fields (cf. equation 1.7).

It seems possible that this difference could be investigated experimentally by the recently developed pulsed field technique. A careful analysis of the oscillations may be required, since the difference between these two predictions is not apparent on every half-cycle.

6. THE ELECTRICAL CONDUCTIVITIES OF GRAPHITE

Let us now evaluate the electrical conductivities of graphite parallel and perpendicular to the graphite planes. We shall assume that τ does not depend significantly on $\boldsymbol{k}$.

Following A, we have for the conductivity in the direction of the unit vector $\boldsymbol{u}$:

$$\sigma(\boldsymbol{u}) = -\frac{2e^2\tau}{h^2}\int\frac{df_0}{dE}\left[\int_{E=\text{const.}}(\boldsymbol{u}\,.\,\boldsymbol{n})^2|\text{grad}_k E|\,dS_k\right]dE \tag{6.1}$$

where the inner integral is taken over a surface of constant energy, and $n\,dS_k$ is the vector element of area on this surface.

For our $E(\boldsymbol{k})$ relation, we shall use equation (5.22), which is valid provided $E \ll \gamma_0 \simeq 2{\cdot}6$ eV.

The integral in (6.1) is easily transformed into an integral over K and an integral over E, by projecting the surface of constant energy onto the plane $k_z = 0$. A factor of 4 is introduced because of the equivalence of the six corners of the Brillouin zone, and because of the two projections onto the plane $k_z = 0$ coming from above and below this plane.

When u is chosen in the graphite plane and perpendicular to it, we find respectively:

$$\sigma_{\text{n}} = -\frac{e^2\tau}{2\pi h^2}\int\frac{df_0}{dE}\left[\int\frac{(\partial E/dK)^2}{(\partial E/\partial k_z)}\,.\,8\pi K\,dK\right]dE \tag{6.2}$$

$$\sigma_{\perp} = -\frac{2e^2\tau}{2\pi h^2}\int\frac{df_0}{dE}\left[\int\left(\frac{\partial E}{\partial k_z}\right)8\pi K\,dK\right]dE. \tag{6.3}$$

Let us now look at the range of the inner integral. As long as we are dealing with low temperatures, df_0/dE will be a sharply peaked function at $E = \zeta$, which is much greater than $2\gamma_1$. From (5.22), it follows that the constant energy surfaces for $E > 2\gamma_1$ are open endless tubes of variable cross-section. Hence, the range of K is:

$$\frac{1}{\hbar v}\cdot(E^2-2\gamma_1 E)^{\frac{1}{2}} \leqslant K \leqslant \frac{1}{\hbar v}\cdot(E^2+2\gamma_1 E)^{\frac{1}{2}}.$$

However, for higher temperatures df_0/dE is not sufficiently peaked to exclude the contributions to the conductivity from $E < 2\gamma_1$. We then write:

$$\frac{-2\pi h^2\sigma_{\text{n}}}{e^2\tau} = \int_{-\infty}^{-2\gamma_1} f_0'C_1(E)\,dE + \int_{-2\gamma_1}^{0} f_0'C_2(E)\,dE + \int_{0}^{2\gamma_1} f_0'C_3(E)\,dE + \int_{2\gamma_1}^{\infty} f_0'C_4(E)\,dE \tag{6.4}$$

$$\frac{-2\pi h^2\sigma_{\perp}}{2e^2\tau} = \int_{-\infty}^{-2\gamma_1} f_0'D_1(E)\,dE + \int_{-2\gamma_1}^{0} f_0'D_2(E)\,dE + \int_{0}^{2\gamma_1} f_0'D_3(E)\,dE + \int_{2\gamma_1}^{\infty} f_0'D_4(E)\,dE \tag{6.5}$$

where $C_l\,(E)$, $D_l\,(E)$ stand for the inner integrals in (6.2) and (6.3) respectively, with the proper range of integration in each case.

Because of the simplification of (6.4) and (6.5) at very low temperatures, the zero temperature conductivities are easily evaluated.

We find:

$$\sigma_{\parallel}(0) = \frac{8\pi e^2\tau}{h^2 c}\cdot\zeta_0 \tag{6.6}$$

$$\sigma_{\perp}(0) = \frac{2\pi e^2\tau}{h^2}\cdot\frac{\gamma_1^2 c}{(\hbar v)^2}\cdot\zeta_0. \tag{6.7}$$

And hence:

$$\frac{\sigma_{\parallel}(0)}{\sigma_{\perp}(0)} = \frac{4(\hbar v)^2}{c^2\gamma_1^2} \tag{6.8}$$

With $a = 2{\cdot}46\text{A}^0$, $c = 6{\cdot}74\text{A}^0$, $\gamma_0 = 2{\cdot}5$ eV, $\gamma_1 = 0{\cdot}005$ eV we find:

$$\frac{\sigma_{\parallel}(0)}{\sigma_{\perp}(0)} = 10^5. \tag{6.9}$$

KRISHNAN and GANGULI(16) found a ratio of about 10^5. DUTTA(17) reports a ratio of between 10^4 and 10^5, while PRIMAK and FUCHS(18) report a considerably lower ratio. The experiment is however a difficult one, and it is easy, because of the large anisotropy, to underestimate the ratio of $\sigma_{\parallel}/\sigma_{\perp}$, while it seems impossible to get too large a value in any experiment. This has been pointed out by MROZOWSKI.(13)

We now proceed to the evaluation of the two principal conductivities for arbitrary temperature. The inner integrals in equations (6.4) and (6.5) can all be done analytically. The final results can be written in the following form:

$$\sigma_{\parallel}(T) = \frac{4e^2\tau}{h^2}\cdot\frac{\gamma_1^2}{c(kT)}\int_{-\infty}^{+\infty}\operatorname{sech}^2\left[\frac{x-\zeta/\gamma_1}{2kT/\gamma_1}\right]F(x)\,dx \tag{6.10}$$

where

$$F(x) = x\left\{\frac{\pi}{2}+\sin^{-1}\left(\frac{x}{2}\right)-\frac{x}{2(1-x^2)^{\frac{1}{2}}}\cdot\log\left[\frac{((4-x^2)(1-x^2))^{\frac{1}{2}}+2-x^2}{x}\right]\right\} \qquad 0 \leqslant x \leqslant 1$$

$$= \frac{2\pi}{3}-\frac{\sqrt{3}}{2} \qquad x = 1$$

$$= x\left\{\frac{\pi}{2}+\sin^{-1}\left(\frac{x}{2}\right)-\frac{x}{2(x^2-1)^{\frac{1}{2}}}\cdot\left[\frac{\pi}{2}-\sin^{-1}\left(\frac{2-x^2}{x}\right)\right]\right\} \qquad 1 \leqslant x \leqslant 2$$

$$= x\left\{\pi-\frac{\pi}{2}\cdot\frac{x}{(x^2-1)^{\frac{1}{2}}}\right\} \qquad x \geqslant 2$$

($F(x)$ is symmetric about $x = 0$).

$$\sigma_{\perp}(T) = \frac{e^2\tau c}{2h^2}\cdot\frac{\gamma_1^4}{(kT)(\hbar v)^2}\int_{-\infty}^{+\infty}\operatorname{sech}^2\left[\frac{x-\zeta/\gamma_1}{2kT/\gamma_1}\right]G(x)\,dx \tag{6.11}$$

where

$$
\begin{aligned}
G(x) &= x^2\left\{-(4-x^2)^{\frac{1}{2}}+2x\left[\frac{\pi}{2}+\sin^{-1}\left(\frac{x}{2}\right)\right]+2(1-x^2)^{\frac{1}{2}}.\log\left[\frac{((4-x^2)(1-x^2))^{\frac{1}{2}}+2-x^2}{x}\right]\right\} && 0 \leqslant x \leqslant 1\\
&= \frac{4\pi}{3}-\sqrt{3} && x = 1\\
&= x^2\left\{-(4-x^2)^{\frac{1}{2}}+2x\left[\frac{\pi}{2}+\sin^{-1}\left(\frac{x}{2}\right)\right]-2(x^2-1)^{\frac{1}{2}}.\left[\frac{\pi}{2}-\sin^{-1}\left(\frac{2-x^2}{x}\right)\right]\right\} && 1 \leqslant x \leqslant 2\\
&= x^2\{2\pi x-2\pi(x^2-1)^{\frac{1}{2}}\}. && x \geqslant 2
\end{aligned}
$$

($G(x)$ is symmetric about $x = 0$).

Equations (6.10) and (6.11) can now be evaluated numerically for any temperature. This is done as follows: $F(x)$ and $G(x)$ are evaluated once and for all, for the entire range of x required. Then T, γ_1 and $\zeta(T)$ are chosen (the latter from Fig. 1) and the integral can be evaluated by any of the standard approximate methods.

A numerical evaluation shows that the ratio $\sigma_{\parallel}(T)/\sigma_{\perp}(T)$ is almost independent of temperature between 0°K and 600°K.

$$
\frac{\sigma_{\parallel}(T)}{\sigma_{\perp}(T)} \simeq \frac{\sigma_{\parallel}(0)}{\sigma_{\perp}(0)} = 10^5. \tag{6.12}
$$

Experimentally, DUTTA(17) reports a variation by a factor of ~ 2 over this range.

Thus, our results show that $\sigma_{\parallel}$ and $\sigma_{\perp}$ exhibit the same temperature dependence (within about 1 or 2 per cent). Agreement with experiment could of course be obtained by attributing *different* temperature dependences to the two relaxation times parallel and perpendicular to the two graphite planes. However, such an assignment implies that τ is $\boldsymbol{k}$-dependent and thus violates our original assumption. It is reasonable to suppose that in graphite the relaxation time is indeed a markedly anisotropic function of $\boldsymbol{k}$. Until more is known about the relaxation time, it does not seem profitable to extend this simple calculation.

An approximation which is sometimes made, is that τ depends on $\boldsymbol{k}$ through the energy only. In this case, τ factors outside the inner integrals in equations (6.2) and (6.3), since these are integrals over constant energy surfaces. Then, at low temperatures, the ratio of $\sigma_{\parallel}/\sigma_{\perp}$ is independent of τ, since the outer integrations in equations (6.2) and (6.3) will involve a δ-function. At higher temperatures, the ratio $\sigma_{\parallel}/\sigma_{\perp}$ will however depend on τ even in this approximation.

We conclude that the low temperature value of $\sigma_{\parallel}/\sigma_{\perp}$ predicted by our choice of γ_0, γ_1 and ζ_0 can probably be trusted and is in fair agreement with experiment.

7. THE HALL COEFFICIENT IN GRAPHITE

Let us now evaluate the zero field Hall coefficient for graphite. To do this, we shall use the same approximation as was used in the conductivity calculation, namely that τ is independent of $\boldsymbol{k}$. Again we shall find that at low temperatures, our result will be independent of τ, if τ is a function of energy only, and not a general function of $\boldsymbol{k}$.

When the magnetic field H lies along the z-axis (in our case, the c-axis in graphite), the general formula for the zero field Hall coefficient is.(29)

$$
A_{H\to 0} = \frac{-8\pi^3}{2e}\,\frac{\displaystyle\int\left[\frac{\partial E}{\partial k_y}\left(\frac{\partial^2 E}{\partial k_x{}^2}\right)-\frac{\partial E}{\partial k_x}\left(\frac{\partial^2 E}{\partial k_x\partial k_y}\right)\right].\frac{\partial E}{\partial k_y}.\frac{df_0}{dE}.d^3k}{\displaystyle\int\left(\frac{\partial E}{\partial k_x}\right)^2\frac{df_0}{dE}\,d^3k.\int\left(\frac{\partial E}{\partial k_y}\right)^2\frac{df_0}{dE}\,d^3k} \tag{7.1}
$$

Using the $E(\boldsymbol{k})$ relation given by (5.22), and a procedure analagous to that used in calculating the electrical conductivities, equation (7.1) can be transformed to:

$$A_{H\to 0} = \frac{-\pi^2}{e}\,\frac{\displaystyle\int \frac{df_0}{dE}\left[\int \left(\frac{\partial E}{\partial K}\right)^3 \frac{dK}{(\partial E/\partial k_z)}\right] dE}{\left\{\displaystyle\int \frac{df_0}{dE}\left[\int \left(\frac{\partial E}{\partial K}\right)^2 \frac{K\,dK}{(\partial E/\partial k_z)}\right] dE\right\}^2} \tag{7.2}$$

As in the case of the conductivity, these integrals are easily evaluated at very low temperatures, because of our assumption that $\zeta_c \simeq 0{\cdot}06$ eV $\gg \gamma_1 \simeq 0{\cdot}005$ eV. The result for the zero field Hall coefficient at absolute zero of temperature is:

$$\underset{\mathrm{H}\to 0}{A(0)} = -\frac{\pi c(\hbar v)^2}{2e\zeta_0{}^2} \simeq -0{\cdot}705\frac{\mathrm{cm}^3}{\mathrm{C}}. \tag{7.3}$$

The numerical value is obtained if we use:

$$a = 2{\cdot}46\ \text{Å}; \qquad c = 6{\cdot}74\ \text{Å}; \qquad \gamma_0 = 2{\cdot}5\ \text{eV};$$
$$\zeta_0 = 0{\cdot}06\ \text{eV}.$$

KINCHIN(30) has measured the zero field Hall coefficient for a single crystal of graphite, and reports a value of $-0{\cdot}69$ cm^3/C at very low temperatures, in good agreement with that predicted by equation (7.3).

In the general case of arbitrary temperature, the outer integrals in (7.2) must again be done numerically. One can transform equation (7.2) into:

$$\underset{H\to 0}{A\,(T)} = -\frac{\pi^2}{2e}\cdot\frac{(\hbar v)^2 c(kT)}{\gamma_1{}^2}\cdot\frac{\displaystyle\int_{-\infty}^{+\infty} \operatorname{sech}^2\left[\frac{x-\zeta/\gamma_1}{2kT/\gamma_1}\right] K(x)\,dx}{\left\{\displaystyle\int_{-\infty}^{+\infty} \operatorname{sech}^2\left[\frac{x-\zeta/\gamma_1}{2kT/\gamma_1}\right] F(x)\,dx\right\}^2} \tag{7.4}$$

where

$$K(x) = -\frac{x(4-x^2)^{\frac{1}{2}}}{1-x^2}+\frac{x(2-x^2)}{(1-x^2)^{3/2}}.\log\left[\frac{((4-x^2)(1-x^2))^{\frac{1}{2}}+2-x^2}{x}\right] \qquad 0 \leqslant x \leqslant 1$$

$$= \sqrt{3} \qquad x = 1$$

$$= \frac{+x(4-x^2)^{\frac{1}{2}}}{x^2-1}-\frac{x(2-x^2)}{(x^2-1)^{3/2}}.\left[\frac{\pi}{2}-\sin^{-1}\left(\frac{2-x^2}{x}\right)\right] \qquad 1 \leqslant x \leqslant 2$$

$$= \frac{\pi x(x^2-2)}{(x^2-1)^{3/2}} \qquad x \geqslant 2$$

($K(x)$ is antisymmetric about $x = 0$).

and $F(x)$ is defined by (6.10).

A numerical evaluation of $A(T)$ yields Fig. 7. Basically, the behaviour of the Hall coefficient is due to the shift of the Fermi level with temperature. As the temperature is raised, the Fermi level moves towards the degeneracy point, and hence more and more positive carriers contribute. However, there will always be an excess of negative carriers, and hence the Hall coefficient approaches zero for high temperatures but remains negative. The peculiar behaviour of the Hall coefficient between 100°K and 300°K is due to the numerator of equation (7.4). This integral has a maximum value in this temperature range, which results in a Hall coefficient slightly lower than the zero temperature value.

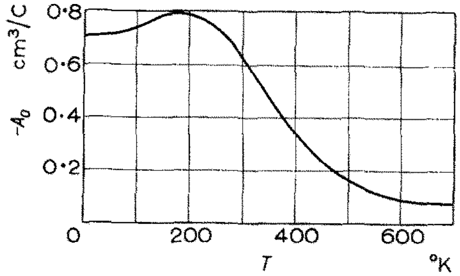

FIG. 7. The variation of the Hall coefficient with temperature.

The various experimental investigations of the Hall coefficient have led to rather widely varying results.(10,30,31) Our low temperature value agrees with a reasonable extrapolation of the results of KINCHIN, while the trend we predict at high temperatures seems in agreement with all relevant measurements. On the other hand, SOULE(31) gets very much larger values than those obtained by other investigators at low temperatures and high fields. He also gets a small *positive* Hall coefficient for fields less than one kilogauss at 4·2°K. These results are in definite disagreement with the predictions of our model.

8. THE TRANSVERSE MAGNETO-RESISTANCE IN GRAPHITE

Finally, we calculate the transverse magneto-resistance, the magnetic field being applied along the c-axis of graphite. If we again make our previous assumptions about τ, we will find that the ratio $\Delta\rho/\rho$ is proportional to τ^2. Thus, comparison with experiment will, at best, predict a relaxation time τ.

Following JONES and ZENER,(29) we write for the ratio of the change in resistivity to the resistivity:

$$\frac{\Delta\rho}{\rho} = \left(\frac{eH\tau}{\hbar^2 c}\right)^2 \cdot \frac{I_3}{I_1 . I_2} \tag{8.1}$$

where

$$I_1 = -\int \frac{df_0}{dE}\left(\frac{\partial E}{\partial k_x}\right)^2 d^3k$$

$$I_2 = -\int \frac{df_0}{dE}\left(\frac{\partial E}{\partial k_y}\right)^2 d^3k$$

$$I_3 = \int \frac{df_0}{dE}\left(\frac{\partial E}{\partial k_y}\right)\Omega\frac{\partial E}{\partial k_x}\, d^3k \,.\int \frac{df_0}{\partial E}\left(\frac{\partial E}{\partial k_x}\right)\Omega\frac{\partial E}{\partial k_y}\, d^3k - \int \frac{df_0}{dE}\left(\frac{\partial E}{\partial k_y}\right)^2 d^3k \,.\int \frac{df_0}{dE}\left(\frac{\partial E}{\partial k_x}\right)\Omega^2\frac{\partial E}{\partial k_x}\, d^3k$$

$$\Omega = \left(\frac{\partial E}{\partial k_y}\right)\frac{\partial}{\partial k_x} - \left(\frac{\partial E}{\partial k_x}\right)\frac{\partial}{\partial k_y}$$

The transformation of these integrals into integrals over $K = [k_x^2 + k_y^2]^{\frac{1}{2}}$ is straightforward but tedious. At low temperatures, where the derivative of the Fermi distribution is sharply peaked at $E = \zeta_0$, we find:

$$\frac{I_3}{I_1 . I_2} = \frac{-\left[\int \left(\frac{\partial E}{\partial K}\right)^3 \frac{dK}{|\partial E/\partial k_z|}\right]^2 + \int \left(\frac{\partial E}{\partial K}\right)^2 \frac{K\,dK}{|\partial E/\partial k_z|} \cdot \int \left(\frac{\partial E}{\partial K}\right)^4 \frac{dK}{K|\partial E/\partial k_z|}}{\left[\int \left(\frac{\partial E}{\partial K}\right)^2 \frac{K\,dK}{|\partial E/\partial k_z|}\right]^2} \tag{8.2}$$

Under the assumption that $\zeta_0 > 2\gamma_1$, the integrals have the range $\hbar vK = (\zeta_0^2 - 2\gamma_1\zeta_0)^{\frac{1}{2}}$ to $\hbar vK = (\zeta_0^2 + 2\gamma_1\zeta_0)^{\frac{1}{2}}$. The integrals are easily evaluated in a power series of γ_1^2/ζ_0^2. To the lowest non-zero order we find:

$$\frac{\Delta\rho}{\rho} = \left(\frac{eH\tau}{\hbar^2 c}\right)^2 \cdot \frac{(\hbar v)^4 \gamma_1^2}{2\zeta_0^4}. \tag{8.3}$$

This result may now be compared with the experiments of KINCHIN.(30) Using the various values of $\Delta\rho/\rho$ and H given in KINCHIN's paper and our previous choice of parameters γ_0, γ_1, ζ_0 equation (8.3) predicts:

$$\tau \simeq 4-6 \times 10^{-11} \text{ sec.} \qquad (T = 4.2°\text{K})$$

GALT *et al.*(32) report a relaxation time of approximately 10^{-11} sec, using the cyclotron resonance technique. Thus, agreement seems very satisfactory. We shall discuss the cyclotron resonance result a little more fully in the conclusions.

SUMMARY AND CONCLUSIONS

The basis for our model of graphite is a small interplanar interaction plus a certain number of excess electrons. Perhaps the most striking feature of this model is its simplicity. Only three parameters are incorporated in it (γ_0, γ_1, and ζ_0), yet the basic features of most of the properties of graphite in external fields are explained. The most unsatisfactory result is obtained for the amplitudes of the de Haas–Van Alphen effect fluctuations, which turn out to be far too large even when estimated from a simplified three-dimensional model. It may be argued that if the density of states within the nth level had not been replaced by the sum of three δ-functions, the amplitudes would have been further reduced. Although some reduction of the amplitudes would occur, the major source of the trouble lies elsewhere. As long as the magnetic energy levels are narrow as compared to their spacing, large fluctuations (and discontinuities) will occur. We must conclude that there is some other source of level broadening, which we have not considered. The fact that the observed oscillations are smaller than the theoretically predicted ones is in line with what has been found to be the case in many other substances. In Li, Na, Cu, Ag and Au for example, no oscillations have yet been observed, although theoretically one has reason to expect them. These difficulties are discussed in a very illuminating article by CHAMBERS.(33)

The form of the energy relations we have used were derived within the framework of the tight binding approximation. However, SLONCZEWSKI(34) has shown that the same form for these relations can also be obtained by group theoretical methods. It therefore seems improbable that the difficulties with the susceptibility oscillations have their origin in this approximation.

We have calculated the magneto-resistance to order H^2 only. An exact calculation, which leads to a saturation factor, is possible for graphite. However, since such a calculation is based on the Boltzmann equation, one can have confidence in the results only for magnetic fields which are small enough so that quantum effects are unimportant. In graphite, the condition for the validity of the Boltzmann equation is that $sv^2\tau/2\hbar\zeta \ll 1$. At low temperatures this condition breaks down at fields between 1000 and 10,000 gauss.

Finally, we have stated that our magneto-resistance result corresponds to a value of the relaxation time which is in fair agreement with the value found by GALT *et al.*(32) by cyclotron resonance. Cyclotron resonance results seem to indicate the presence of positive carriers. In their publication GALT *et al.* state that the presence of these carriers is uncertain, since a similar effect is under certain circumstances observed due to extremely eccentric energy surfaces.(35) In a recent private communication with one of us (P.R.W.), GALT expressed the view that positive carriers are almost certainly present and that the relaxation time is probably as long as 10^{-9} seconds. If these more recent findings are correct, they are difficult to reconcile with our model because of the position of the Fermi surface.

It may be that the reduction in the absorption near $H = 0$ is a magneto-resistance effect. CHAMBERS(36) has proposed that such an effect exists in bismuth. If our model of excess electrons is correct, then bismuth and graphite should behave quite similarly, that is, graphite should behave more like a poor metal than a semiconductor, and hence CHAMBER's explanation may also apply to graphite. Further investigation is necessary before these differences can be understood. In this connection, the previously mentioned measurement of the de Haas–Van Alphen effect would be of interest, since such an experiment would test the general features of our model.

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