some support to Shoenberg's conclusion that the degeneracy temperature is very small.

The simplest two-band model will not account for all of the observed piezoresistance effects. For if we assume that the extrema of both bands are on the $\mathbf{k}_z$ axis, the energy surfaces are ellipsoids of revolution. about this axis. It can be shown[8] that for such a model the shear coefficient combination $\frac{1}{2}(\rho_{14}+2\rho_{41})$ vanishes. Actually, in bismuth this coefficient has the fairly large value[9] 13.2×10^{-9} ohm-cm/kgcm^{-2}, corresponding to a dimensionless elastoresistance coefficient of about 30. In order to explain this coefficient, it is necessary to assume that at least one of the bands has extrema which are not on the $\mathbf{k}_z$ axis and which, consequently, are at least three in number and are transformed into one another by the symmetry operations of the crystal.

We can thus conclude that a multivalley model of bismuth which explains the piezoresistance effects must have the following features: (1) current carriers from two bands, and (2) one band with a multiplicity of extrema. The magnitude of the effects suggests that the energy difference between the extrema of the two bands is small. A model of bismuth in which the conduction band has three minima and the valence band has one extremum on the $\mathbf{k}_z$ axis has been proposed to explain the de Haas-van Alphen[2-3] and galvanomagnetic effects.[1,4,6]

More extensive experimental study of the piezoresistance effects would be of value in the working out of further details of the energy bands of bismuth. Measurements which completely determine the piezoresistance tensor would allow the elastoresistance coefficients to be calculated and various deformation potential constants to be found. It is difficult to determine parameters of the individual bands from measurements on pure bismuth alone, because the effects are due to both holes and electrons. However, by doping with elements from other columns of the periodic table, materials with conduction by predominantly one type of carrier can be prepared, and piezoresistance studies on such materials would be sensitive to details of the structure of the conduction and valence bands.

PHYSICAL REVIEW VOLUME 104, NUMBER 3 NOVEMBER 1, 1956

Diamagnetism of Graphite

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(Received April 19, 1956)

The conduction-electron magnetic susceptibility of graphite has been calculated by using the Wallace two-dimensional band structure. The energy levels induced by the magnetic field are calculated by the method of Luttinger and Kohn, taking into account the large (in this case) effects of band-to-band transitions which are not included in the Landau-Peierls treatment. Agreement with the susceptibility observed at high temperatures is obtained with a choice of 2.6 ev for the resonance-integral parameter γ_0. The details of the de Haas-van Alphen effect cannot be reproduced, indicating that a more complicated band structure is needed to account for the low-temperature experiments.

1. INTRODUCTION

THE diamagnetic susceptibility of pure crystalline graphite is large and anisotropic. The difference between the susceptibility parallel to the principal axis and that perpendicular to the principal axis is -21.5×10^{-6} emu/g at room temperature, and the magnitude increases with decreasing temperature.[1] The susceptibility perpendicular to the principal axis[2] is about equal to the free-atom susceptibility of -0.5×10^{-6} emu/g.

Ganguli and Krishnan[1] showed that the temperature dependence of the anisotropic part of the susceptibility is the same as that of a two-dimensional free-electron gas with certain characteristics. Their model has been extended by Mrozowski.[3] However, such a model is not in accord with recent calculations of the electron energy band structure of graphite.[4-6] Further, the work of Hove[7] and the present paper demonstrate that the temperature dependence of the susceptibility is principally due to the Fermi-Dirac statistics.

Several calculations of the susceptibility[7-9] have been made on the Wallace model, using the Landau-Peierls[10] formula for the diamagnetic susceptibility of conduction electrons. The most detailed calculation is that by Hove. He found that though the correct dependences of the susceptibility upon temperature and impurity concentration were obtained, the magnitude of the

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[1] N. Ganguli and K. S. Krishnan, Proc. Roy. Soc. (London) **A117**, 168 (1941).

[2] K. S. Krishnan, Nature **133**, 174 (1934).

[3] S. Mrozowski, Phys. Rev. **85**, 609 (1952).

[4] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[5] C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London) **A65**, 815 (1952).

[6] D. F. Johnston, Proc. Roy. Soc. (London) **A227**, 349 (1955).

[7] J. E. Hove, Phys. Rev. **100**, 645 (1955).

[8] R. Smoluchowski, Revs. Modern Phys. **25**, 178 (1953).

[9] W. P. Eatherly, see discussion following reference 8.

[10] R. Peierls, Z. Physik **80**, 763 (1933). See also A. H. Wilson, Proc. Cambridge Phil. Soc. **49**, 292 (1953).

theoretical susceptibility was about forty times too small. Adams[11] has critized the use of the Landau-Peierls formula in cases where two or more bands are near in energy at the same point in *k*-space (as is the case in graphite). In such cases, he argued, the band-to-band transitions caused by the magnetic field may make large contributions to the susceptibility.

In this paper the energy levels in the presence of a magnetic field are calculated for the simpler (two-dimensional) Wallace band structure; using the formalism of Luttinger and Kohn,[12] which is especially designed to treat the effects of perturbations on degenerate and nearly-degenerate bands. The susceptibility is obtained by calculating the free energy and taking the appropriate derivative. It will be seen that the correct order of magnitude and temperature dependence are obtained for high temperatures.

2. MAGNETIC ENERGY LEVELS

The reduced Brillouin zone for graphite (see Fig. 1) is in the form of a hexagonal pill-box of height $2\pi/c_L$, where c_L is the spacing between identical layer planes. In Wallace's "two-dimensional" tight-binding calculation,[4] the valence and conduction bands are degenerate along the six vertical edges of the zone (*HH* and *H'H'*). The energy is independent of the vertical coordinate and, near a zone edge, is proportional to the distance from the zone edge. Following Wallace, we write

$$\epsilon(\kappa)=\pm\tfrac{1}{2}\sqrt{3}\gamma_0 a\kappa=\pm\hbar v\kappa, \qquad (2.1)$$

where ϵ is the energy (relative to the energy at the zone edge), κ is the distance in *k* space from the zone edge, *a* is the spacing between identical atoms in a layer plane, and γ_0 is a parameter which is estimated to be between 0.9 and 3 ev. Expression (2.1) neglects higher order terms in $a\kappa$, but we are concerned only with the band structure near the zone edge where $a\kappa$ is small. The plus sign refers to the conduction band and the minus sign refers to the valence band. In the far right side of (2.1), we have used the fact that the velocity is given by the derivative of the energy with respect to $\hbar k$, so that *v* is the common magnitude of the velocities of the carriers near the zone edge.

It is interesting to find the energy spectrum in the presence of a magnetic field, using semiclassical theory. The semiclassical spectrum differs slightly from the exact spectrum, and the difference is important for the magnetic susceptibility. In the presence of a magnetic field (*H*) parallel to the principal axis, the carriers precess around the zone edge in circular orbits. According to Onsager,[13] the area of an orbit in *k* space is quantized by

$$A=\pi\kappa_n^2=(n+\tfrac{1}{2})(2\pi e/\hbar c)H. \qquad (2.2)$$

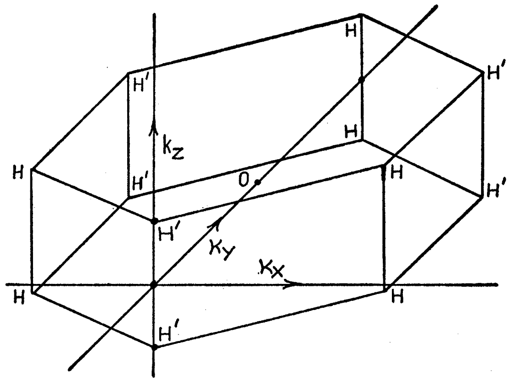

FIG. 1. The reduced Brillouin zone for graphite. Equivalent points in *k* space are labeled with the same letter. Note that the origin of coordinates illustrated is not at the origin of *k* space (0).

Using the abbreviation $s=eH/\hbar c$, we may then write

$$\kappa_n=[(2n+1)s]^{\frac{1}{2}}, \quad \epsilon_n=\pm\hbar v[(2n+1)s]^{\frac{1}{2}}. \qquad (2.3)$$

The same result can also be derived by a physical argument similar to one given for free electrons by Mott and Jones.[14] As the behavior in *k* space is the same as for a two-dimensional free electron gas, the counting of states is also the same. Thus the degeneracies of the levels are all equal and proportional to the magnetic field strength.

We now proceed to the exact calculation of the energy spectrum, using the method of Luttinger and Kohn. The details of their method can be found in the original paper (hereafter referred to as LK). In brief their procedure is: the total Hamiltonian is written down in terms of base functions which are the unperturbed solutions at a degeneracy point in *k* space times plane-wave factors $\exp[i\boldsymbol{\kappa}\cdot\mathbf{r}]$; the coupling between the degenerate states and all others is removed to first order by a canonical transformation, yielding a set of coupled differential equations. The equations which we use are a slightly generalized version of Eq. (IV.13) of LK,[15,16]

$$\begin{aligned}\textstyle\sum_{j'}[(\kappa_\alpha-\delta_{x\alpha}is\partial/\partial\kappa_y)D_{jj'}{}^{\alpha\beta}(\kappa_\beta-\delta_{\beta x}is\partial/\partial\kappa_y)\\ +(\hbar/m)(\kappa_\alpha-\delta_{x\alpha}is\partial/\partial\kappa_y)p_{jj'}{}^{\alpha}]B_{j'}(\kappa)=\epsilon B_j(\kappa). \qquad (2.4)\end{aligned}$$

The quantity ϵ is an energy eigenvalue in the field, $B_j(\kappa)$ is the wave function in *k* space, *j* and *j'* refer to the degenerate states, $p_{jj'}{}^{\alpha}$ is the αth Cartesian component of a momentum matrix element, and the numbers $D_{jj'}{}^{\alpha\beta}$ [defined by Eq. (IV.9) in LK] are analogous to effective-mass components. The repeated indices α and β are summed over *x*, *y*, *z*. The $B_j(\kappa)$ are required by the boundary conditions to be periodic functions of *k*

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[11] E. N. Adams II, Phys. Rev. **89**, 633 (1953).

[12] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[13] L. Onsager, Phil. Mag. 43, 1006 (1952). Note that our definition of *k* space differs from his by a factor 2π.

[14] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 202.

[15] The equations have been rewritten so as to correct the error in (IV.13) due to violation of the commutation rules (see the discussion in reference 16). The sign difference is due to the fact that LK write *e* for the electron charge and we write it $-e$. Note also that we do not use the convention $\hbar=1$.

[16] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

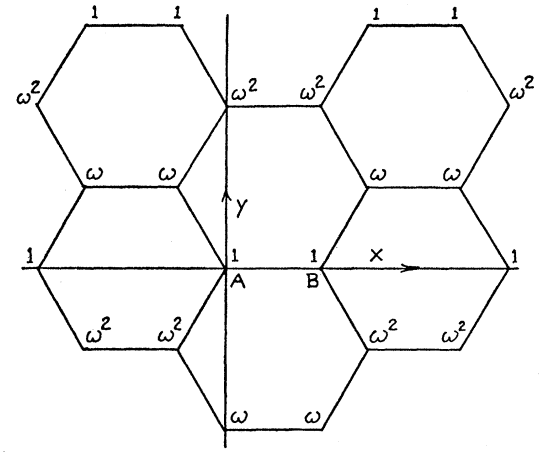

FIG. 2. A graphite layer plane.

(with the periodicity of the reciprocal lattice). However, as we will be interested in wave functions which are highly localized in the Brillouin zone, we may substitute the requirement that the $B_j(\kappa)$ vanish for large values of κ. The generalization of Eq. (IV.13) to cover the case in which there are matrix elements of momentum between the degenerate states is easily performed but is important for the present work.

For the purpose of calculating the low-field susceptibility, all terms in the energy up to order s^2 are potentially important. In this regard (2.4) is incomplete as it is only correct to second order in the quantities $(\kappa_\alpha-\delta_{x\alpha}is\partial/\partial\kappa_y)$. For example, in the extreme tight binding limit, the atomic diamagnetism comes from a term which is second order in s and second order in κ_α, or fourth order in $(\kappa_\alpha-\delta_{x\alpha}is\partial/\partial\kappa_y)$. However, we shall neglect the effects of terms not included in (2.4) on the grounds that such effects are probably of the order of the atomic susceptibility, which is small compared to the total susceptibility. We shall also neglect the terms involving $D_{jj'}{}^{\alpha\beta}$. There are two kinds of terms involved, those due to the part of $D_{jj'}{}^{\alpha\beta}$ which is symmetric with respect to interchange of α and β, and those due to the antisymmetric part. We assume that the symmetric part of $D_{jj'}{}^{\alpha\beta}$ is zero, as otherwise there would be terms in the unperturbed energy proportional to κ^2. The antisymmetric part gives a term linear in s which, in the extreme tight binding limit, reduces to the coupling between the atomic orbital angular momentum and the magnetic field.[16] We shall neglect the contribution of this term to the susceptibility as it is zero for free carbon atoms, and it seems plausible that for the solid it should not exceed the atomic susceptibility. Finally, we neglect the Pauli spin paramagnetism. In addition to the fact that the neglected parts of the susceptibility are judged to be small, they should also be very nearly isotropic. We compare the calculated susceptibility with the anisotropy in the observed susceptibility so that the error due to the neglected terms should be quite small.

In order to use Eq. (2.4) to find the energy spectrum, we must know the momentum matrix elements $p_{jj'}{}^{\alpha}$. We shall calculate the matrix elements directly from Wallace's wave functions, though the form of the result obtained is more general. The structure of a single layer plane of graphite is shown in Fig. 2. Note that there are two atoms (A and B) in the basic unit cell. Wallace's tight-binding wave functions for the valence and conduction bands are linear combinations of Bloch waves made up of $2p_z$ orbitals on A and B atoms. Because of the degeneracy, any linear combination of the two Bloch waves corresponding to a point on the edge of the zone is an eigenfunction. We choose a wave function ϕ_1 based solely on A atoms and another ϕ_2 based solely on B atoms. The coefficients of the orbitals in the Bloch sums (for a specific choice of phases) are indicated in Fig. 2, where $\omega=\exp[2\pi i/3]$. The case illustrated corresponds to a k vector on an HH edge.

We assume that the momentum matrix element between atomic orbitals based on different atoms vanishes unless the atoms are nearest neighbors in the same plane. By symmetry, the only nonzero component of such a matrix element is that directed along the line joining the two atoms. We write the matrix element between the A and B atoms labeled in Fig. 2 as

$$\int d^3r X_A(\mathbf{r})p_x X_B(\mathbf{r})=-\tfrac{2}{3}ip_0, \qquad (2.5)$$

where X_A and X_B are the orbitals (which we have chosen to be real). The momentum matrix elements between the normalized Bloch wave functions are now given by

$$p_{12}{}^x=(1-\tfrac{1}{2}\omega-\tfrac{1}{2}\omega^2)(-\tfrac{2}{3}ip_0)=-ip_0, \qquad (2.6a)$$

$$p_{12}{}^y=(\tfrac{1}{2}\sqrt{3}\omega-\tfrac{1}{2}\sqrt{3}\omega^2)(-\tfrac{2}{3}ip_0)=p_0. \qquad (2.6b)$$

The diagonal matrix elements vanish. Slonczewski[17] has shown by use of group theory that the form (2.6) for the matrix elements holds in general for the two-dimensional lattice. Thus we shall make use of the form of (2.6), but not depend upon Eq. (2.5). In fact, we shall replace p_0 by mv, for then Eq. (2.4) yields the result (2.1) for the unperturbed energies.

When we use the momentum matrix elements calculated above and neglect the $D_{jj'}{}^{\alpha\beta}$, the system of Eqs. (2.4) becomes

$$\hbar v(-i\kappa_x-s\partial/\partial\kappa_y+\kappa_y)B_2=\epsilon B_1, \qquad (2.7a)$$

$$\hbar v(i\kappa_x+s\partial/\partial\kappa_y+\kappa_y)B_1=\epsilon B_2. \qquad (2.7b)$$

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[17] J. C. Slonczewski, Ph.D. thesis, Rutgers University, 1955 (unpublished). The work also contains an estimate of p_0 using the tight-binding method but taking into account all overlap integrals. The result corresponds to a γ_0 of 2.3 ev.

The solution to the set of equations is

$$B_1=2^{-\frac{1}{2}}u_n(\kappa_y/s^{\frac{1}{2}})\exp[-i\kappa_x\kappa_y/s]\delta(\kappa_x-\kappa_x'), \tag{2.8a}$$

$$B_2=\pm 2^{-\frac{1}{2}}u_{n-1}(\kappa_y/s^{\frac{1}{2}})\exp[-i\kappa_x\kappa_y/s]\delta(\kappa_x-\kappa_x'), \tag{2.8b}$$

$$\epsilon=\pm\hbar v(2ns)^{\frac{1}{2}}=\pm\nu(ns)^{\frac{1}{2}}. \tag{2.8c}$$

The u_n are normalized harmonic oscillator wave functions and n takes on all positive integer values. For the case of $n=0$, u_{-1} is interpreted to be zero, and the normalizing factor $2^{-\frac{1}{2}}$ on B_2 should be removed. The solutions can easily be checked by noting that the left sides of (2.7a) and (2.7b) contain the raising and lowering operators, respectively. The apparent lack of symmetry between A and B atoms is due to the choice of phase and choice of gauge for the vector potential. The momentum matrix for states belonging to points on the $H'H'$ edge is the complex conjugate of the one for HH. This fact causes the solutions for the $H'H'$ edge to be asymmetric in the opposite sense from (2.8), so that there is symmetry in the complete set of solutions. Note that the exact energy spectrum is the same as the semiclassical spectrum except that $n+\frac{1}{2}$ is replaced by n.

The degeneracies of the levels can be found in the following manner. The Fourier transforms of the B's are factors in the direct-space wave function. The complex exponential factor in B causes the center of the direct-space wave function to be at $y'=\kappa_x'/s$. Limiting y' to be within a normalization volume then limits κ_x', and the counting of states proceeds exactly as in the free-electron case.[18] The number of states per volume associated with a single value of n and a single choice of sign in (2.8) is given by

$$w=8(2\pi)^{-3}(2\pi/c_L)(2\pi s)=qs. \tag{2.9}$$

The factor 8 in (2.9) is the product of three factors 2, representing: (1) the spin degeneracy, (2) the site degeneracy (the Brillouin zone can be cut up and reassembled so there are two lines of degeneracy, HH and $H'H'$), and (3) the twofold degeneracy due to the stacking of two kinds of planes in the graphite lattice (Wallace uses a double-height Brillouin zone instead). It is important to note that there are the same number of states belonging to $n=0$ as to any other single value of n and single choice of sign. We may think of the $n=0$ levels as being shared between the valence and conduction bands.

3. CALCULATION OF THE SUSCEPTIBILITY

Before making a rigorous calculation of the susceptibility, we shall present a rough calculation which gives some insight into the origin of the large diamagnetism. The reason for the diamagnetism is qualitatively this[18]: when the magnetic field is turned on, groups of states, which were originally distributed in energy, coalesce to the original average energy of the group. In the absence of the field the lower energy states in each group were preferentially occupied, so that creating the field raises the total energy of the electrons. Thus the system is diamagnetic. We now calculate the contribution to the susceptibility due to the condensation into the $n=0$ level. The total energy in the absence of the field of the group of electrons which condense to the level is given by

$$E=\int_{-\lambda}^{\lambda}g_0(\epsilon)f(\epsilon)\epsilon d\epsilon, \tag{3.1}$$

where $\lambda=\nu(s/2)^{\frac{1}{2}}$ and $g_0=2q\epsilon/\nu^2$ is the density of states in energy in the absence of the field and f is the Fermi-Dirac distribution function. For small magnetic fields the level splitting is small compared to the thermal energy. In that case we have

$$E\cong 4\int_0^{\lambda}(q\epsilon/\nu^2)\epsilon^2(\partial f/\partial\epsilon)_{\epsilon=0}=\tfrac{1}{4}q\nu^2s^2(\partial f/\partial\epsilon)_{\epsilon=0}. \tag{3.2}$$

As the total energy of the group in the magnetic field is zero, the increase in energy is $-E$. Neglecting the difference between the free energy and the total energy, the contribution to the susceptibility is given by $(\partial E/\partial H)/H$, yielding

$$\chi_0\cong-(q\nu^2/8)(e/\hbar c)^2\,\mathrm{sech}^2(\zeta/2KT)/KT, \tag{3.3}$$

where K is Boltzmann's constant and ζ is the energy of the Fermi level. Similar calculations show that the contribution to the susceptibility from the other levels is negligible. The quantity χ_0 is about three times larger than the susceptibility calculated below, the overestimate being due to the neglect of the increase in entropy with magnetic field. As might be expected, the same type of calculation using the semiclassical spectrum yields a negligible susceptibility. The existence of the $n=0$ levels which are shared by the bands depends upon the matrix elements connecting bands. Thus all the conduction electron diamagnetism of the two-dimensional model is due to band-to-band transitions. The reason that the diamagnetism is large is that fast-moving electrons are involved (i.e., γ_0 is large), a situation which is analogous to the existence of a small effective mass.

We now proceed to the more rigorous calculation using the following expression (derived in Appendix A) for the Helmholtz free energy:

$$F=N\zeta+E_0+\int d\epsilon\phi(\epsilon)(-\partial f/\partial\epsilon). \tag{3.4}$$

The energy ϵ is measured from the degeneracy point (zone edge) and the limits of integration are from $-\infty$ to ∞. The quantity N is the excess of the number of electrons per volume over the number which would just fill the valence bands. Thus N could have either

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[18] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 584.

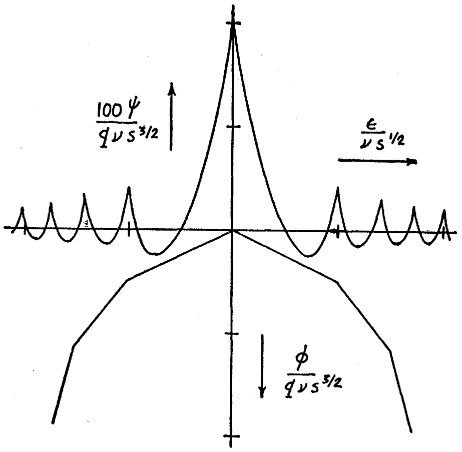

FIG. 3. A plot of the functions ϕ and ψ *versus* the energy. Note that ψ is magnified by a factor 100 relative to ϕ.

sign and is equal to zero for pure graphite. The quantity E_0 is the total energy, in the presence of a magnetic field, that the completely filled valence bands would have. The quantity $\phi(\epsilon)$, which is related to what the free energy at absolute zero would be if ϵ were the Fermi energy, is given by

$$\phi(\epsilon)=\int_0^\epsilon dx(x-\epsilon)g(x). \tag{3.5}$$

The quantity $g(\epsilon)$ is the density of states in the presence of the field, and may be expressed as

$$g(x)=qs\sum_{n=-\infty}^{\infty}\delta[x-\nu(n/|n|)(|n|s)^{\frac{1}{2}}], \tag{3.6}$$

where δ is the Dirac delta function. Let m be the largest integer such that $m\leqslant(\epsilon/\nu)^2/s$. Then ϕ is

$$\phi=qs\left[\sum_{n=1}^{m}\nu(ns)^{\frac{1}{2}}-(m+\tfrac{1}{2})|\epsilon|\right]. \tag{3.7}$$

We perform the sum using Euler's formula,[19] obtaining

$$\sum_{n=1}^{m}n^{\frac{1}{2}}\cong\frac{2}{3}m^{\frac{3}{2}}+\frac{1}{2}m^{\frac{1}{2}}+\frac{1}{24}m^{-\frac{1}{2}}-0.209. \tag{3.8}$$

For large values of ϵ, we have

$$\phi\cong-\tfrac{1}{3}q|\epsilon|^3/\nu^2-0.209q\nu s^{\frac{3}{2}}. \tag{3.9}$$

The first term in (3.9) is the value of ϕ if there were no magnetic field. The second term, when integrated in (3.4), cancels the part of E_0 which depends upon the magnetic field strength. Thus the interesting quantity to us is the difference between (3.7) and (3.9). We may write that the change in the quantity $F-N\zeta$ due to the magnetic field is

$$\Delta(F-N\zeta)=\int_{-\infty}^{\infty}d\epsilon\psi(-\partial f/\partial\epsilon), \tag{3.10}$$

where

$$\psi=\phi+\tfrac{1}{3}q|\epsilon|^3/\nu^2+0.209q\nu s^{\frac{3}{2}}. \tag{3.11}$$

The quantities ϕ and ψ are sketched in Fig. 3. Note that ψ oscillates about zero, with an amplitude which decreases with increasing ϵ.

The calculation of the susceptibility in the high-temperature—low-field limit is now easily carried out. Specifically, we assume that the level splitting is small compared to the thermal energy, $KT\gg\nu s^{\frac{1}{2}}$. The derivative of the Fermi function then does not vary much over one oscillation of ψ. As the average value of ψ is negligible except for the first few oscillations, we may evaluate $\partial f/\partial\epsilon$ at $\epsilon=0$ and factor it out of the integral. The integral over ψ then yields

$$\Delta(F-N\zeta)=0.088q\nu^2s^2\operatorname{sech}^2(\zeta/2KT)/4KT. \tag{3.12}$$

Now ζ is actually a function of s, obtained by minimizing F with respect to ζ. However the explicit derivative of ζ with respect to s does not contribute to the susceptibility and as we are interested in the low field limit, we may use the zero-field value for ζ. The susceptibility per unit volume is obtained from $\chi=-(\partial F/\partial H)/H$, so that

$$\chi=-0.044q\nu^2(e/\hbar c)^2\operatorname{sech}^2(\zeta/2KT)/KT. \tag{3.13}$$

Converting to the susceptibility per gram, and substituting from (2.8) and (2.7c) for q and ν, we have

$$\chi=-0.044(4/\pi c_L)^{\frac{3}{2}}(\gamma_0a)^2(e/\hbar c)^2 \times\operatorname{sech}^2(\zeta/2KT)/\rho KT, \tag{3.14}$$

where $\rho=2.22$ g/cm^3 is the density of graphite. Putting $a=2.46$ A and $c_L=6.74$ A, we obtain

$$\chi=-0.0014_6\gamma_0^2\operatorname{sech}^2(\zeta/2KT)/T\text{ emu/g}, \tag{3.15}$$

where γ_0 is in ev and T in degrees Kelvin. The experimentally determined anisotropic susceptibility for pure material and at high temperatures is[1] $-0.010/T$ emu/g. The experimental data can be reproduced by making a choice of $\gamma_0=2.6$ ev, which is within the range of theoretical estimates!

When the energy level spacing is larger than the thermal energy, (3.10) gives the de Haas-van Alphen effect. Instead of making a complete calculation here, we shall show by simple arguments that the two-dimensional model cannot fit the observed data.[20,21] The frequency of oscillation of the susceptibility is the frequency with which magnetic energy levels are swept through the Fermi surface. The condition that at absolute zero the electrons just occupy the first n levels is $N=(n+\frac{1}{2})qs$. The values of H for which this situation

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[19] See, for example, J. Pierpont, *Functions of a Complex Variable* (Ginn and Company, Boston, 1914), p. 320.

[20] D. Shoenberg, Trans. Roy. Soc. (London) **245**, 1 (1952).

[21] T. G. Berlincourt and M. C. Steele, Phys. Rev. **98**, 956 (1955).

occurs are given by $1/H_n=(n+\frac{1}{2})qe/\hbar cN$. Thus the susceptibility is periodic in $1/H$ with a period of $qe/\hbar cN=2e/\hbar c\kappa_F{}^2=ev^2/\hbar c\zeta^2$, where κ_F stands for the values of κ at the Fermi surface. The result is a special case of the general formula derived by Onsager.[13]

If one uses the value of γ_0 estimated above, and the experimental period of 2.15×10^{-5} gauss^{-1}, $|\zeta|$ becomes 0.065 ev. Thus $\zeta/2KT$ is so large that the zero-field susceptibility is negligible. Also, as the average value of ψ is zero for large ϵ, it follows that the susceptibility oscillates about zero. This prediction disagrees with the experimentally observed average of about -30×10^{-6} emu/g.

We may estimate the amplitude of oscillation of the susceptibility by taking the maximum derivative of ψ with respect to s at $\epsilon\cong\zeta$. Such an estimate neglects temperature damping of the oscillations, which suppresses the oscillations at fields below which the level splitting is equal to the thermal energy. The maximum derivative is approximately $q\zeta$, which yields an estimate of $0.01\gamma_0{}^2MK/\zeta$ for the amplitude. The integer $M=(\zeta/v)^2/s$ is the index of the maximum, counting from the high field end (the estimate does not hold for $M<1$). Thus at 10 kilogauss ($M\simeq2$) the theoretical amplitude would be about 100×10^{-6} emu/g, which is a factor 50 too large. However, any deviation of the energy surfaces from the cylindrical form would tend to reduce the amplitude,[13] as the total susceptibility would be a sum of contributions with a distribution of frequencies. It is interesting to note that Shoenberg's analysis of his data[20] disclosed another weaker contribution with a period of $\frac{3}{4}$ of that of the main contribution.

4. SUMMARY AND CONCLUSIONS

Perhaps the chief accomplishment of the present paper is the demonstration that the large magnitude of the susceptibility of graphite can be accounted for, at least as well as other electronic properties, by the current type of band structure calculations. Though we have calculated for the simplest model, all models have in common the degeneracy of bands at the zone edge; and it is this feature which causes the large diamagnetism. The two-dimensional model seems adequate at high temperatures, giving the correct dependence on temperature and impurity concentration,[7,8,9] as well as the right magnitude. Presumably, use of a more sophisticated model would give a satisfactory account of the low-temperature data.

The results should also be of interest in regard to the general theory of conduction-electron diamagnetism.[10,11,22] We have found a sizable susceptibility for a case in which the Landau-Peierls formula give zero [the energy surfaces (2.1) have zero Gaussian curvature], thus justifying the ideas of Adams.[11] Note that, as should be expected, the Landau-Peierls result holds when the Fermi level is several KT away from the degeneracy point; for then $\chi\cong0$.

The author is indebted to Dr. D. B. Bowen and Dr. J. L. Powell for helpful conversations on the subject of this paper.

APPENDIX A

The free energy per volume of a system of electrons is given by

$$F-N_T\zeta=-KT\int_{\epsilon(0)}^{\infty}d\epsilon g\ln\{1+\exp[(\zeta-\epsilon)/KT]\},\tag{A.1}$$

where N_T is the total number of electrons per unit volume and $\epsilon(0)$ is the energy of the lowest state. Two partial integrations yield

$$F-N_T\zeta=\int d\epsilon\phi_T(\epsilon)(-\partial f/\partial\epsilon),\tag{A.2}$$

where

$$\phi_T(\epsilon)=-\int_{\epsilon(0)}^{\epsilon}dx\int_0^x dyg(y)=\int_{\epsilon(0)}^{\epsilon}dx(x-\epsilon)g(x).\tag{A.3}$$

The second form in (A.3) has been obtained by another partial integration. From the second form it can be seen that $\phi_T(\epsilon)$ represents the value that the quantity $F-N_T\zeta$ would have at absolute zero if $\epsilon=\zeta$. At finite temperature, $F-N_T\zeta$ is then given by the sum of a distribution of its possible zero-temperature values, weighted by the function $-\partial f/\partial\epsilon$. Equation (A.2) has been used by several authors.[23–25] Sondheimer and Wilson[25] have shown that ϕ_T is the Laplace transform of the classical partition function.

We wish to obtain a form for F which involves integrals from the zero of energy (chosen at the zone edge) instead of integrals from $\epsilon(0)$. Thus we write

$$\phi_T(\epsilon)=\phi(\epsilon)+E_0-\epsilon N_0,\tag{A.4}$$

where

$$E_0=\int_{\epsilon(0)}^{0}dxg(x)x,\tag{A.5}$$

$$N_0=\int_{\epsilon(0)}^{0}dxg(x),\tag{A.6}$$

and ϕ is given by (3.5). We also write $N_T=N+N_0$. Then substitution of (A.4) into (A.3) gives (3.4), with the additional assumption that $\zeta-\epsilon(0)\gg KT$.

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