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Theory of Diamagnetism of Graphite

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The conduction-electron diamagnetism has been calculated for the three-dimensional band structure of graphite. The magnetic energy levels are found and the susceptibility calculated by analytically carrying out the free energy sum. Agreement with experiment is found for values of the band parameters nearly equal to those which give agreement with the de Haas-van Alphen effect and other phenomena. The value of γ_0 is found to be 2.8 ± 0.1 ev. The results indicate the γ_1 is about 0.27 ev and Δ is about 0.025. The other band parameters do not have an important influence upon the value of the susceptibility. The relation to the general treatments of conduction-electron diamagnetism is also discussed.

1. INTRODUCTION

THE problem of explaining the large diamagnetic susceptibility of graphite in terms of its electron energy band structure has been a troublesome one. The application of the Landau-Peierls formula[1,2] to the band structure of Wallace[3] (or its refinements) produces a result much too small. The use of the simple Landau-Peierls formula in cases which involve band degeneracies (as is the case in graphite) was criticized by Adams.[4] A few years ago, the large effects of the band-to-band transitions induced by the magnetic field (not included in the Landau-Peierls formula) were calculated for the simplified "two-dimensional" band structure.[5] The correct high-temperature susceptibility was obtained, but the low-temperature oscillations (de Haas-van Alphen effect) were not correctly given. On the other hand, a proper choice of band parameters for the "three-dimensional" model does give agreement with the de Haas-van Alphen effect[6] and cyclotron resonance.[7] However, Haering and Wallace[8] have argued on plausible grounds that the large susceptibility can only be obtained from the "two-dimensional" model or something very close to it. It is the purpose of this paper to present a calculation which yields a large susceptibility for the same "three-dimensional" model that gives agreement with the other phenomena.

The method used is a direct one. The magnetic energy levels are found and the derivative of the free energy evaluated analytically. The results are of some interest with regard to the general theory of conduction-electron diamagnetism. A discussion is made of the relation to the formulas of Adams[4] and of Hebborn and Sondheimer.[9]

2. HAMILTONIAN AND MAGNETIC ENERGY LEVELS

We shall construct the Hamiltonian in the magnetic field using the method of Luttinger and Kohn.[10] The advantage of this method is that it allows the important interaction between the degenerate bands to be treated accurately using a relatively simple Hamiltonian. The disadvantage is that it is difficult to calculate all effects which give a term to the free energy proportional to the square of the magnetic field. However, it will be argued that the terms neglected are small, and the calculated susceptibility matches the large experimental value.

We begin with the Hamiltonian derived from group theory by Slonczewski and Weiss.[11] There are four bands of interest with regard to conduction properties: two almost unoccupied and two almost completely occupied. All four are near in energy in the vicinity of the six vertical edges of the hexagonal Brillouin zone. It is only necessary to consider states very near the zone edges, so that the Hamiltonian may be expanded in powers of the distance from the edge. In the vertical direction (parallel to the c axis) the Hamiltonian is expanded in a Fourier series (the tight-binding approximation converges rapidly in this direction due to the large separation between graphite layer planes).

In writing the Hamiltonian we use the notation of reference 6. Cylindrical coordinates (σ,α,ξ) are used in which the distances from the zone edge in the x and y directions are $\kappa_x=-(2\sigma/3^{\frac{1}{2}}a_0)\sin\alpha$ and $\kappa_y=(2\sigma/3^{\frac{1}{2}}a_0)\times\cos\alpha$, and the vertical distance from the center of the zone is $k_z=\xi/c_0$, where a_0 and c_0 are the lattice parameters. The Hamiltonian in the absence of the magnetic field is then

$$H=\begin{bmatrix} E_1 & 0 & H_{13} & H_{13}^* \\ 0 & E_2 & H_{23} & -H_{23}^* \\ H_{13}^* & H_{23}^* & E_3 & H_{33} \\ H_{13} & -H_{23} & H_{33}^* & E_3 \end{bmatrix}, \tag{2.1a}$$

where

$$E_1=\Delta+\gamma_1\Gamma+\tfrac{1}{2}\gamma_5\Gamma^2, \tag{2.1b}$$

$$E_2=\Delta-\gamma_1\Gamma+\tfrac{1}{2}\gamma_5\Gamma^2, \tag{2.1c}$$

$$E_3=\tfrac{1}{2}\gamma_2\Gamma^2, \tag{2.1d}$$

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[11] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

$$H_{13}=2^{-\frac{1}{2}}(-\gamma_0+\gamma_4\Gamma)\sigma\exp(i\alpha), \tag{2.1e}$$

$$H_{23}=2^{-\frac{1}{2}}(\gamma_0+\gamma_4\Gamma)\sigma\exp(i\alpha), \tag{2.1f}$$

$$H_{33}=\gamma_3\Gamma\sigma\exp(i\alpha), \tag{2.1g}$$

with the abbreviation, $\Gamma=2\cos(\frac{1}{2}\xi)$. The only difference from reference 6 in the above equations is the inclusion of the γ_5 term in E_1 and E_2, in order to make them consistent with E_3. The diagonalization of the above Hamiltonian yields formulas for the variation of energy with wave number in the vicinity of the zone edge. Higher order terms in σ are unnecessary in dealing with properties of the carriers, as the maximum σ values of interest are no more than 0.1.

The introduction of the magnetic field by the method of Luttinger and Kohn involves the replacement of the quantity κ_x by $\kappa_x+(ie\mathcal{H}/\hbar c)\partial/\partial\kappa_y$, where e is the magnitude of the electronic charge, $\mathcal{H}$ is the magnetic field (parallel to the z axis), $\hbar$ is Planck's constant, c the velocity of light, and the vector potential is given by $\mathbf{A}=(-\mathcal{H}y,0,0)$. Care must be taken to preserve the order of the multiplication in the original Hamiltonian, as the operator replacing κ_x does not commute with κ_y. In working out the second order Hamiltonian, new terms are found which are linear in the magnetic field.[12] The effect of such terms on the present calculation is discussed in Appendix A, where it is concluded that they are small.

The modification of the Hamiltonian (2.1) is easily accomplished by working out the changes in the quantities $\sigma\exp(\pm i\alpha)=\mp i\sigma_x+\sigma_y$, which become $\frac{1}{2}3^{\frac{1}{2}}a_0 \times[\kappa_y\mp i\kappa_x\pm(e\mathcal{H}/\hbar c)\partial/\partial\kappa_y]$. If the Hamiltonian is now transformed by $H'=SHS^{-1}$, $S=\exp(-i\kappa_x\kappa_y\hbar c/e\mathcal{H})$, the κ_x term is eliminated. We rewrite the operator which replaces $\sigma\exp(i\alpha)$ as $b^{\frac{1}{2}}a^\dagger$, where $b=3a_0^2e\mathcal{H}/2\hbar c$, $a^\dagger=2^{-\frac{1}{2}}(u+\partial/\partial u)$, and $u=(\hbar c/e\mathcal{H})^{\frac{1}{2}}\kappa_y$. It is seen that $a^\dagger$ is the lowering operator in terms of the dimensionless variable u [i.e., if ψ_n is a harmonic oscillator wave function, then it holds that $a^\dagger\psi_n(u)=n^{\frac{1}{2}}\psi_{n-1}(u)$]. Similarly, $\sigma\exp(-i\alpha)$ is replaced by $b^{\frac{1}{2}}a$ where a is the raising operator $(a\psi_n=(n+1)^{\frac{1}{2}}\psi_{n+1})$. If γ_3 is neglected, the eigenvector can be written as $(C_1\psi_n,C_2\psi_n,C_{31}\psi_{n+1}, C_{32}\psi_{n-1})$, where the C's are determined by the algebraic Hamiltonian,

$$H=\begin{bmatrix} E_1 & 0 & -(\frac{1}{2}B)^{\frac{1}{2}}(1-\nu)(n+1)^{\frac{1}{2}} & -(\frac{1}{2}B)^{\frac{1}{2}}(1-\nu)n^{\frac{1}{2}} \\ 0 & E_2 & (\frac{1}{2}B)^{\frac{1}{2}}(1+\nu)(n+1)^{\frac{1}{2}} & -(\frac{1}{2}B)^{\frac{1}{2}}(1+\nu)n^{\frac{1}{2}} \\ -(\frac{1}{2}B)^{\frac{1}{2}}(1-\nu)(n+1)^{\frac{1}{2}} & (\frac{1}{2}B)^{\frac{1}{2}}(1+\nu)(n+1)^{\frac{1}{2}} & E_3 & 0 \\ -(\frac{1}{2}B)^{\frac{1}{2}}(1-\nu)n^{\frac{1}{2}} & -(\frac{1}{2}B)^{\frac{1}{2}}(1+\nu)n^{\frac{1}{2}} & 0 & E_3 \end{bmatrix}. \tag{2.2}$$

In the above, $B=\gamma_0^2b=q\mathcal{H}$ and $\nu=\gamma_4\Gamma/\gamma_0$. Use of the harmonic oscillator wave functions is valid only if the wave functions centered on different edges of the zone do not overlap. Overlap would produce broadening of the levels.[13] If γ_3 is not neglected the simple eigenvector chosen is not correct, as the γ_3 term couples it to those of quantum number $n\pm3$. This coupling breaks down the dipole selection rule and gives rise to the harmonics in the cyclotron resonance. To calculate the effect of the γ_3 term on the magnetic susceptibility would cause considerable complications. Therefore, we shall ignore it here on the basis of the following crude estimate. If all of the band parameters except γ_3 were zero, then the Hamiltonian would have the same form as the two-dimensional Hamiltonian with γ_3 replacing γ_0. As γ_3 is approximately 0.1 of γ_0, and as the two-dimensional susceptibility is proportional to the square of γ_0, we see that the susceptibility with γ_3 alone would be of the order of 0.01 of the observed value.

The secular equation derived from the Hamiltonian (2.2) can be written

$$B^2n(n+1)-(n+\tfrac{1}{2})B\left(\frac{E-E_1}{(1-\nu)^2}+\frac{E-E_2}{(1+\nu)^2}\right)(E-E_3) +\frac{(E-E_3)^2(E-E_1)(E-E_2)}{(1-\nu^2)^2}=0. \tag{2.3}$$

The equation reduces to the correct "two-dimensional" secular equation if all parameters except γ_0 are set equal to zero. If γ_0 and γ_1 are kept, the result of Haering and Wallace[8] is obtained. The same secular equation (except with $\nu=0$) has been published without its derivation by Uemura and Inoue.[14] Recently, Sato[15] has published a derivation of the energy levels for the case of γ_0 and γ_1 not zero. His results disagree with those of this paper and with those of references 8 and 14. His mistake seems to be in assuming a certain symmetry in the eigenvector which does not hold in the presence of the field.

The derivation given above does not hold if $n=0$. However, three solutions of the type $(C_1\psi_0,C_2\psi_0,C_{31}\psi_1,0)$ and one of the type $(0,0,C_{31}\psi_0,0)$ can be found. Furthermore, these four energies are the same as those found from Eq. (2.3) with $n=0$.

The finding of the magnetic energy levels involves the solution of the quartic equation. Though formulas exist for such solutions, they are not very useful here. Instead, we give approximate formulas for the energy levels in special cases and present a relation which will be used below in performing certain sums. We note that to find the quantum number in terms of the energy it is only necessary to solve a quadratic equation. For

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[14] Y. Uemura and M. Inoue, J. Phys. Soc. Japan **13**, 382 (1958).

[15] H. Sato, J. Phys. Soc. Japan **14**, 609 (1959).

many purposes, such a form is adequate. We find

$$(n+\tfrac{1}{2})B=\frac{(E-E_3)}{2}\left(\frac{E-E_1}{(1-\nu)^2}+\frac{E-E_2}{(1+\nu)^2}\right)$$
$$\pm\left\{\left[\frac{E-E_3}{2}\left(\frac{E-E_1}{(1-\nu)^2}-\frac{E-E_2}{(1+\nu)^2}\right)\right]^2+\frac{B^2}{4}\right\}^{\frac{1}{2}}. \quad (2.4)$$

If the $B^2/4$ term under the radical is ignored, (2.4) becomes the same as the secular equation in the absence of the magnetic field, except that $\gamma_0{}^2\sigma^2$ is replaced by $(n+\frac{1}{2})B$. This is an example of Onsager's rule,[16] which will hold for energies far from the band edge, except at the top and bottom of the zone (where $\Gamma=0$). At the top and bottom of the zone, we have the exact result:

$$E=\tfrac{1}{2}\Delta\pm[(\tfrac{1}{2}\Delta)^2+(n,\,n+1)B]^{\frac{1}{2}}. \quad (2.5)$$

For small quantum numbers, the levels are approximately

$$E=E_3+\{-\tfrac{1}{2}(n+\tfrac{1}{2})(\omega_1+\omega_2)$$
$$\pm[\tfrac{1}{4}(n+\tfrac{1}{2})^2(\omega_1-\omega_2)^2+\tfrac{1}{4}\omega_1\omega_2]^{\frac{1}{2}}\}B, \quad (2.6a)$$

$$E=E_1+(n+\tfrac{1}{2})\omega_1 B, \quad (2.6b)$$

$$E=E_2+(n+\tfrac{1}{2})\omega_2 B, \quad (2.6c)$$

where $\omega_1=(1-\nu)^2/(E_1-E_3)$ and $\omega_2=(1+\nu)^2/(E_2-E_3)$. The above formulas hold provided that neither E_1 nor E_2 is equal to E_3. Note that one of the levels in Eq. (2.6a) is equal to E_3 for $n=0$. This loss of zero-point energy resembles the result for the "two-dimensional" model. For the special case that $\nu=0$, $\Delta=0$ and $\gamma_2=\gamma_5$ (so that $\omega_1=-\omega_2$), Eq. (2.6a) reduces to

$$E=E_3\pm[n(n+1)]^{\frac{1}{2}}B/(E_1-E_3). \quad (2.7)$$

The above formula is interesting as it clearly shows the transition from "quantum behavior" to "classical behavior" as n increases, i.e., $[n(n+1)]^{\frac{1}{2}}$ goes to $n+\frac{1}{2}$ for large n.

When E_1 and E_3 are equal, and not equal to E_2, the levels are (still for small n):

$$E=E_3\pm(1-\nu)[(n+\tfrac{1}{2})B]^{\frac{1}{2}}, \quad (2.8a)$$

$$E=E_3-n(n+1)\omega_2 B/(n+\tfrac{1}{2}), \quad (2.8b)$$

$$E=E_2+(n+\tfrac{1}{2})\omega_2 B. \quad (2.8c)$$

Similar formulas hold when E_3 is equal to E_2.

The degeneracy of the levels is found in the usual way[17] by applying boundary conditions to the factor $\exp(i\kappa_x\kappa_y\hbar c/e\mathcal{H})$ which multiplies the wave functions expressed in the original coordinates. The number of states per volume in an interval $d\xi$ for each energy level is

$$(e\mathcal{H}/\hbar c c_0\pi^2)d\xi=(\beta\mathcal{H}/2\pi)d\xi. \quad (2.9)$$

In the above formula the spin degeneracy and the site degeneracy (there are two complete lines of degeneracy inside a single Brillouin zone) are included.

3. CALCULATION OF THE SUSCEPTIBILITY

Before performing the more rigorous calculation of the susceptibility we shall make a rough estimate which gives some insight into the origin of the large diamagnetism. We shall use the simple formula (2.7), and (2.6b) and (2.6c) with ν equal to zero. If in (2.7) the $[n(n+1)]^{\frac{1}{2}}$ were replaced by $n+\frac{1}{2}$, the susceptibility would be correctly given by the Landau-Peierls formula. As it is known that the Landau-Peierls term is too small, we shall neglect it and investigate the contribution of the correction proportional to $[n(n+1)]^{\frac{1}{2}}-(n+\frac{1}{2})\simeq-1/(8n)$. The correction produces diamagnetism as it raises the energy of the lower band (which is more fully occupied) and lowers the energy of the upper band, thus raising the total energy. The sum $\mp\sum(1/n)$ can be approximated by $-\int d\epsilon/\epsilon$, with $\epsilon=E-E_3$. Thus the increase in energy is approximately

$$\delta E=-(\beta\mathcal{H}/2\pi)\int d\xi\int d\epsilon\, Bf(\epsilon)/[8\epsilon(E_1-E_3)], \quad (3.1)$$

where f is the Fermi-Dirac distribution function. The limits on the ξ integral are $\pm\pi$. The limits on the ϵ integral are cutoff points which a more careful investigation yields as $\pm(E_1-E_3)$. The singularity at $\epsilon=0$ comes from our Taylor expansion of $[n(n+1)]^{\frac{1}{2}}$ and could be eliminated. However, as the sign of ϵ changes, the resulting total integral is finite. The susceptibility due to (3.1) is then

$$\chi=(\beta q/2\pi)\int d\xi\int d\epsilon\, f(\epsilon)/[4\epsilon(E_1-E_3)]. \quad (3.2)$$

The quantity βq is equal to $(e/\hbar c)^2(3a_0{}^2/\pi c_0)\gamma_0{}^2$. To obtain χ in emu/g, and use energies expressed in ev, the value of βq is $1.435\times10^{-6}\gamma_0{}^2$. The value of the ϵ integral at low temperature is finite if the Fermi level (ζ) is between E_1 and E_2. The value is approximately $\ln|(E_1-E_3)/(\zeta-E_3)|$, which is somewhat more than two. The integral over ξ, divided by 2π, is then about $1/4\gamma_1\approx1$. Thus, a rough estimate of the low-temperature susceptibility is about $-3\gamma^2{}_0\times10^{-6}$ emu/g. If γ_0 is about 3 ev, the estimated susceptibility is about -30×10^{-6}, of the same order as the experimental result.[18] If the Fermi level is far below the band edge, the susceptibility will be small as the f in (3.2) will be small. If the Fermi level is far above the band edge, or if the temperature is very high, the contribution from the positive and negative regions of ϵ will tend to cancel and reduce the susceptibility. Thus the rough estimate above has the right order of magnitude, and the right

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qualitative dependence upon temperature and Fermi level. For a two-dimensional band structure it has been shown that most of the diamagnetism comes from the region between the $n=0$ level (for which $E=E_3$) and the $n=1$ levels ($E=E_3\pm B^{\frac{1}{2}}$). In the present case, the source of the diamagnetism is spread over the energy region $\pm(E_1-E_3)$. The two cases may be considered as being equivalent, for if we let all parameters but γ_0 go to zero, then the level with $n=0$ near E_1 becomes equal to $E_3+B^{\frac{1}{2}}$. Thus, the energy region of the width about E_1-E_3 has collapsed to the region between the levels which are numbered 0 to 1 in the "two-dimensional" scheme. Though the argument which Haering and Wallace presented is correct in that a large susceptibility does not come from the $n=0$ level in the three-dimensional case, their argument does not apply as the source of susceptibility is now spread out over a finite energy region.

The calculation presented below will show that the above considerations are essentially correct. As we have seen, the large susceptibility comes from the departure from Onsager's rule. This departure is due to the fact that the raising and lowering operators appear alone in the Hamiltonian, and not in symmetrical combinations. It is the form of the momentum matrix which determines the form of the Hamiltonian, and the form of the momentum matrix on the Brillouin zone edge is determined solely by the crystal structure.

We now present the more rigorous calculation of the susceptibility. The free energy per unit volume is given by

$$F=N\zeta+\beta\mathcal{H}\sum\nolimits_{i,n} g(E_{in}), \tag{3.3a}$$

$$g(E)=-kT\ln\{1+\exp[(\zeta-E)/kT]\}, \tag{3.3b}$$

where N is the total number of electrons per unit volume, k is Boltzmann's constant, T is the absolute temperature, and i is the branch index which specifies one of the four solutions of (2.4) for a given n. We assign the values of i in the order of increasing energy, with $i=1$ corresponding to the lowest energy. Note that these indices will not correspond to those used to describe the energies on the zone edges in the absence of the magnetic field. The highest and lowest energies are the solutions for which the minus sign is chosen in (2.4).

We shall perform the sum on n by the Euler-Maclaurin sum formula,[19] which may be written:

$$\sum\nolimits_n g(n)\cong\tfrac{1}{2}g(0)+\tfrac{1}{2}g(\infty)+\int_0^\infty dn\, g(n)+(1/12)g'(n)\,|_0^\infty. \tag{3.4}$$

To use the formula we must know the behavior of the energy levels at the end points, which was worked out in the previous section. We must also be able to carry out the indicated integration. We write $\int dn$ as $\int dE\, d(n+\frac{1}{2})/dE$ and note that we do not need to know the energy levels, merely n as the function of E, which is given by Eq. (2.4). In the free energy sum, the terms for $n=\infty$ vanish for the two upper branches. For the two lower branches, we sum to a large quantum number which is chosen such that the total number of states summed over is independent of the magnetic field. When this is done, no term proportional to $\mathcal{H}^2$ enters the free energy from the $n=\infty$ terms. We perform a partial integration, obtaining

$$\tfrac{1}{2}g(0)+\int_0^\infty dn\, g(n)=-\int dE(n+\tfrac{1}{2})f(E). \tag{3.5}$$

In the above, we use the fact that the Fermi function is given by $f=\partial g/\partial E$. The limits on the second integral are from E_{i0} to ∞. The free energy can then be written:

$$F=N\zeta+\beta\mathcal{H}\int d\xi \sum\nolimits_i F_i, \tag{3.6a}$$

$$F_i=-\int dE\ (n+\tfrac{1}{2})f(E)-(\partial E_{i0}/\partial n)f(E_{i0})/12. \tag{3.6b}$$

To find the susceptibility we calculate $\chi=-(\partial F/\partial\mathcal{H})/\mathcal{H}=-q^2(\partial F/\partial B)/B$. In taking the derivative we regard ζ as a constant. We find

$$\chi=(1/2\pi)\int d\xi\, \beta q(D+I), \tag{3.7a}$$

$$D=\sum\nolimits_i\left[-\tfrac{1}{2}f(E_{i0})\frac{\partial E_{i0}}{\partial B}+\frac{1}{B}\frac{\partial}{\partial B}\left(\frac{B}{12}f(E_{i0})\frac{\partial E_{i0}}{\partial n}\right)\right], \tag{3.7b}$$

$$I=\sum\nolimits_i\int dE\, f(E)\frac{1}{B}\frac{\partial}{\partial B}[B(n+\tfrac{1}{2})]=\sum\nolimits_i\int dE\, f(E)\theta. \tag{3.7c}$$

The first term in D comes from the derivative of the lower limit of the integral in (3.6b). Operating on (2.4) we obtain

$$\theta=\pm[(E-E_3)^2\Omega^2+B^2]^{-\frac{1}{2}}/8, \tag{3.8a}$$

$$\Omega=-[(E-E_1)/(1-\nu)^2]+[(E-E_2)/(1+\nu)^2], \tag{3.8b}$$

where the plus sign holds for branches 2 and 3, and the minus sign holds for branches 1 and 4. Because of the difference in sign, the integral for branch 1 is completely cancelled by part of the integral for branch 2, so that the two together give an integral from E_{20} to E_{10}. A similar result holds for branches 3 and 4. This is the origin of the cutoff mentioned earlier.

We are interested in the field-independent susceptibility, so now may let B approach zero. We treat first the case that $E_1>E_3>E_2$. Then $E_{40}=E_1$, $E_{10}=E_2$,

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[19] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, 1950), 4th ed., p. 127.

$E_{20}=E_{30}=E_3$. The end-point term can be evaluated by formulas (2.6). The result for the term D (at $B=0$) is

$$D=-(1/12)\{\omega_1[f(E_1)-f(E_3)]+\omega_2[f(E_2)-f(E_3)]\}. \quad (3.9)$$

In evaluating the term I, we first perform a partial integration and then let B approach zero. The integral between E_{30} and E_{40} becomes

$$\int dE\, f(E)\theta=-f(E_{30})\phi_1(E_{30})-\int dE\,(\partial f/\partial E)\phi_1(E), \quad (3.10a)$$

where

$$\phi_1(E)=\int dx\,\theta(x). \quad (3.10b)$$

The integration in (3.10b) is from E_1 to E. The same sort of result is obtained for the integral from E_{10} to E_{20}, with the exception that the integral defining ϕ_2 is taken from E_2 to E. It can be shown that the terms involving $f\phi$ from the two intervals cancel for small B. The integration to find $\phi_1(E_{30})$ [or $\phi_2(E_{20})$] is made difficult by the fact that Ω depends upon E. However, one may integrate from E_{30} to an intermediate energy small enough that the change of Ω may be neglected, but large enough that B may be neglected in continuing the integral to E_1. It is important to note that the cancellation is not obtained if B is set to zero before evaluating the ϕ's.

It is, however, permissible to set $B=0$ to obtain the ϕ in the second term in (3.10a). This can be shown by direct calculation, but the following simple argument should suffice. Setting B to zero affects the values of ϕ only over a very small energy range. Therefore, it does not affect the integral of ϕ, but the first term in (3.10a) involves evaluating ϕ for the small argument. The formulas for the ϕ's are then

$$\phi_1=\frac{1}{8\Omega_0}\ln\left(\frac{(E-E_3)(E_1-E_2)}{\Omega(E_1-E_3)(1+\nu)^2}\right), \quad (3.11a)$$

and

$$\phi_2=\frac{1}{8\Omega_0}\ln\left(\frac{(E-E_3)(E_1-E_2)}{\Omega(E_2-E_3)(1-\nu)^2}\right). \quad (3.11b)$$

The expression for I becomes

$$I=\int_{E_3}^{E_1}dE\left(-\frac{\partial f}{\partial E}\right)\phi_1-\int_{E_3}^{E_2}dE\left(-\frac{\partial f}{\partial E}\right)\phi_2. \quad (3.12)$$

Formulas (3.7a), (3.9), and (3.12) then give the complete susceptibility. It can be shown that if $E_1-E_3=E_3-E_2$ and $\nu=0$, the contribution of the term I to the susceptibility is the same as our rough estimate (3.2).

For the case that $E_1>E_2>E_3$, we have $E_{20}=E_3$, $E_{30}=E_2$, $E_{40}=E_1$, and $E_{10}=E_3-\frac{1}{2}B(\omega_1+\omega_2)$. In this case, we must evaluate the integral from E_{20} to E_{10} before allowing B to go to zero. The result can be put in exactly the same form as above.

The derivations above do not apply to the special cases of E_1 or E_2 equal to E_3, or of E_1 equal to E_2. Detailed calculations for these special cases have been performed, and the results agree with the limiting behavior of the above formulas. For the case $E_1=E_2$, which corresponds to the top and bottom of the Brillouin zone, so that $\nu=0$, the result is

$$D+I=(1/3)[f(\Delta)-f(0)]/\Delta. \quad (3.13)$$

This formula goes over to the "two-dimensional" result as Δ approaches zero, yielding a susceptibility which is proportional to the derivative of the Fermi function evaluated at the degeneracy energy. The numerical coefficient in (3.13) is about 5% different from that in reference 5. The discrepancy is due to the different methods of calculation. A direct calculation for the "two-dimensional" case using the method of this paper agrees with the limit of (3.13), so that it is the correct result. For the case, $E_1=E_3$, the Euler formula is not valid starting from the level for which $n=0$. However, if the $n=0$ levels are included exactly and the sum formula used from $n=1$, the calculation is valid. The result in this case also agrees with the limit of (3.12).

If the temperature is very high, so that kT is much greater than $|E_1-E_3|$ or $|E_2-E_3|$, then the "two-dimensional" result holds for the entire susceptibility. At low temperatures the integral term (I) is much more important than the difference term (D) (which is always paramagnetic). In the high-temperature limit, the integral term gives a contribution equal to 1.5 of the total, and the difference term cancels the extra 0.5.

We have programmed an electronic computer to evaluate the susceptibility formula numerically. The integrations are done by Simpson's rule, using enough intervals so that the final result is good to $\pm0.1\times10^{-6}$ emu/g. The results for a particular set of band parameters are shown in Fig. 1. The results represent the carrier diamagnetism, i.e., the contribution to the orbital diamagnetism from the states near in energy to the Fermi level. We estimate that the carrier diamagnetism with the magnetic field perpendicular to the c axis is very small. Firstly, the "cyclotron effective masses" are about twelve times heavier than those for the parallel case.[6] Secondly, the interband interaction does not have a large effect in this orientation, so that the Landau-Peierls formula is valid. For the same γ_0 and γ_1, the Landau-Peierls formula gives about one-seventh of the present result for the field parallel to the c axis.[1] Thus the carrier diamagnetism perpendicular to the c axis is about one-thousandth of that for the parallel case, so that our results represent the anisotropy in the carrier diamagnetism. If all other contributions are isotropic we may compare our results with the

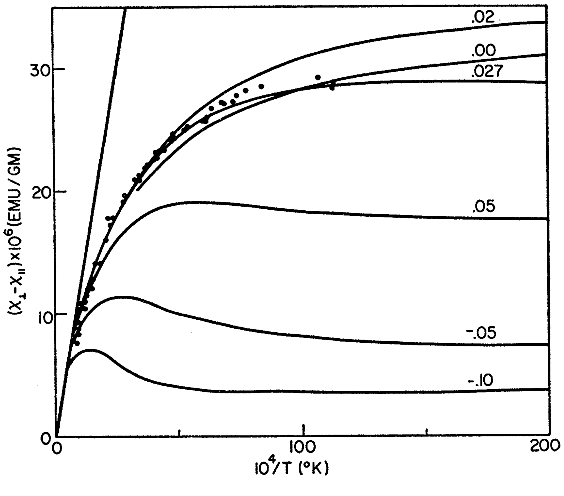

FIG. 1. The magnetic susceptibility of graphite. The circles represent the data of Ganguli and Krishnan (reference 18). The curves are calculated for the following band parameters: $\gamma_0=2.8$ ev, $\gamma_1=0.27$ ev, $\gamma_2=0.02$ ev, $\gamma_4=-0.03$ ev, $\gamma_5=0.02$ ev, and $\Delta=0.025$ ev. The straight line is the "two-dimensional" susceptibility for $\gamma_0=2.8$ ev and $\zeta=0$. The numbers on the curves give the Fermi level in ev. The 0.027-ev level corresponds to pure graphite. The 0.05 ev level corresponds to 10^{-4}/atom more electrons than holes; while the levels 0.02, 0.0, -0.05, and -0.10 correspond, respectively, to 0.25×10^{-4}, 1.0×10^{-4}, 3.7×10^{-4}, and 6.6×10^{-4} more holes per atom than electrons per atom.

measured susceptibility anisotropy.[18] The diamagnetism of the inner shell electrons, and the Pauli spin paramagnetism are isotropic. Pacault and Marchand[20] assume that there is also a London-type diamagnetic anisotropy. They empirically extrapolate the results for aromatic molecules to graphite, obtaining about -1×10^{-6} emu/g. However, we have recently been able to to show that the London diamagnetism and the carrier diamagnetism are the same for graphite.[21] In Fig. 1, we compare with the directly measured anisotropy.

Calculations have been made for a variety of values of the band parameters. As might be expected, the high-temperature susceptibility is determined by γ_0 alone. For values of the parameters of the order of magnitudes deduced from the de Haas-van Alphen effect and cyclotron resonance, the susceptibility at 1000°K is about 90% of the "two-dimensional" susceptibility. The only other parameter which has an appreciable effect upon the value of the susceptibility above 300°K is γ_1. The values of γ_0 and γ_1 used in Fig. 1 were chosen to fit the experimental curve at high temperatures. If the experimental magnitude is reduced by 1×10^{-6} emu/g, the values of both parameters are reduced approximately 0.1 ev. The value of γ_0^2/γ_1 for the parameters in Fig. 1 is somewhat different from the value deduced from the de Haas-van Alphen effect and the cyclotron resonance. Reducing their magnitudes increases the discrepancy. At 100°K, the parameter Δ has an effect, and its value was chosen to obtain agreement at that temperature. The other parameters, if kept within reasonable limits, have no effect upon the value of the susceptibility. The values of these parameters used for Fig. 1 were chosen to give rough agreement with the de Haas-van Alphen effect. The parameters used give the correct de Haas-van Alphen periods, and electron and holes masses of $0.03m_0$ and $0.06m_0$ (where m_0 is the free-electron mass) for a Fermi level of 0.029 ev.

Note that in Fig. 1 the susceptibility versus temperature curves are given for a variety of Fermi levels. In this paper, we are chiefly concerned with pure graphite, which corresponds to a Fermi level of approximately 0.027 ev for the band parameters used. However, the curves for the other Fermi levels should represent the behavior of impure graphite. In the three-dimensional band structure, the Fermi level for a constant excess (or deficit) of electrons over holes depends very little upon temperature. Thus, each curve in Fig. 1 corresponds approximately to the excess of electrons or holes noted in the caption. We shall not attempt to make a detailed comparison between these curves and the experiments, though the results seem to be qualitatively in accord with bromination results[22] if it is assumed that 2% of the bromine atoms are ionized. This estimate differs by a factor 10 from that in reference 22. It is interesting to note that the curves predict a maximum in the susceptibility as a function of temperature for very impure graphite. To the author's knowledge, such a maximum has not yet been observed.

The calculations presented above are valid in the limit of very small magnetic fields. However, there is experimental and theoretical evidence that the results can apply to the actual measurements. Lumbroso-Bader and Marchand[23] have carefully searched for field dependence of the susceptibility of purified single crystals. They find that the variation at room temperature is less than 0.5% from 3 to 12 kilogauss. From the present derivation, we see that field dependence would be important when B is greater than $(E-E_3)\Omega$ over an appreciable fraction of the energy range. For a field of 10 kilogauss, B is about 10^{-3} ev. As Ω is usually about 1 ev, the fact that $\mathcal{H}$ is not zero affects only a small part of the total energy range. Also, we have used an electronic computer to calculate numerically the susceptibility at finite fields. The effect of the two lower bands, if completely full, was calculated by the Euler-Maclaurin sum formula, and the free energy sums for electrons and holes calculated term by term. The results at 50 kilogauss agree within 2% with those from formula (3.12), except at low temperatures where the de Haas-van Alphen effect is important. Thus at 10 kilogauss we would expect the variation to be less than 1%.

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4. DISCUSSION

The most important result in the present work is the demonstration that the "three-dimensional" band model is capable of explaining the observed diamagnetic susceptibility. As the same model gives a good account of several other properties, it seems to be well established. Of course, the exact values of the parameters are subject to revision.

It is appropriate here to discuss the relation of our work to that of Pacault and Marchand.[20] These authors have been able to obtain a good fit of experimental susceptibility data for a wide range of graphite types. They use a simple formula derived for a two-dimensional electron gas. (The model specifies a constant effective mass, and is not to be confused with the "two-dimensional" band structure mentioned in this paper.) Theoretically, our model should be more correct for perfect graphite (though the agreement with experiment is not better). However, the band structure we use does not apply to small crystals, which have an energy gap between the valence and conduction bands. On the other hand, their model is plausible for the small crystals. Marchand[24] has proposed that their formula be reinterpreted for perfect graphite. Our results are so complicated that we have not yet been able to show the relation to their formula, though the numerical agreement is good. We do make a conjecture concerning the small crystal graphites. We note that increasing (or decreasing) the parameter Δ more than $2\gamma_1$ produces an energy gap.[11] Though the effect of reducing the size is certainly more complicated, changing Δ may give the qualitative effect. The susceptibility for a large Δ would be given by (3.13) which resembles the formula of Pacault and Marchand.

It is also of interest to compare our results with general calculations of the conduction electron diamagnetism. In particular, we shall compare with the treatments of Adams[4] and Hebborn and Sondheimer,[9] which yield complete formulas. These formulas are general in that they include all effects which contribute to the low-field susceptibility; however, they do not *a priori* apply to cases involving band degeneracy. Their formulas are very complicated and contain many terms, so it is of some value to see which terms correspond to the large susceptibility we have calculated. We may take a clue from formula (3.2), which as we saw is responsible for the large value of the diamagnetism. We replace the integral over ϵ by $\int d\sigma^2(\pm\gamma_0^2)/(E_1-E_3)$ (as in this simple case, $\epsilon=\gamma_0^2\sigma^2/(E_1-E_3)$, in the absence of the magnetic field). We then obtain a result proportional to the integral over k space of $[\gamma_0^2/(E_1-E_3)]^2 f(\epsilon)/\epsilon$. Now the difference between the energies of the two middle bands (2 and 3) is 2ϵ, so that the expression has the form of the Fermi function divided by an interband energy difference. These terms are called χ_3 and χ_4 by Hebborn and Sondheimer. (Of course, we could perform the partial integration to get a term containing $\partial f/\partial\epsilon$, but it would be multiplied by the logarithm function which has no analog in the general formulas.) Furthermore, only the term $\int(\partial u_l^*/\partial x)(\partial u_n/\partial k_2)d\tau$ in χ_4 contributes a factor $[\gamma_0^2/(E_1-E_3)]^2$, so that it is the source of the large susceptibility. In the Adams paper, it is χ_3 which contains the large effect. In particular, it is the part of χ_3 involving the operator s. In fact, Adams evaluated χ_3 for a particular model and noted that it included terms which had opposite signs in two bands, such that there would be a contribution to the susceptibility if the bands were not equally occupied. Next, we consider the question of degeneracy. The general treatment should give a correct result except when $\epsilon=0$. From our calculation, we have seen that the error at $\epsilon=0$ cancels out of the final result. Thus it appears that the general formulas could be used to calculate the susceptibility correctly for the three-dimensional case. Since this is true, we must explain why the present method was used. Firstly, the method used seemed simpler. The evaluation of all the terms in the general formula would be a formidable task. Secondly, the method used provides more insight into the cause of the large diamagnetism, though it is hoped that an even better physical understanding can be gained in the future. Lastly, it provided a careful investigation which justifies the use of the general formulas.

APPENDIX A

We shall now discuss the effect of higher order terms which were left out of the Hamiltonian (2.2). The higher terms come from the elimination by perturbation theory of all states not included in the four-band sub-Hamiltonian. There are two types of terms which enter. There are those in which the quantity κ_x in the sub-Hamiltonian of the type (2.1) are replaced by the operator $\kappa_x+(ie\mathcal{H}/\hbar c)\partial/\partial\kappa_y$. These terms (above the first order) have a small effect as the terms of higher order in σ have a small effect. There are, however, other terms which appear because the operator does not commute with κ_y. For example, the second-order terms in the operator contain a term which is linear in the magnetic field and is given by

$$T_{rs}=(e\mathcal{H}\hbar/m^2c)\sum_n(P_{rn}^xP_{ns}^y-P_{rn}^yP_{ns}^x)/(E_r-E_n), \quad (A.1)$$

where $r, s=1, 2, 31, 32$ are the indices for the four bands on the zone edge, n is the index for all other bands, and P_{rn}^x is the matrix element of the x component of the momentum. The effect of this term, which is analogous to the orbital angular momentum, is to add to the Hamiltonian the following matrix:

$$\delta H=\begin{bmatrix} 0 & D_{12}\mathcal{H} & 0 & 0 \\ D_{12}\mathcal{H} & 0 & 0 & 0 \\ 0 & 0 & D_{33}\mathcal{H} & 0 \\ 0 & 0 & 0 & -D_{33}\mathcal{H} \end{bmatrix}. \quad (A.2)$$

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The above matrix can be found by using the form for the general momentum matrices found by Slonczewski. From that work we have an important result: all of the subgroups possible at a general point on the zone edge are included in the four bands. This means that when (2.2) is treated exactly, it includes effects of the type represented by (A.2). Let us illustrate this statement. Suppose that we are dealing with a case in which E_1, E_2, and E_3 are all different. Further, suppose that we are interested only in the two bands derived from 31 and 32, so that we may eliminate bands 1 and 2 by perturbation theory. We would then find in our two-band sub-Hamiltonian terms like those given by D_{33} in Eq. (A.2). The same kind of argument holds if we eliminate bands 31 and 32 and keep bands 1 and 2. Of course, if E_1 or E_2 is equal to E_3, we cannot use perturbation theory, but the *type* of interaction does not change. As the differences between E_1 or E_2 and E_3 are of the order of tenths of electron volts, and as the nearest state in energy to the four bands of interest is several electron volts away, the effect of the terms in (A.2) must be small compared to those already present in (2.2).

Still higher terms could contribute. For example, the fourth-order terms produce the analog to the free-atom diamagnetism. We will not give a complete discussion of the higher terms. However, we have shown that the second-order terms are negligible, and the order of magnitude of the fourth-order terms is probably of the order of the free-atom diamagnetism, which is small (0.5×10^{-6} emu/g).

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Infrared Absorption and Valence Band in Indium Antimonide*

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Infrared absorption is studied at near liquid helium temperature for *n*- and *p*-type degenerate samples of various carrier concentrations. The absorption in *p*-type samples, at photon energies larger than the energy gap, depends on the hole concentration. The results show that the valence band is warped and that the energy at $k=0$ is very close to the maximum energy of the band. A step in the absorption of *n*-type samples is observed which gives an estimate of $\sim0.012m$ for the effective mass of light holes. The long wavelength absorption in *p*-type samples is characteristic of intervalence band transitions.

INTRODUCTION

INFRARED studies of indium antimonide have contributed a large amount of experimental information about the conduction band which is consistent with a model of an energy minimum at the center of the Brillouin zone and an effective mass varying with energy. Observations of a change of absorption edge with the concentration of conduction electrons[1,2] gave a rough estimate of the effective mass for the conduction band. Consistent values of the effective mass have been obtained from various types of experiments including cyclotron resonance,[3] reflection and absorption at long wavelengths,[4] Faraday rotation,[5] and magneto-oscillatory effect.[6] The reflection and absorption studies made on samples of various carrier concentrations explored a considerable range of the conduction band, giving the variation of effective mass with energy. The magneto-oscillatory effect experiments gave an estimate of the gyromagnetic ratio for the conduction electrons.

Experimental information about the valence band, including the results of infrared studies, is not as conclusive, as uncertainty is involved in the interpretation of some of the observations. Theoretical treatments suggest that the valence band resembles to some extent that of germanium and silicon but that there may be a number of energy maxima due to the lack of the center of symmetry.[7,8] Estimates of the effective mass for holes, varying from $0.1m$ to $0.2m$, have been deduced from different types of measurements;[4,9] for a complicated band structure, masses obtained from different

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