Diamagnetism of graphite*†‡

M. P. Sharma,‡ L. G. Johnson, and J. W. McClure
Department of Physics and Institute of Theoretical Science, University of Oregon, Eugene, Oregon 97403
(Received 4 September 1973)

A calculation of the diamagnetism of graphite including the effects of trigonal warping of the Fermi surfaces has been performed using Fukuyama’s formulation of the diamagnetism of Bloch electrons. Inclusion of the trigonal warping increases the diamagnetism by about 13% at low temperatures and reduces it by about 1% at high temperatures. A paramagnetic constant is used to represent all effects not associated with the free carriers. The experimental diamagnetism can be fitted quite well using values of the energy band parameters which give agreement with the de Haas–van Alphen effect, optical absorption, and magnetoreflection experiments.

I. INTRODUCTION

The diamagnetism of graphite is large and anisotropic.1,2 Several years ago a calculation was published3 which gave agreement with experiment and which showed that the large diamagnetism has an interband origin. However, since that time a great deal more has been learned about the energy-band structure of graphite. The values of the energy-band parameters used in the previous calculation are in disagreement with more recent experiments. In particular, it is now known that the trigonal warping of the Fermi surfaces, which was neglected in the previous calculation, is very significant.4 In order to resolve these discrepancies, we have made a new calculation of the diamagnetism which includes the trigonal warping.

Until recently, the general formulas available for calculating the diamagnetism of band electrons have been very complicated.5 In the previous calculation of the diamagnetism of graphite3 it was considered easier to solve for the Landau levels directly and then evaluate the partition sum. Such a method works well if the Fermi surface has rotational symmetry about the magnetic-field direction,6 but would be very awkward for the case of trigonal warping. Recently Fukuyama7 has published a new general formula for the diamagnetism of band electrons which is much simpler than previous formulas.

In Sec. II, we transform Fukuyama’s formula in order to simplify the subsequent calculation. In Sec. III, we work out the diamagnetism of graphite, and in Sec. IV we compare the results with experiment and draw conclusions.

II. MODIFICATION OF FUKUYAMA’S FORMULA

Fukuyama’s expression7 for the magnetic susceptibility of Bloch electrons when the magnetic field is in the z direction is

\[
\chi = \left( \frac{e^2/\hbar c^2}{\pi^2} \right) k_B T \sum_n \int d^3 k T \text{Tr}[g \gamma^x \gamma^y \gamma^z \gamma^g]. \tag{2.1}
\]

Atomic units (energy in Ry) have been used; \( \gamma^x, \gamma^y \) are components of the momentum matrix, \( g \) is the Matsubara Green’s function,

\[
g = (\varepsilon_n + \mu - 3\xi)^{-1}, \tag{2.2}
\]

where \( \varepsilon_n = (2n+1)\pi k_B T, 3\xi \) is the Hamiltonian in the absence of the magnetic field, and \( \mu \) is the energy of the Fermi level. The sum on \( n \) is from \( -\infty \) to \( \infty \); the integral on \( k \) is over the Brillouin zone, and the trace is taken with respect to the band indices. The susceptibility is dimensionless (emu/cm²), and the spin degeneracy is included. Fukuyama7 has shown that the formula is equivalent to the previous more complicated formulas when the Matsubara sum on \( n \) is performed before the matrix algebra and the integrations are carried out. Working out the matrix algebra first simplifies the calculation in some cases, including the present one. The formula is valid in any representation, but we will work in the \( \vec{k} \cdot \vec{p} \), or Luttinger-Kohn (LK) representation,9 in which

\[
\gamma^x_{\mu \nu} = \frac{1}{2} \frac{\partial \gamma_{\mu \nu}}{\partial k_\xi} + \delta_{\mu \nu} k_\xi. \tag{2.3}
\]

The first modification we make takes advantage of the symmetry of the model Hamiltonian for graphite, which depends upon \( k_x \) and \( k_y \) only through \( k_z = 2^{-1/2}(k_x + ik_y) \). We define \( \gamma^* = 2^{-1/2}(\gamma^x + i\gamma^y) \) and substitute into Eq. (2.1), producing several terms. The cyclic invariance of the trace can be used to eliminate terms with three \( \gamma^* \) factors and one \( \gamma^x \), and vice versa. The fact that the susceptibility is invariant under rotation about the magnetic-field direction eliminates terms with four \( \gamma^x \) factors or four \( \gamma^* \) factors, so that

\[
\chi = \left( \frac{e^2/\hbar c^2}{\pi^2} \right) k_B T \sum_n \int d^3 k T \text{Tr}[\gamma^x \gamma^y \gamma^z \gamma^g - \frac{1}{2} \gamma^* \gamma^* \gamma^y \gamma^g]. \tag{2.4}
\]

The result can be made more compact by a se-
ries of partial integrations. From Eq. (2.3) and the definitions of \( h_4 \) and \( \gamma^* \), we have

\[
\frac{\partial h_4}{\partial \gamma^*} = 2 \gamma^*,
\]

\[
E(0) = \int d^2k \left( \frac{\partial^2}{\partial \gamma^* \partial \gamma^*} \right) Tr(\gamma^* \gamma^*) = 0,
\]

(2.5a, 2.5b)

where \( I \) and \( O \) are the unit and null matrices, respectively. Combining with Eq. (2.2) we obtain a result similar to Fukuyama's,

\[
\frac{\partial g}{\partial h_4} = 2 \gamma^* \gamma^*.
\]

(2.6)

These relations allow us to take derivatives and to perform partial integrations on the expression

\[
\int d^2k \frac{\partial^2}{\partial \gamma^* \partial \gamma^*} Tr(\gamma^* \gamma^*) = 0,
\]

(2.7)

which vanishes because the trace is periodic in \( k \) space. The result is

\[
\int d^2k Tr(\gamma^* \gamma^* \gamma^* \gamma^* \gamma^* \gamma^*) = \frac{1}{2} \int d^2k Tr(\gamma^* \gamma^* \gamma^* \gamma^* \gamma^* \gamma^*),
\]

(2.8)

from which follows

\[
\chi = \left( \frac{c^2/hc^2}{4 \pi^2} \right) h_4 T \sum_n \int d^2k
\]

\[
\times Tr(\gamma^* \gamma^* \gamma^* \gamma^* \gamma^* \gamma^*). \quad (2.9)
\]

Use of Eq. (2.6) then produces the form

\[
\chi = \left( \frac{c^2/hc^2}{4 \pi^2} \right) h_4 T \sum_n \int d^2k
\]

\[
\times Tr \left[ \frac{1}{2} \gamma^* \gamma^* \gamma^* \gamma^* \gamma^* \gamma^* \right]. \quad (2.10)
\]

Either Eq. (2.9) or Eq. (2.10) is more convenient for the case of graphite than Eq. (2.1), but the latter form has only four matrices to be multiplied together.

We now specialize to the \( \overrightarrow{k} \cdot \overrightarrow{p} \) approximation, in which a truncated sub-Hamiltonian is used in a small region of \( k \) space. Neglecting the dependence of the energy-band structure upon temperature and doping, all contributions to the magnetic susceptibility which depend upon the temperature or small changes in the Fermi level come from states very near the Fermi level for pure material. Thus we can write the susceptibility as the contribution calculated using the sub-Hamiltonian in the small region plus a term independent of temperature and Fermi level which comes from the rest of the occupied bands and the integral over the rest of the Brillouin zone. The region of integration for the contribution from the \( \overrightarrow{k} \cdot \overrightarrow{p} \) sub-Hamiltonian should be the region in which the \( \overrightarrow{k} \cdot \overrightarrow{p} \) approximation is valid. However, we extend the integration to infinity in the \( k_x k_y \) plane (provided the integral converges) and call this contribution to the susceptibility \( \chi' \). If the bands are far above or far below the Fermi level everywhere outside the region in which the \( \overrightarrow{k} \cdot \overrightarrow{p} \) model is valid, then the correction to \( \chi' \) due to the extension of the region of integration is a constant and may be combined with the constant contribution already mentioned. This condition is met in graphite.

In the \( \overrightarrow{k} \cdot \overrightarrow{p} \) approximation a subset of bands are chosen which are close in energy to each other, but are far from all other bands. In the "full" version of the approximation a transformation is made which removes to first order the interaction between the chosen bands and all other bands, leaving a sub-Hamiltonian quadratic in \( k \). In the "bare" version, such as the Slonczewski-Weiss model for graphite, only the linear terms in \( k \) are kept. In this section we will treat the case of the "full" approximation, though in Sec. III we specialize to the "bare" case.

Since we now have a finite sub-Hamiltonian, the Green's function can be obtained by simple matrix inversion,

\[
g = N/D,
\]

(2.11)

where \( N \) is the transpose of the matrix of cofactors, and \( D \) is the determinant, of the matrix \( e^+ + \mu - \mathcal{H} \). It can be shown that the \( \gamma \)'s are still given by the derivatives of the sub-Hamiltonian, but the second half of Eq. (2.3) is no longer true. The \( \gamma \)'s are linear in \( k \), so that the derivatives of the \( \gamma \)'s are constant matrices,

\[
\frac{\partial \gamma^*}{\partial k_x} = \frac{\partial \gamma^*}{\partial k_y} = \Omega,
\]

(2.12a)

\[
\frac{\partial \gamma^*}{\partial k_z} = \omega, \quad \frac{\partial \gamma^*}{\partial k_z} = \omega'.
\]

(2.12b)

We will now use the above results, together with Eq. (2.6), which is still valid when the sub-Hamiltonian is quadratic in \( k \), to change Eq. (2.10) to a form which is easier for calculation. If we substitute (2.11) into (2.10), one term of the result involves \((\gamma^* N \partial / \partial h_4)^2\). The elements of the matrix \( N \) are power series in \( k \) (for the \( 4 \times 4 \) bare \( \overrightarrow{k} \cdot \overrightarrow{p} \) matrix of graphite, \( N \) is cubic in \( k \) and \( \partial N / \partial h_4 \) is a simpler matrix, so that this term is simpler to evaluate than Eq. (2.10). The other terms in the expression for the susceptibility can be expressed in terms of derivatives of \( D \) and traces of very simple operators. For example, one term involves

\[
Tr(\gamma^* N \gamma^* N) = D^2 Tr(\gamma^* \gamma^* \gamma^* \gamma^*)
\]

\[
= \frac{1}{2} D^2 Tr \left( \gamma^* \frac{\partial g}{\partial h_4} \right).
\]
DIAMAGNETISM OF GRAPHITE

\[ -\frac{1}{2} D^2 \left( \frac{\partial}{\partial k_\perp} \text{Tr}(\gamma^g) - \text{Tr}(\omega^g) \right), \]  
\[ (2.13) \]

and the remaining terms can be expressed as a derivative of the above term plus simple corrections. Finally, \[ \text{Tr}(\gamma^g) = \text{Tr}(\gamma^N)/D \] can be eliminated using the theorem

\[ \frac{\partial D}{\partial k_\perp} = \sum_{\{A\}} \frac{\partial}{\partial k_\perp} \left( \gamma + \mu - \mu \right) \rho_{\{A\}} \frac{\partial D}{\partial \left( \gamma + \mu - \mu \right) \rho_{\{A\}}} \]
\[ = -2 \sum_{\{A\}} \gamma^N \rho_{\{A\}} = -2 \text{Tr}(\gamma^N). \]  
\[ (2.14) \]

Using the above results and the cyclic invariance of the trace, we arrive at

\[ x_{sr} = \frac{1}{4\pi^2} \left( \frac{\varepsilon^2}{\hbar c} \right)^2 k_B T \sum_n \int d^2 k \left\{ \frac{1}{2} \text{Tr}(\omega^g) - \frac{1}{D} \frac{\partial D}{\partial k_\perp} \left( \frac{1}{2} \frac{\partial}{\partial k_\perp} \text{Tr}(\omega^g) + \frac{2}{D} \right) \right\} \]
\[ - \frac{1}{2D^2} \left( \frac{\partial D}{\partial k_\perp} \right)^2 \text{Tr}(\omega^g) - \frac{1}{2D^2} \left[ \text{Tr} \left( \frac{\gamma - D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} \right) + \frac{1}{2D} \frac{\partial D}{\partial k_\perp} \left( \frac{\partial D}{\partial k_\perp} \right)^2 \right] \]
\[ - \frac{2}{D} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} - \frac{2}{D} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\parallel} \frac{\partial D}{\partial k_\parallel} \} \]  
\[ (2.15) \]

As pointed out before, this form involves simpler matrix algebra than Eq. (2.10).

The result (2.15) still has the disadvantage that after the Matsubara sum has been performed, the \( D^4 \) in the denominator will give rise to a third derivative of the Fermi distribution function with respect to energy, while the standard formulas for diamagnetism involve the Fermi function and its first derivative only. To avoid this difficulty, we make a series of partial integrations in the \( k_\parallel k_\parallel \) plane. The surface terms vanish as, in the case of graphite, the integrand falls off as \( k \to \infty \) and we have extended the integration to infinity. The integrations are made by noting that

\[ \frac{1}{D^4} \frac{\partial D}{\partial k_\perp} = -\frac{1}{3} \frac{\partial}{\partial k_\perp} \frac{1}{D^3}, \]

and similar relations. The final result is

\[ x = \frac{1}{4\pi^2} \left( \frac{\varepsilon^2}{\hbar c} \right)^2 k_B T \sum_n \int d^2 k \left\{ \frac{1}{2} \text{Tr}(\omega^g) - \frac{1}{2D^2} \right\} \text{Tr}(\omega^g) - \frac{1}{2D^2} \left( \frac{\partial D}{\partial k_\perp} \right)^2 \text{Tr}(\omega^g) \]
\[ \left[ \frac{1}{2D^2} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\parallel} \frac{\partial D}{\partial k_\parallel} \right] \]  
\[ (2.17) \]

where

\[ \mathcal{L} = \frac{1}{6} \left[ \frac{4}{D^2} \left( \frac{\partial D}{\partial k_\perp} \right)^2 - \frac{1}{D^2} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\parallel} \frac{\partial D}{\partial k_\parallel} \right] - \frac{1}{2D^2} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\perp} \frac{\partial D}{\partial k_\parallel} \frac{\partial D}{\partial k_\parallel} \left[ \frac{1}{2D} \frac{\partial D}{\partial k_\perp} \right] \]  
\[ (2.18) \]

Though the result looks more complicated than Eq. (2.10), it is in fact easier to evaluate.

III. APPLICATION TO GRAPHITE

The Slonczewski-Weiss (SW) Hamiltonian describes the four electron energy bands that produce the Fermi surface near the H-K edge of the Brillouin zone. The form of the Hamiltonian is given by

\[ 3\mathcal{C} = \begin{pmatrix} E_1 & O & H_{13} & H_{13}^* \\ O & E_2 & H_{23} & -H_{23}^* \\ H_{13}^* & H_{23} & E_3 & H_{33} \\ H_{13} & -H_{23} & H_{33}^* & E_3 \end{pmatrix}. \]  
\[ (3.1) \]

In order to write the matrix elements conveniently in terms of \( k_\parallel \) (defined relative to the zone edge), we make a 90° rotation in the coordinate system from that previously used. Accounting for the factor 2^{1/2} in the definition of \( k_\parallel \), the matrix elements can be written as

\[ E_1 = \Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_3 \Gamma^2, \]  
\[ (3.2a) \]
\[ E_2 = \Delta - \gamma_1 \Gamma + \frac{1}{2} \gamma_3 \Gamma^2, \]  
\[ (3.2b) \]
\[ E_3 = \frac{1}{2} \gamma_2 \Gamma^2, \]  
\[ (3.2c) \]
\[ H_{13} = \frac{1}{2} \sqrt{3} \left( -\gamma_0 + \gamma_4 \Gamma \right) a_0 k_\perp, \]  
\[ (3.2d) \]
\[ H_{23} = \frac{1}{2} \sqrt{3} \left( \gamma_0 + \gamma_4 \Gamma \right) a_0 k_\perp, \]  
\[ (3.2e) \]
\[ H_{33} = \left( \frac{1}{2} \right)^{1/2} \gamma_3 \Gamma a_0 k_\perp, \]  
\[ (3.2f) \]

where \( \Gamma = 2 \cos \left( \frac{1}{2} \phi \right) \), \( c_0 \) is the lattice parameter in the \( \varepsilon \) direction, perpendicular to the basal plane, \( a_0 \) is the in-plane lattice parameter, and \( \Delta \) and the \( \gamma_i \) are the energy-band parameters defined previously.\(^{3,12}\)

The SW Hamiltonian is the "bare" \( \mathbf{k} \cdot \mathbf{p} \) approximation in the \( k_\parallel k_\parallel \) plane. Therefore, in calculating the magnetic susceptibility with the magnetic
field parallel to the $z$ axis, we drop all terms coming from parts of the Hamiltonian quadratic in $k_x k_y$, including the $g^2$ term which came from the $k^2$ on the diagonal of the full $k^2$ Hamiltonian. Thus the only term kept in Eq. (2.17) is $J$, for which we need $\gamma^3 N/k_e$, $D$, and the various derivatives of $D$.

The SW Hamiltonian gives the following expression for $D$,

$$D = e_s^2 e_1 e_2 - 2 e_s e_1 \gamma_0^3 \zeta_x + \gamma_0^3 (1 - \nu^2) e_2 \zeta_z^2$$

$$+ \gamma_0 \sum_{i=1}^{3} \zeta_i \zeta_i + \gamma_0^3 (1 - \nu^2) e_2 \zeta_z^2$$

$$+ \gamma_0 \sum_{i=1}^{3} \zeta_i \zeta_i + \gamma_0^3 (1 - \nu^2) e_2 \zeta_z^2$$

where

$$e_s = \frac{1}{2} e_1 (1 + \nu)^2 + \frac{1}{2} e_2 (1 - \nu)^2.$$  

(3.3a)

$$\zeta_x = \frac{\zeta_1^2 + \zeta_2^2 + \zeta_3^2}{2}$$

(3.3b)

\[ \mathcal{L} = \left( \frac{3}{2} D \right)^2 \gamma_0^3 \zeta_x \zeta_y \zeta_z + \frac{3}{2} \gamma_0^3 (1 - \nu^2) \zeta_z^2 + \frac{1}{2} \gamma_0^3 (1 - \nu^2) \zeta_z^4 - 4(1 - \nu^2)^2 D_0 \]

$$+ \gamma_0 \sum_{i=1}^{3} \zeta_i \zeta_i + \gamma_0^3 (1 - \nu^2) e_2 \zeta_z^2$$

$$+ \gamma_0 \sum_{i=1}^{3} \zeta_i \zeta_i + \gamma_0^3 (1 - \nu^2) e_2 \zeta_z^2$$

(3.4)

where

$$D_0 = \left[ e_1 e_2 - \frac{\nu}{2} \gamma_0^3 (1 - \nu^2) \zeta_z \right] e_3 e_3 + \frac{1}{2} \gamma_0^3 (1 + \nu^2) \zeta_z$$

is the determinant $D$ with $\gamma_0 = 0$, and $\zeta_z^2 = 2 \zeta_x \zeta_y$. We have used Eq. (3.3a) so that all the dependence on azimuthal angle is in $D$.

Up to this point the calculation is exact in terms of the SW Hamiltonian. However, the angular dependence of $J$ makes the subsequent calculation complicated. We now assume that the effect of $\gamma_0$ is small, and expand in powers of $\gamma_0^3/\gamma_0$. Since the first-order contribution is zero by symmetry, we retain terms through second order in $\gamma_0^3/\gamma_0$. With these considerations, the integral on $k_x k_y$ can be easily performed in polar coordinates, giving a sum of terms that are ratios of polynomials in $\zeta_z$, some of which are multiplied by $\ln(e_2/e_1)$. The $k_z$ integration must be done numerically, so we next proceed with the Matsubara sum on $n$. The logarithms can be converted to simple poles by introducing a dummy integration,

$$\ln[(\zeta_n + \mu - E)/(\zeta_n + \mu - E)] = \int_{E_z}^{E_z} dE/(\zeta_n + \mu - E),$$

(3.5)

which puts the result in a form that makes the sum on $n$ easy to carry out by transforming to contour integrals in the complex energy plane.

We call the susceptibility calculated using the SW Hamiltonian $\chi_{SW}$. The value of $\chi_{SW}$ is twice $\chi_{2p}$ in Eq. (2.17) as there are two inequivalent $H-K$ axes in the Brillouin zone. The result for $\chi_{SW}$ can be written in two parts,

$$\chi_{SW} = \chi_0 + \delta \chi,$$

(3.6)

where $\chi_0$ is independent of $\gamma_0$ and $\delta \chi$ is the correction to second order in $\gamma_0$. After carrying out the sums and rearranging terms, we find

$$\chi_n = -N_0 \Gamma_3 \frac{(1 - \nu)^2}{12 \left( \frac{f(E) - f(E_1)}{E_3 - E_1} \right)} \left[ \frac{(1 + \nu)^2}{12 \left( \frac{f(E) - f(E_2)}{E_3 - E_2} \right)} \right]$$

$$+ \frac{(1 - \nu)^2}{8 \nu} \left[ \int_{E_3}^{E_3} \frac{f(E)}{E_3 - L} \ln \left( \frac{1 - \nu^2 (E_3 - E_2)}{(1 + \nu)^2 (E_3 - E_1)} \right) \right]$$

(3.7a)

where

$$L = \left[ E_1 (1 + \nu)^2 - E_2 (1 - \nu)^2 \right] / 4 \nu,$$

$$N_0 = \left( \omega \hbar c \right)^2 (2 \gamma_0^3 / 2 \gamma_0^3 c_0),$$

(3.7b)

and where $\zeta = \zeta_0 k_z$, the limits on $\xi$ are from $-\pi$ to $\pi$, and $f(E)$ is the Fermi distribution function.

The normalization $N_0$ contains the extra factor two due to the two inequivalent $H-K$ axes in the Brillouin zone. Also, we find

$$\delta \chi = -N_0 \gamma_0^3 \frac{\pi}{4} \int_{E_z}^{E_z} dE \frac{\partial}{\partial E_z} \left[ \int_{E_z}^{E_z} \frac{G(E_z) - G(E_2)}{E_3 - E_2} dE \right],$$

(3.7b)
\[ + G(E_3) \ln \left( \frac{1 - \nu}{1 + \nu} \right)^2 + G_3(E_3) - \frac{3}{2} f(E_3) \]  

(3.8a)

where

\[ G(E) = f(E) \left( (x_1 + x_2)/(x_1 - x_2)^2 \right) \]

\[ \times \left( x_1^2 + 2 x_1 x_2 + 4 x_2^2 \right), \]

(3.8b)

\[ G_3(E) = \frac{1}{2} f(E) \left( (x_1 + x_2)/(x_1 - x_2)^2 \right). \]

(3.8c)

and where \( x_1 = (1 + \nu)^2(E - E) \) and \( x_2 = (1 - \nu)^2(E - E_3) \). The expression for \( \chi_0 \) in Eq. (3.7a) is equivalent to that previously obtained.\(^3\)

The high-temperature limit has been used to estimate\(^8\) the value of the parameter \( \gamma_0 \). It should be instructive to see if the terms due to the inclusion of trigonal warping could alter the high-temperature limit of \( \chi_{SW} \). To second order in \((\gamma_4/\gamma_0)\), the high-temperature limits are

\[ x_0 = -\pi N(\gamma_0^2 - \frac{2}{3} \gamma_4^2) / 6b \chi_x, \]

(3.9a)

\[ \delta x = \pi N(\nu(1 - \frac{3}{2} \gamma_4^2) / 6b \chi_x. \]

(3.9b)

The corrections due to \( \gamma_4 \) are small as for usual parameters \((\gamma_4/\gamma_0)^2 \approx 0.3\% \). Typical values of \( \gamma_0 \) and \( \gamma_4 \) indicate about a 1% correction to the high-temperature limit of \( \chi_{SW} \) due to \( \gamma_3 \).

At low temperature, \( x_0 \) is approximately proportional to \( \gamma_4^2/\gamma_1 \) and \( \delta x \) is approximately proportional to \( \gamma_4^2/\gamma_2 \). Thus the fractional correction at low temperatures is \((\gamma_4/\gamma_0)^2 \gamma_4^2 \), significantly larger than the high-temperature correction \((\gamma_3/\gamma_0)^2 \).

To obtain \( \chi_{SW} \) as a function of temperature and Fermi level, the integrations on \( \chi_0 \) and \( \chi_x \) must be done numerically. It is economical of computer time to first evaluate \( \chi_{SW} \) at zero temperature. In the zero-temperature limit, the Fermi function becomes a "step" function in \( \nu - E \), so that the energy integrations and differentiations in Eqs. (3.7a) and (3.8a) can be done analytically. Care must be taken in the numerical integration on \( \chi_x \) due to the appearance of singularities. For intrinsic material, \( \mu = -0.024 \) eV, about \( \frac{1}{4} \) of \( x_0 \) comes from the region near \( \mu = E_\chi \), which we take to be a slice whose thickness is 10% of the \( K^-H \) distance. About 75% of \( \chi_x \) comes from the same region, which is also where the Fermi-surface "legs" are located. However, we cannot correlate this contribution with the details of the Fermi surface as we have made a power expansion in \( \gamma_3 \).

The zero-temperature susceptibility as a function of Fermi level is shown in Fig. 1. For all values of \( \gamma_0 \) there is a logarithmic singularity at \( \mu = \gamma_0(\Delta/\gamma_3) \approx 0 \) if \( \gamma_3 \) and \( \Delta \) have the same signs. The effect of \( \gamma_3 \) is to introduce inverse-square-root singularities on either side of \( \mu = 2\gamma_3 \). The susceptibility is strongly diamagnetic when the Fermi level is near the doubly-degenerate \( E_3 \) band, weakly diamagnetic or paramagnetic in most of the rest of the overlap region, near zero outside the overlap region, \(-0.764 \mu < 0.764 \) eV.

FIG. 1. Magnetic susceptibility of graphite at 0°K as a function of Fermi level. The magnetic field is parallel to the \( c \) axis. The calculation is for the Slonczewski-Weiss band model with the parameter values: \( \gamma_0 = 3.11 \) eV, \( \gamma_1 = 0.376 \) eV, \( \gamma_2 = -0.0208 \) eV, \( \gamma_4 = 0.197 \) eV, \( \gamma_3 = -0.01 \) eV, and \( \Delta = -0.012 \) eV. The solid curve is for \( \gamma_3 = 0.29 \) eV and the broken curve is for \( \gamma_3 = 0.0 \). The susceptibility changes sign at \( \mu = \pm 0.4 \) eV, and is zero outside the overlap region, \(-0.764 \mu < 0.764 \) eV.

This method is particularly suitable because of the limited range of \( \mu \) in which \( \chi_{SW} (\mu, 0) \) is nonzero. The infinite singularities in \( \chi_{SW} (\mu, 0) \) are all integrable, but special care must be taken in the numerical method. Our calculations reproduce the previous result\(^3\) when the same energy-band parameters are used. The use of Eq. (3.10) clearly indicates that the effects of thermal variation in the model parameters are not included. These effect will be discussed in Sec. IV.

The variation with temperature in the Fermi level was taken into account. The computer program calculated the difference in hole and electron concentrations at each temperature and Fermi level chosen.\(^{16}\) It then used an interpolation scheme to find the Fermi level for any specified excess carrier concentration, and the susceptibility appropriate to that Fermi level.

IV. DISCUSSION OF RESULTS

Our numerical calculations show that the effect of taking \( \gamma_3 = 0.3 \) eV while the other parameters have reasonable values is to increase the diamag-
netism by about 13% at low temperatures and reduce it by about 1.2% at high temperatures. Thus the crude estimate given earlier is valid only at high temperatures. We will see below that the increase in diamagnetism at low temperatures is essential in fitting the experimental data.

The most complete data for the magnetic susceptibility of pure graphite as a function of temperature was taken by the torque method, which gives the magnetic anisotropy $\chi_3 - \chi_1$, where $\chi_3$ is the magnetic susceptibility along the $c$-axis and $\chi_1$ is that perpendicular to the $c$ axis. The most modern data was taken by Poquet et al., and is in fair agreement with the older data of Ganguli and Krishnan. Our calculation shows that $\chi_3$ is equal to $\chi_{3w}$ plus a constant (independent of temperature and Fermi level). The theoretical expression for $\chi_1$ has a similar form. It has been estimated that the temperature-dependent part of $\chi_1$ is only about one-thousandth of the temperature-dependent part of $\chi_3$, so that we will adopt the expression

$$\chi_3 - \chi_1 = \chi_{3w} + \chi_B,$$

where $\chi_3$ is independent of temperature and Fermi level, and combines the previous constant with $\chi_B$. In our work $\chi_B$ is a disposable constant which is used to obtain a good fit to the data. It would, however, be interesting to calculate $\chi_B$. We have calculated one of the contributions to $\chi_B$, the correction coming from the extension of the region of integration to infinity. We choose the radius of the cylindrical region of integration to be one-tenth the $K$-$M$ distance and find a value of $2.4 \times 10^{-8}$ cm$^3$/g (we now divide the theoretical susceptibility by the density of graphite at 0 K, 2.22 g/cm$^3$, to obtain the specific susceptibility). Effects which are nearly isotropic, such as the Pauli paramagnetism and the diamagnetism of the 1s bands, will not contribute importantly to the magnetic anisotropy.

Our assumption that $\chi_3$ is constant could be criticized on the grounds that the measured $\chi_3$ is temperature dependent, varying by about $0.4 \times 10^{-6}$ cm$^3$/g. However, this quantity is difficult to measure, and if the sample is bent the measured value is a combination of the true $\chi_1$ and the temperature-dependent $\chi_3$. In any case, the variation is small compared to the magnetic anisotropy, though it is about twice the discrepancy of fit in our best results.

In fitting the experimental results, we have assumed that the samples are perfectly pure and that the energy-band structure does not change with temperature. Our best result is shown in Fig. 2. It is seen that the fit is quite satisfactory, except at 20 °K. As will be discussed below, the band parameters used in the calculation give agreement with a number of other experimental results.

![Fig. 2. Magnetic anisotropy of graphite as a function of inverse temperature. The circles are the experimental data for pure graphite (Ref. 2). The numbers on the curves represent $(p - m) \times 10^4$, where $p$ and $m$ are the numbers of free holes and electrons per carbon atom. The curves are calculated using the parameters listed in the caption of Fig. 1, and with $\chi_B = 2.0 \times 10^{-6}$ cm$^3$/g.](image)

We have calculated the magnetic susceptibility versus temperature for a wide variety of sets of band parameters. The procedure was to fix the values of $\gamma_0$, $\gamma_b$, $\gamma_d$, and $\Delta$, and to choose values of $\gamma_1$, $\gamma_2$, and $\gamma_4$ which gave agreement with the majority de Haas–van Alphen periods and effective masses, and with the valence-band effective mass at point $K$. Fixing both the valence- and conduction-band effective masses at point $K$ gives agreement with the magnetoreflection results from point $K$. A least-squares technique was used, as there were five experimental data and three parameters. The five quantities were always fit within or almost within the experimental uncertainties. Values of these and other properties for the band parameters used in Fig. 2 are listed in Table I.

The high-temperature susceptibility depends almost exclusively upon $\gamma_0$ and $\chi_B$. In the previous work $\chi_B$ was not included and $\gamma_0$ had to be set to 2.8 eV in order to obtain agreement with the high-temperature results. However, the magnetoreflection results at the $H$ point yield that $\gamma_0 = 3.11 \pm 0.05$ eV. In the previous work $\gamma_1$ had to be chosen as small as 0.27 eV in order to obtain a large enough diamagnetism at low temperatures. This conflicts with the value from the infrared absorption, $\gamma_1 = 0.4$ eV, and the values of $\gamma_d$ and $\gamma_1$ used violate the relation $\gamma_d^2/\gamma_1 \approx 25$ eV, which is obeyed by the de Haas–van Alphen effect, cyclo-tron resonance, and magnetoreflection at the $K$ point. In addition, the parameter set used in previous work does not agree with the other information derived from the de Haas–van Alphen effect and magnetoreflection. However, the increase in the low-temperature diamagnetism due to $\gamma_3$ allows
TABLE 1. Comparison of experimental and theoretical properties for the energy-band parameters listed in the caption of Fig. 1 and for a Fermi level of $-0.0246$ eV.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>de Haas–van Alphen frequencies (in tesla)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>majority electron</td>
<td>$6.62 \pm 0.13^a$</td>
<td>6.67</td>
</tr>
<tr>
<td>minority hole 1</td>
<td>$4.83 \pm 0.10^a$</td>
<td>4.76</td>
</tr>
<tr>
<td>minority hole 2</td>
<td>$0.33 \pm 0.02^a$</td>
<td>0.23</td>
</tr>
<tr>
<td>Effective masses (divided by free-electron mass)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>majority electron</td>
<td>$0.089 \pm 0.002^a$</td>
<td>0.058</td>
</tr>
<tr>
<td>minority hole 1</td>
<td>$0.040 \pm 0.002^a$</td>
<td>0.041</td>
</tr>
<tr>
<td>minority hole 2</td>
<td>$0.006^a$</td>
<td>0.003</td>
</tr>
<tr>
<td>valence band at $K$</td>
<td>$0.105 \pm 0.003^a$</td>
<td>0.106</td>
</tr>
<tr>
<td>$(p-n) \times 10^5$</td>
<td>$\pm 0.04/\text{atom}^a$</td>
<td>0.02/atom</td>
</tr>
<tr>
<td>$\frac{1}{2}(p+n) \times 10^4$</td>
<td>$(2.5 \pm 0.3)/\text{atom}^a$</td>
<td>2.2/atom</td>
</tr>
</tbody>
</table>

$^a$Reference 18.
$^b$Reference 26.
$^c$References 27 and 28.
$^d$Reference 4.


A larger $\gamma_1$ to be chosen and the use of the constant $\chi_b$ allows $\gamma_0$ to have other values. In fact, it is possible to fit the susceptibility data with $\gamma_0$ values ranging at least from 2.8 to 3.2 eV. In our discussion, a reasonable fit to the magnetic anisotropy means that the maximum deviations after the optimum $\chi_b$ is chosen are less than $0.4 \times 10^{-6}$ cm$^3$/g.

The parameters $\gamma_3$ and $\Delta$ have important effects upon the magnetic anisotropy, while the effect of $\gamma_0$ is minor. For fixed values of $\gamma_0$ and $\gamma_3$ we can make a reasonable fit by adjusting $\Delta$ and $\chi_b$. Thus for $\gamma_0 = 3.11$ eV and $\gamma_3 = 0.29$ eV, the values in the range $\Delta = -0.01 \pm 0.002$ eV give good fits, but if $\gamma_0 = 0.21$ eV, $\Delta$ must be chosen less than $-0.02$ eV. The value $\gamma_0 = 0.29$ eV has been found by Schroeder et al. from the K-point magnetoreflection results, while Ushio et al. found $\gamma_0 = 0.21$ eV from the cyclotron-resonance results. The analysis of the magnetoreflection at the $H$ point indicates that $|\Delta| = 0.008 \pm 0.004$ eV, which favors the higher value of $\gamma_3$. Negative values of $\Delta$ in this range are consistent with the minority carrier de Haas–van Alphen frequency from the $H$ point being the lower of the two observed values. To obtain agreement with the higher minority frequency (or with the average of the two frequencies, as proposed by Woollam) requires $\Delta$ values of the order of $0.004$ eV or larger. To fit the susceptibility with such $\Delta$ values would require a $\gamma_0$ of at least 0.35 eV. Thus the parameter set used in Fig. 2 agrees with the diamagnetism, de Haas–van Alphen effect, optical absorption, and magnetoreflection at both the $H$ and $K$ points. It disagrees with the $\gamma_3$ value found from the cyclotron resonance and with the alternant interpretations of the minority-carrier de Haas–van Alphen effect. The changes necessary to agree with the latter two results are incompatible.

Since we now calculate the susceptibility per unit mass, there is no temperature dependence due to the change in the volume of the unit cell, but the values of the energy-band parameters do depend upon the temperature. However, at high temperature where the band parameters have changed the most, the susceptibility depends chiefly upon the value of $\gamma_0$. The $a$ spacing (in-plane) changes by about 0.1%, from 0 to 2000 K, which would cause a change in $\gamma_0$ of only about 0.4%, a negligible effect in the present work. In contrast, the change in the $c$ spacing in the same temperature range is 5.6%, though it is only 0.5% from 0 to 300 K. Estimates of the rate of change of the band parameters with $c$ spacing were taken from the de Haas–van Alphen experiments as a function of pressure. The rate of change of the susceptibility with each band parameter was calculated directly. The results are that the temperature dependencies of $\gamma_1$ and $\Delta$ have the largest effects, and the total effect could cause deviations of $\pm 0.4 \times 10^{-6}$ cm$^3$/g. As pointed out before, this error is small compared to the magnetic anisotropy, but is about twice the maximum deviation in our best fit.

The most serious discrepancy is at 20 K, where the experiment is $2.0 \times 10^{-6}$ cm$^3$/g more diamagnetic than the theory, an error of 6.6%. This discrepancy remains about the same for all the parameter sets tested. One possible explanation is that the power series in $\gamma_3$ is not accurate enough. A priori, since the $\gamma_3^2$ term made a 13% correction, one would expect the $\gamma_3^4$ term to make a correction of $0.5 \times 10^{-6}$ cm$^3$/g. However, the coefficient of the $\gamma_3^4$ term could be four times larger than expected. Another possibility is experimental error. Shoenberg's de Haas–van Alphen data at 1.27 K oscillate about $-30.7 \times 10^{-6}$ cm$^3$/g. This is in good agreement with the data of Poquet et al. at 20 K. Our calculations show that the susceptibility changes by less than $0.1 \times 10^{-6}$ cm$^3$/g between 0 and 20 K. However, Shoenberg has stated that his magnetic-field calibration was probably off a few percent. His de Haas–van Alphen periods are 4% higher than those of Berlincourt and Steele and 8% higher than those of Soule et al., so that the corrected average magnetic anisotropy is $-29.5 \times 10^{-6}$ cm$^3$/g or $-28.4 \times 10^{-6}$ cm$^3$/g. In the data of Berlincourt and Steele the average is about $-34 \times 10^{-6}$ cm$^3$/g, but the average depends upon temperature and magnetic-field strength, so the value is unreliable. It would be useful if a new measurement of the low-temperature diamagnetism could
be made.

We have also compared with the data on the magnetic susceptibility as a function of boron content at 300 K. Boron is known to be an acceptor in the graphite single crystal. In Fig. 3 we plot the experimental data for the magnetic anisotropy versus the boron content and the theoretical curve for the magnetic anisotropy versus the excess hole density (assuming the rigid-band model). There is a discrepancy for pure material due to the discrepancy between the data of Poquet et al. (to which the theory was fitted) and the data of Soule. Soule measured $\chi_A$ and $\chi_I$ directly, and the anisotropy is obtained by subtraction. We assume that the discrepancy is due to the difficulty of measuring $\chi_A$ and recalculate the theory with a different $\chi_A$ chosen to agree with Soule's data. We also follow Soule and assume that a fixed fraction of the boron ionizes, producing the dashed curve, which is in reasonable agreement with experiment. There is also data on the diamagnetism of boronated polycrystalline graphite as a function of temperature. The data qualitatively agree with the family of curves in Fig. 2, but differs quantitatively. This may be due to the difference between single and polycrystalline samples.

**ACKNOWLEDGMENTS**

The authors wish to thank Dr. H. Fukuyama for useful discussions, and Mr. K. Johnson for writing and testing the program for choosing the band parameters to fit the de Haas–von Alphen properties and the subroutine for calculating the carrier densities. Thanks are also due to Professor M. S. Dresselhaus and colleagues for communicating their results prior to publication.

*Work supported by the National Science Foundation under Grant No. GP-29086.
†Based on a thesis submitted by one of the authors (M.P.S.) in partial fulfillment of the requirements for the Ph.D. degree at the University of Oregon.
§Present address: Instituto de Física, Universidade Estadual de Campinas, Barão Geraldo, Campinas, Brazil.
3J. W. McClure, Phys. Rev. 119, 606 (1960). The factors $\pi$ in Eqs. (2.8a), (2.11a), and (2.11b) should be factors $\pi$. This misprint did not affect the numerical work.
13For further details of the calculations, see M. P. Sharma, Ph.D. dissertation (University of Oregon, 1973) (unpublished), to be available from University Microfilm Corporation, Ann Arbor, Mich. 48106.
W. W. Toy, C. R. Hewes, and M. S. Dresselhaus, Carbon (to be published).


D. Schoenberg, Trans. R. Soc. Lond. 245, 1 (1952).

D. Shoenberg (private communication).

