Theory of magnetic susceptibility of graphite intercalation compounds

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The orbital magnetic susceptibility (χ_{or}^c) of graphite intercalation compounds is calculated for $\vec{H} \| \vec{c}$ using a tight-binding model for the π-electron energy bands and the compact expression for χ_{or}^c derived by Fukuyama, which includes both intraband and interband terms. The results are presented as an approximate analytic expression for χ_{or}^c as a function of Fermi level μ ($0 < \mu \lesssim 3$ eV) and temperature. For $\mu/k_B T \ll 1$ the susceptibility is large and diamagnetic (due to interband transitions), while for $k_B T \ll \mu \lesssim 3$ eV, χ_{or}^c is paramagnetic (mainly due to intraband transitions) in contrast to the usual Landau-Peierls diamagnetism of conduction electrons in parabolic bands. Furthermore, χ_{or}^c is shown to be a sensitive function of μ and hence of the conduction-electron charge distribution in each graphite layer. We show that this theory accounts for the main features of the experimental data (stage and temperature dependence of χ_{or}^c) and suggest that measurements of the stage dependence of χ_{or}^c can be used to estimate the c-axis screening length in graphite intercalation compounds.

I. INTRODUCTION

Graphite intercalation compounds (GIC) are characterized by high basal-plane conductivities and by an ordered sequence of n carbon and one intercalant layer, with n defining the stage of the material.[1] The c-axis charge distribution of the carriers donated to the carbon by the intercalant is a problem of current experimental[2,3] and theoretical[4] interest. While early studies[5] assumed a uniform distribution of charge in all the graphite layers, recent theoretical[4] and experimental[2,3] evidence indicates that the screening of the intercalant layer should result in a localization of the charge near the carbon layers which bound the intercalate. In this paper we calculate the magnetic susceptibility of a single graphite layer for a wide range of Fermi energies and show how our results can be used to interpret the susceptibility measurements in GIC (Refs. 6–8) to yield information about the charge distribution along the c axis.

Although the susceptibility of intrinsic graphite is large and diamagnetic,[9,10] recent experiments,[7,8] in alkali GIC have shown that the susceptibility χ^c for the magnetic field parallel to the crystalline c axis ($\vec{H} \| \vec{c}$) is paramagnetic. Furthermore, the ratio of χ^c to the (estimated) Pauli (spin-only) contribution to the susceptibility (χ_P), increases rapidly as a function of stage, varying from $\simeq 2$ in stage 1 to 17 in stage 4. Since the *anisotropy* in the susceptibility also increases with stage, the observed enhancement of χ^c over χ_P cannot be attributed to Coulomb enhancement[11] of χ_P which should be isotropic. The calculations presented here indicate that the large paramagnetic values observed for χ^c in GIC arise from a *paramagnetic* orbital susceptibility. In addition, the stage and

temperature dependence of the experimental data can be understood in the light of our calculations which use the formula for the orbital susceptibility (χ_{or}^c) derived by Fukuyama.[12] This formalism has been used by Sharma *et al.*[9] to calculate the magnetic susceptibility of intrinsic graphite. However, the calculations of Ref. 9 use the Slonczew-ski-Weiss (SW) model[13] which was developed to treat the band structure for the small (~ 0.024 eV) values of the Fermi energies and carrier concentration ($\sim 10^{-4}$ per carbon atom) appropriate to pure graphite. Since the Fermi energy in GIC can be as large as 1–2 eV (corresponding to $\sim 10^{-1}$ carriers per carbon atom), a more general calculation is necessary for the understanding of the magnetic susceptibility of these materials.

In Sec. II we review the single-layer, tight-binding model[14] for the electronic energy-band structure of graphite which will be used in the calculations of χ_{or}^c in Secs. II–IV. In order to simplify our calculations, we transform Fukuyama's formula using some manipulations suggested in Ref. 9. In Sec. III we calculate χ_{or}^c analytically for very small and very large values of the Fermi energy. Our results reduce to those previously obtained in Ref. 15 for small values of the Fermi energy. In the limit of both high temperatures and small values of the Fermi energy, our results reduce to those obtained in Ref. 9 where the (three-dimensional) SW model was used.

Section IV contains the most significant result of our calculation—an (approximate) analytic form for χ_{or}^c as a function of both temperature and Fermi level μ for $0 < \mu \leq 3$ eV. For $\mu \ll k_B T$ we show that χ_{or}^c is diamagnetic ($\chi_{or}^c < 0$), while for $\mu \geq 4k_B T$ χ_{or}^c is paramagnetic ($\chi_{or}^c > 0$). For large values of $\mu \simeq 3$ eV, the paramagnetism of χ_{or}^c is due to the negative value of one component of the effective-

mass tensor near the saddle point in the density of states. This is in contrast to the usual result $\chi_{or}^c < 0$ (Landau diamagnetism[16]) for parabolic bands near an energy minimum or maximum. The results of the single-layer model for χ_{or}^c are applied to the case of GIC in Sec. V, where the interpretation of the experimental results and the limitations of the theory are also discussed. (For the details of the experiments and their interpretation see the preceding paper.[8])

II. TIGHT-BINDING MODEL AND FUKUYAMA FORMULA

In this section, we rewrite Fukuyama's formula for χ_{or}^c in a form convenient for calculations in the tight-binding model. The tight-binding model for graphite is reviewed, and an explicit form for the orbital and Pauli susceptibilities is given in terms of $\vec{k}$-space integrals.

The general formula for χ_{or}^c derived by Fukuyama[12] for $\vec{H} \| \vec{c}$ is

$$\chi_{or}^c = \left(\frac{e}{\hbar c}\right)^2 k_B T \frac{1}{8\pi^3} \sum_n \int d\vec{k}\, \text{Tr}(\gamma_x g \gamma_y g \gamma_x g \gamma_y g) . \tag{1}$$

In Eq. (1) χ_{or}^c is dimensionless and the spin degeneracy has been included; g is the Matsubara Green's function[17]

$$g = (\epsilon_n - \mathcal{H})^{-1} , \tag{2}$$

where $\epsilon_n = (2n+1)\pi i k_B T + \mu$, $\mathcal{H}$ is the Hamiltonian matrix, and μ is the Fermi energy. The matrix γ_i $(i = x, y)$ is the product of the matrix representation of the momentum operator and the factor $\hbar/m$, while the integral is over the first Brillouin zone and n runs from $-\infty$ to ∞. Equation (1) is valid in any basis where $\mathcal{H}$ is diagonal in $\vec{k}$ but not necessarily in the band indices. This expression for χ_{or}^c has the following interpretation.[18] An electron is given an impulse in the x direction (γ_x), propagates (g), is given an impulse in the y direction (γ_y), propagates (g), etc., until it is back where it started from. Thus the electron orbit is a closed path which represents a magnetic moment.

In order to calculate χ_{or}^c for a large range of Fermi energies, we use the tight-binding representation for the graphite energy bands,[14] which yields an expression for the energy $E(\vec{k})$ which is periodic in $\vec{k}$ space. Furthermore, since the details of the c-axis interactions and charge distributions are presently unknown in GIC for $n > 1$, we use a two-dimensional model for the π bands of each graphite layer. The Fermi energy can then be written

$$\mu = \mu_i + V_i , \tag{3}$$

where i is an index specifying the graphite layer, μ_i represents the contribution to the Fermi level

from the carriers in that layer, and V_i is the potential at layer i due to the screened intercalant layer. Our treatment is thus a first approximation to the complete band structure of GIC, since we assume that the intercalate potential provides a constant shift of the two-dimensional graphite bands of *each* layer. The electron charge density in each layer is thus an adjustable parameter in our theory. The advantage of this approach is its tractability in a calculation of χ_{or}^c and the presence of only one adjustable parameter (μ_i) which is of direct physical significance. In Secs. II–IV we shall deal with the properties of a single graphite layer, so we replace μ_i by μ, which will be termed the Fermi level in these sections.

In a tight-binding model which treats only the π band of graphite, a nearest-neighbor approximation yields[14]

$$\mathcal{H} = \begin{pmatrix} 0 & H(\vec{k}) \\ H^*(\vec{k}) & 0 \end{pmatrix} , \tag{4}$$

where

$$H(\vec{k}) = \gamma_0 \left(e^{ik_x a/\sqrt{3}} + 2 \cos\frac{k_y a}{2} e^{-ik_x a/2\sqrt{3}} \right) . \tag{5}$$

Here a is the in-plane graphite lattice constant, while recent estimates[9] of γ_0 indicate $\gamma_0 = 3.11$ eV. Since the matrix g^{-1} is now finite, it can be inverted to yield

$$g = \frac{N}{D} = \frac{1}{D} \begin{pmatrix} \epsilon_n & H(\vec{k}) \\ H^*(\vec{k}) & \epsilon_n \end{pmatrix} , \tag{6}$$

where

$$D = \epsilon_n^2 - E^2 , \tag{7a}$$

$$E^2 = H(\vec{k})H^*(\vec{k}) . \tag{7b}$$

By symmetry, matrix elements of the momentum operator $(\vec{p}^{op})$ between two π orbitals centered at nearest-neighbor sites separated by $\vec{R}_i$ are proportional to $\vec{R}_i$. From the tight-binding expression for $H(\vec{k})$ it can be seen that

$$\vec{\gamma} = \alpha \nabla_k H(\vec{k}) , \tag{8}$$

where α is a proportionality constant. From a $\vec{k} \cdot \vec{p}$ expansion of the Hamiltonian near the K point in Brillouin zone where $H(\vec{k}) = 0$,[13,15] one can show that in our units $\alpha = 1$.

In Appendix A we show that the susceptibility can be rewritten

$$\chi_{or}^c = \left(\frac{e}{\hbar c}\right)^2 \frac{1}{8\pi^3} k_B T \sum_n \int d\vec{k} \frac{1}{D^2}(\chi_I + \chi_{II} + \chi_{III} + \chi_{IV}) \tag{9}$$

where χ_I, χ_{II}, χ_{III}, and χ_{IV} are given by

$$\chi_I = \tfrac{1}{3}(D_{xy}^2 - D_{yy}D_{xx}) - \mathrm{Tr}(\gamma_x N\gamma_x N_{yy}),\qquad(10a)$$

$$\chi_{II} = -\tfrac{1}{2}D_{yy}\,\mathrm{Tr}(\Omega N) - \tfrac{1}{2}D_y\,\mathrm{Tr}(\Omega N_y),\qquad(10b)$$

$$\chi_{III} = -\tfrac{1}{2}D_y\,\mathrm{Tr}(\Omega_y N),\qquad(10c)$$

$$\chi_{IV} = -\mathrm{Tr}(\omega N\gamma_x N_y) - \mathrm{Tr}(\gamma_x N\omega N_y).\qquad(10d)$$

In Eqs. (10), Ω and ω are matrices defined by

$$\Omega = \frac{\partial \gamma_x}{\partial k_x} \quad \text{and} \quad \omega = \frac{\partial \gamma_x}{\partial k_y},\qquad(10e)$$

while the subscripts (x, y) on N and D indicate differentiation with respect to (k_x, k_y), respectively. This form for χ_{or}^c is valid for any Hamiltonian matrix where Eq. (8) applies and $H(\vec{k})$ is periodic in $\vec{k}$ space. This is in contrast to Eq. (2.17) of Ref. 9 which is an approximation designed to treat only the linear terms in an expansion of $H(\vec{k})$. The advantage of Eq. (9) over the original formula for χ_{or}^c [Eq. (1)] is that the dependence on the index n is contained only in the factor $1/D^2$ in our case. Furthermore, if $H(\vec{k})$ is now expanded to order k^2, $\chi_{III} = 0$, while if only the linear terms in $H(\vec{k})$ are kept, only χ_I is nonzero.

We now perform the sum over the index n. For the 2×2 Hamiltonian matrix of Eq. (4) the factor D^{-2} can be rewritten as

$$\frac{1}{D^2} = \frac{1}{2E}\frac{\partial}{\partial E}\frac{1}{D},\qquad(11)$$

where we have used Eq. (7). Furthermore we can write

$$\frac{1}{D} = \frac{1}{2E}\left(\frac{1}{\epsilon_n - E} - \frac{1}{\epsilon_n + E}\right).\qquad(12)$$

Using the fact that[19]

$$k_B T \sum_n (\epsilon_n - E)^{-1} = f(E - \mu),\qquad(13)$$

where $f(E - \mu)$ is the Fermi factor, we find that

$$k_B T \sum_n \frac{1}{D^2} = \frac{1}{2E}\frac{\partial}{\partial E}\left(\frac{f(E-\mu) - f(-E-\mu)}{2E}\right).\qquad(14)$$

The orbital susceptibility as a function of $\epsilon_0 \equiv \mu/\gamma_0$ can be rewritten using Eq. (14) so that

$$\chi_{or}^c(\epsilon_0) = \chi_0 \int_0^\infty d\epsilon\, h(\epsilon)\left[\frac{1}{2\epsilon}\frac{\partial}{\partial\epsilon}\right.$$
$$\left.\times\left(\frac{f(\epsilon - \epsilon_0) - f(-\epsilon - \epsilon_0)}{2\epsilon}\right)\right].\qquad(15)$$

The integral over ϵ in Eq. (15) is for $\epsilon \geq 0$ only. The existence of two bands with energies $\pm E(\vec{k})$ is accounted for in the $1/D$ factors and by the two Fermi functions in Eq. (15). The constant χ_0 is given by

$$\chi_0 = \left(\frac{e\hbar}{mc}\right)^2 \frac{1}{2\gamma_0\Omega_0} \simeq 2\times10^{-6},\qquad(16)$$

and $\Omega_0 = \tfrac{1}{2}\sqrt{3}\,a^2 c_0$ is the volume of a primitive unit cell of a single layer ($c_0 = 3.35$ Å). In Eq. (15) all energies are scaled by γ_0 so that

$$h(\epsilon) = \left(\frac{2\Omega_0}{8\pi^3}\right)\left(\frac{m}{m^*}\right)^2 \sum_{i=1}^6 \int d\vec{k}\,\delta(\epsilon - \epsilon(\vec{k}))\,\chi_i/(\gamma_0 a)^4,\quad(17)$$

where

$$\frac{m}{m^*} = \frac{\gamma_0 a^2 m}{\hbar^2} \simeq 2.5\qquad(18)$$

is an average effective mass and

$$\chi_1 = \tfrac{1}{3}(D_{xy}^2 - D_{yy}D_{xx}),\qquad(19a)$$

$$\chi_2 = -2\,\mathrm{Re}(H_x^2 H^* H_{yy}^*),\qquad(19b)$$

$$\chi_3 = -D_{yy}\,\mathrm{Re}(H_{xx}H^*),\qquad(19c)$$

$$\chi_4 = -D_y\,\mathrm{Re}(H_{xx}H_y^*),\qquad(19d)$$

$$\chi_5 = -D_y\,\mathrm{Re}(H_{xxy}H^*),\qquad(19e)$$

$$\chi_6 = -4\,\mathrm{Re}(H_x H_{xy}H^* H_y^*).\qquad(19f)$$

In Eq. (19)

$$D_{ij} = \frac{\partial}{\partial k_i}\frac{\partial}{\partial k_j}D,$$

while

$$H_{ij} = \frac{\partial}{\partial k_i}\frac{\partial}{\partial k_j}H(\vec{k}).$$

The Fermi level and temperature dependence of χ_{or}^c are determined by the factor in square brackets in Eq. (15), which contains both interband and intraband terms, while $h(\epsilon)$ depends on the curvature of the bands. We note that while $h(\epsilon)$ can be either positive or negative, its magnitude is proportional to $(m/m^*)^2$. For future reference we give the standard expression for the Pauli contribution to χ^c,[20]

$$\chi_P(\epsilon_0) = \chi_0\frac{\Omega_0}{8\pi^3}\int d\vec{k}\,\delta(\epsilon_0 - \epsilon(\vec{k})).\qquad(20)$$

III. ANALYTIC APPROXIMATIONS

In this section, we use Eqs. (15)–(20) to evaluate the susceptibility analytically near the band minimum ($E = 0$) and the saddle point ($E = \gamma_0$) in the density of states. The general features of χ_{or}^c derived from these calculations—diamagnetism for small μ and paramagnetism for large μ—are corroborated by the more detailed calculations of Sec. IV.

For small values of the Fermi energy, we can

expand $H(\vec{k})$ in $\vec{k}$ near the energy minimum (and degeneracy point) at $\vec{k}=(2\pi/\sqrt{3}a, 2\pi/3a, 0)$. Keeping only the linear terms in this expansion, we find that $\chi_i = 0$ $(i = 2, \ldots, 6)$, while $\chi_1/(\gamma_0 a)^4 = -\frac{3}{4}$. Thus $h(\epsilon)$ is proportional to the density of states and

$$\chi_{or}^c = \chi_0 \left(\frac{m}{m^*}\right)^2 \frac{-\sqrt{3}}{2\pi} \int_0^\infty d\epsilon \frac{\partial}{\partial \epsilon}\left(\frac{f(\epsilon - \epsilon_0) - f(-\epsilon - \epsilon_0)}{2\epsilon}\right) + \bar{\chi} .$$

Here, $\bar{\chi}$ is a constant (independent of ϵ_0) which is due to the neglect of higher order terms in the expanison as well as the extension of the upper limit of integration to ∞. Finally, we find

$$\chi_{or}^c = -\left(\frac{e\hbar}{mc}\right)^2 \frac{1}{8\pi c_0 a^2}\left(\frac{m}{m^*}\right)^2 \frac{1}{k_B T} \operatorname{sech}^2(\mu/2k_B T) + \bar{\chi} ,$$

$$(21)$$

which agrees[21] with the calculation of McClure[15] who derived an expression for χ_{or}^c by summing over the Landau levels obtained in a two-dimensional band model, for $\mu/\gamma_0 \ll 1$. In addition, for high temperatures, our results agree within 1% with the analytic expression for χ_{or}^c derived in Ref. 9 using a three-dimensional SW band structure.

While χ_{or}^c is large and diamagnetic for $\epsilon_0 \ll 1$ (due to interband transitions[15]), near the saddle point in the density of states ($\epsilon_0 \simeq 1$), we find that

$$h(\epsilon) = -\frac{1}{2}\left(\frac{m}{m^*}\right)^2 \rho(\epsilon) , \qquad (22)$$

where $\rho(\epsilon)$ is the density of states, normalized so that $\frac{1}{2}\int_0^\infty \rho(\epsilon) d\epsilon = 1$. Using Eq. (22) in Eq. (15) for $\epsilon \simeq 1$, we find

$$\chi_{or}^c = \chi_0\left[\frac{1}{8}\left(\frac{m}{m^*}\right)^2 \rho(\epsilon_0) + \bar{p}\right] , \qquad (23)$$

where $\bar{p}$ is an interband contribution to χ_{or}^c which is small for $\epsilon_0 \simeq 1$. The orbital susceptibility is thus large and paramagnetic near the saddle point in the density of states. The first term of Eq. (23) can also be derived from a calculation of the Landau-Peierls susceptibility (χ_{LP}^c) which yields[16]

$$\chi_{LP}^c = -\bar{\chi}(m_{xx}^* m_{yy}^*)^{-1}\rho(\epsilon_0) , \qquad (24)$$

where $m_{\alpha\beta}^*$ is the effective-mass tensor and $\bar{\chi}$ is a positive constant. Since $m_{xx}^* m_{yy}^* < 0$ near the saddle point, the susceptibility is paramagnetic for $\epsilon_0 \simeq 1$. This is in contrast to the sign of the orbital susceptibility for ϵ_0 near a band minimum or maximum where $m_{xx}^* m_{yy}^* > 0$ and $\chi_{LP}^c < 0$ for parabolic bands. A comparison of Eqs. (23) and (20) (neglecting $\bar{p}$) indicates that the ratio $r \equiv \chi_{or}^c/\chi_P^c \simeq 1.5$ near the saddle point.

Thus the Fukuyama formula, which includes both interband transitions which dominate for ϵ_0

$\ll 1$ and intraband transitions (Landau-Peierls) which dominate for $\epsilon_0 \simeq 1$, yields both diamagnetism and paramagnetism for χ_{or}^c. The enhancement of the orbital susceptibility over the Pauli contribution for $\epsilon_0 \simeq 1$ as evidenced by the ratio $r \simeq 1.5$ is in general agreement with the susceptibility measurements discussed above.[7,8] In order to derive an expression for χ_{or}^c valid for the range $0 \leq \epsilon_0 \leq 1$, we must evaluate $h(\epsilon)$ [Eq. (17)] numerically. The results of this calculation are discussed in the following section.

IV. FERMI LEVEL AND TEMPERATURE DEPENDENCE OF χ_{or}^c

The section contains the main result of our calculations—an expression for χ_{or}^c as a function of μ and T for $0 < \mu \leq 3$ eV. We present the results of a numerical calculation of the band curvature factor $h(\epsilon)$. These results are fitted to an analytic function of ϵ ($\epsilon = E/\gamma_0$) and the integration of Eq. (15) is performed analytically.

We divide the region of integration ($0 < \epsilon \leq 3$) in Eq. (15) into two parts: region a for $0 \leq \epsilon \leq 1$ and region b for $1 < \epsilon \leq 3$, so that $\chi_{or}^c = \chi_a + \chi_b$. We compute χ_b numerically from a $T = 0$ approximation for the Fermi function in Eq. (15). Since we consider $\epsilon_0 < 1$, χ_b consists of a paramagnetic contribution due to interband transitions, which is independent of temperature and Fermi level for $1 - \epsilon_0 > \tau$ ($\tau = k_B T/\gamma_0 \leq 0.01$). We thus find that $\chi_b \simeq 0.3 \chi_0$. The Fermi level and temperature dependence of χ_{or}^c for $\epsilon_0 < 1$ is thus contained in χ_a.

In order to carefully treat the singular $1/\epsilon^2$ factors in Eq. (15) we fit the results of a numerical integration of $h(\epsilon)$ to the form ($0 \leq \epsilon \leq 1$):

$$h(\epsilon) = -[A\epsilon + B\epsilon^2 + C\epsilon^2 \ln(1 - \epsilon)] . \qquad (25)$$

This fit is motivated by the analytic results of Sec. III, which show that for $\epsilon \simeq 0$ and $\epsilon \simeq 1$, $h(\epsilon)$ is
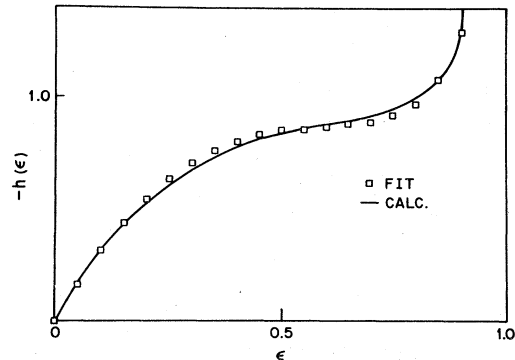

FIG. 1. Plot of the band curvature factor $h(\epsilon)$ defined in Eq. (17). The solid line is the result of a numerical integration of Eq. (17) while the open squares are the fit to this curve calculated from Eq. (25).
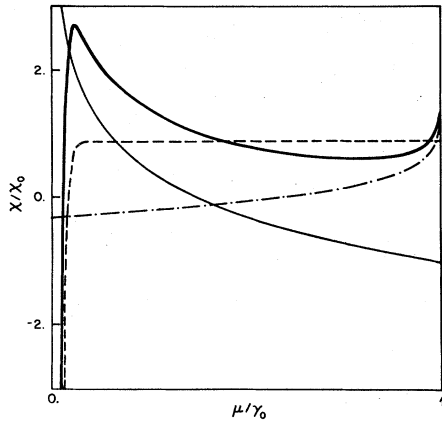
FIG. 2. Fermi-level dependence of χ_{or}^c for $0 \leq \mu/\gamma_0 \leq 1$ for $k_B T/\gamma_0 = 0.0083$ ($T \sim 300$ K). The heavy solid line is χ_{or}^c while the dashed, solid, and dot-dashed lines show the contributions to χ_{or}^c from $\tilde{A}(\epsilon_0)$, $\tilde{B}(\epsilon_0)$, and $\tilde{C}(\epsilon_0)$, respectively [see Eq. (26)]. χ_0 is defined in Eq. (16).

FIG. 3. Temperature dependence of χ_{or}^c as a function of the Fermi level (μ/γ_0). Curves are shown for temperatures $T \simeq 30$, 300, and 750 K. For the Fermi-level dependence χ_{or}^c and χ_p for $0 \leq \mu/\gamma_0 \leq 1$ see Figs. 2 and 3 of the preceding paper (Ref. 8). χ_0 is defined in Eq. (16).

proportional to the density of states which is linear in ϵ near $\epsilon = 0$ and has a logarithmic singularity at $\epsilon = 1$. Figure 1 shows our numerical results for $h(\epsilon)$ as well as a plot of $h(\epsilon)$ calculated from Eq. (25) with the values $A = 3.47$, $B = -4.09$, and $C = -0.79$.

Appendix B contains the details of the integrations of Eq. (15). The result, valid for $0 \leq \epsilon_0 < 1 - \tau$, is

$$\chi_a = \frac{\chi_0}{4}[\tilde{A}(\epsilon_0) + \tilde{B}(\epsilon_0) + \tilde{C}(\epsilon_0)], \qquad (26)$$

$$\tilde{A}(\epsilon_0) = A\left(1 - \frac{1}{2\tau}\text{sech}^2(\epsilon_0/2\tau)\right), \qquad (27a)$$

$$\tilde{B}(\epsilon_0) = B\ln\tau, \quad \epsilon_0/\tau \leq 1 \qquad (27b)$$

$$\tilde{B}(\epsilon_0) = B(1 - \tau/\epsilon_0 + \ln\epsilon_0), \quad \epsilon_0/\tau \geq 1 \qquad (27c)$$

$$\tilde{C}(\epsilon_0) = C\{\ln(1 - \epsilon_0) + [r(1) - r(\epsilon_0)]\}, \qquad (27d)$$

$$r(x) = \sum_{n=1}^{\infty} \frac{x^n}{n^2}. \qquad (27e)$$

In Fig. 2 we plot the various contributions to χ_{or}^c as defined in Eq. (26) for $k_B T/\gamma_0 = 0.0083$ ($T \simeq 300$ K). For $\mu/k_B T \ll 1$, χ_{or}^c is dominated by $\tilde{A}(\epsilon_0)$ and the susceptibility is large and diamagnetic. However, for $\mu/k_B T \geq 1$ this term, which originates from the linear term in an expansion of $E(\vec{k})$ near the K point in the Brillouin zone, approaches a constant paramagnetic value. The peak in χ_{or}^c at $\mu \simeq 8 k_B T$ arises from $\tilde{B}(\epsilon_0)$ which has its origin in the higher-order terms in the expansion of $E(\vec{k})$. Finally, for $\mu \simeq \gamma_0$ the Fermi level dependence of χ_{or}^c is determined by $\tilde{C}(\epsilon_0)$ which has a singularity at $\mu = \gamma_0$ due to the logarithmic singularity in the density of states at the
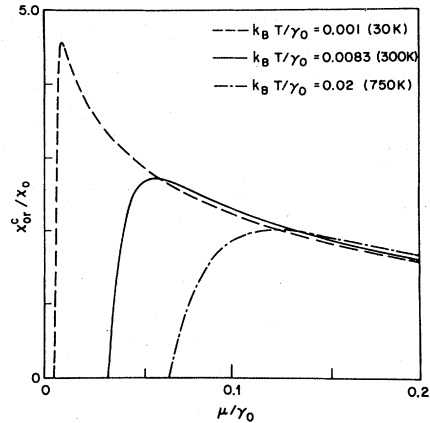
saddle point. On the other hand, the strong Fermi-level dependence of $\tilde{A}(\epsilon_0)$ and $\tilde{B}(\epsilon_0)$ for $\epsilon_0 \ll 1$ arises from the $1/\epsilon^2$ factors in Eq. (15), associated with interband transitions. The temperature dependence of χ_{or}^c near the peak is shown in Fig. 3 where we plot χ_{or}^c/χ_0 as a function of μ/γ_0 for $0 \leq \mu/\gamma_0 \leq 0.2$ for $T = 30$, 300, and 750 K. As indicated in Eq. (27), the peak in χ_{or}^c moves to lower values of μ/γ_0 while the peak height increases as the temperature is lowered. The orbital susceptibility of a single layer of graphite is thus a sensitive function of the Fermi level for $0 < \mu \leq \gamma_0$.

V. DISCUSSION

A detailed comparison of the theory presented here with the experimental data is given in the preceding paper.[8] Here we note that although there are quantitative (factor of 2) differences between our theory and the measured values for χ_{or}^c in the low stage compounds, the simple model presented here is still valuable for the interpretation of the susceptibility experiments, since it correctly predicts the most important features of the data.

(1) The *paramagnetism* of χ_{or}^c for high stage compounds is shown to derive from the presence of the saddle point in the density of states.

(2) The stage dependence of χ_{or}^c and the increase in χ_{or}^c/χ_p from $\simeq 1.4$ ($n = 1$) to 16 ($n = 4$) is shown to arise from the contributions of the interior graphite layers with μ near the peak in χ_{or}^c as shown in Fig. 2. This demonstrates that while χ_p and the specific heat coefficient are sensitive to the charge distribution in the bounding layer

(which contributes the most to the density of states), χ_{or}^c is a sensitive function of the charge distribution in the interior graphite layers. Thus the stage dependence of χ_{or}^c can be used to analyze the c-axis screening length in graphite intercalation compounds.

(3) The observed temperature dependence of χ_{or}^c in stage 4 correlates with a value for μ_i of the order of 0.15 eV for the interior layer, indicating the presence of c-axis screening (μ_i for the bounding layer ~1.5 eV).

Within the context of our simple model, the agreement between theory and experiment could be improved if one could calculate the contribution to χ_{or}^c from the following:

(i) Van Vleck (interband) coupling between the graphite and intercalant conduction bands.

(ii) Electron-electron enhancement of χ_P for the case of the dilute electron gas found in GIC. Larger values for χ_P would result in smaller values for χ_{or}^c in agreement with the theoretical predictions.

(iii) Effects of higher-order interactions in the tight-binding model. To minimize the number of adjustable parameters and to enable us to proceed with a complete calculation using Fukuyama's formula, we have considered only nearest-neighbor graphite-graphite interactions. All interlayer couplings and zone folding due to the intercalate potential were neglected.

Although more realistic band-structure calculations are clearly needed to study the c-axis charge distribution in the higher stage compounds, our single-layer model allows for an interpretation of the experimental results on a layer-by-layer basis as described above and in the preceding paper. This model treats the charge density (and Fermi level) in each level as an adjustable parameter. It is doubtful that a realistic Hamiltonian which contains the interactions of all $6n+1$ atoms in the unit cell (for stage-n Li, for example) could be used in the complete calculation of χ_{or}^c. However, the predictions of realistic calculations of the c-axis charge distribution can be tested against further experimental measurements of χ^c in high stage compounds as interpreted by our single-layer model.

Note added in proof. A summary of this work and of the preceeding paper can be found in Proceedings of International Conference on Layered Materials and Intercalates (Nijmegen, Netherlands, 1979) to be published in Physica.

ACKNOWLEDGMENTS

APPENDIX A

In this Appendix we derive Eq. (9) for χ_{or}^c from Fukuyama's formula [Eq. (1)]. The manipulations of Eq. (1) used here follow closely those of Ref. 9, except that our results are valid throughout the Brillouin zone. We begin by noting the relation discussed in Sec. III:

$$\vec{\gamma} = \nabla_k \mathcal{H}. \tag{A1}$$

Since $gg^{-1} = I$ (I is the unit matrix) we can use Eq. (A1) to write

$$\nabla_k g = g\vec{\gamma}g. \tag{A2}$$

Thus we have

$$\chi_{or}^c = \left(\frac{e}{\hbar c}\right)^2 k_B T \frac{1}{8\pi^3} \sum_n \int d\vec{k}\, \text{Tr}\left(\gamma_x \frac{\partial g}{\partial k_y} \gamma_x \frac{\partial g}{\partial k_y}\right). \tag{A3}$$

In a basis where the Hamiltonian is a finite matrix (e.g., $\vec{k} \cdot \vec{p}$ or tight binding) we write $g = (\epsilon_n - \mathcal{H})^{-1} = N/D$ where these quantities are defined in Sec. II. Writing

$$\frac{\partial g}{\partial k_y} = \frac{1}{D}\frac{\partial N}{\partial k_y} - \frac{1}{D^2}\frac{\partial D}{\partial k_y}N \tag{A4}$$

and substituting Eq. (A4) in Eq. (A3), we find that

$$\chi_{or}^c = \left(\frac{e}{\hbar c}\right)^2 k_B T \frac{1}{8\pi^3} \sum_n (\chi' + \chi'' + \chi'''), \tag{A5}$$

where

$$\chi' = \int d\vec{k}\, \frac{1}{D^2}\text{Tr}\left(\gamma_x \frac{\partial N}{\partial k_y}\right)^2, \tag{A6a}$$

$$\chi'' = -\int d\vec{k}\, \frac{2}{D^3}\frac{\partial D}{\partial k_y}\text{Tr}\left(\gamma_x N \gamma_x \frac{\partial N}{\partial k_y}\right), \tag{A6b}$$

$$\chi''' = \int d\vec{k}\, \frac{1}{D^4}\left(\frac{\partial D}{\partial k_y}\right)^2 \text{Tr}(\gamma_x N)^2. \tag{A6c}$$

We now manipulate χ'' and χ''' so that they are functions of D^{-2} and derivatives of D only.

Using Eq. (A2) we rewrite χ''' as

$$\chi''' = \int d\vec{k}\, \frac{1}{D^2}\left(\frac{\partial D}{\partial k_y}\right)^2 \text{Tr}\left(\frac{\partial}{\partial k_x}(\gamma_x g) - \Omega g\right), \tag{A7}$$

where $\Omega = \partial \gamma_x / \partial k_x$. However, as shown in Ref. 9 and as can be verified explicitly in our model

$$\frac{1}{D}\frac{\partial D}{\partial k_x} = -\text{Tr}(\gamma_x g), \tag{A8}$$

so that

$$\chi''' = \int d\vec{k}\, \frac{1}{D^2} D_y^2 \left(\frac{D_x^2}{D^2} - \frac{D_{xx}}{D^2} - \text{Tr}(\Omega g)\right), \tag{A9}$$

where

$$D_{ij} = \frac{\partial}{\partial k_i}\frac{\partial}{\partial k_j}D.$$

We now perform (two) partial integrations of Eq. (A9) using the fact that the surface integral of a periodic function vanishes. The result is

$$\chi''' = -\int d\vec{k}\frac{1}{D^2}[\tfrac{1}{3}(D_{xx}D_{yy} - D_{xy}^2) + D_y^2 \, \mathrm{Tr}(\Omega g)].\quad\text{(A10)}$$

Another integration by parts of the last term of Eq. (A10) together with an integration by parts of χ'' yields Eqs. (9) and (10) of Sec. II.

APPENDIX B

In this Appendix we discuss the approximations leading to Eq. (26). Using Eqs. (15) and (25), we rewrite χ_a as

$$\chi_a = \chi_0 \int_0^1 d\epsilon(\chi_A + \chi_B + \chi_C),\quad\text{(B1)}$$

$$\chi_A = Ap(\epsilon),\quad\text{(B2a)}$$

$$\chi_B = B\epsilon p(\epsilon),\quad\text{(B2b)}$$

$$\chi_C = C\epsilon p(\epsilon)\ln(1-\epsilon),\quad\text{(B2c)}$$

$$p(\epsilon) = \frac{1}{2}\frac{\partial}{\partial\epsilon}\left(\frac{f(-\epsilon-\epsilon_0) - f(\epsilon-\epsilon_0)}{2\epsilon}\right).\quad\text{(B2d)}$$

χ_A can be integrated directly (see Sec. III). Since χ_C is proportional to ϵ for $\epsilon \ll 1$ and to $\ln(1-\epsilon)$ for $\epsilon \simeq 1$, we evaluate its contribution in the $T = 0$ limit for $p(\epsilon)$, since we are interested in values of ϵ_0 where $0 < \epsilon_0 < 1 - \tau$. The results of the integrations of χ_A and χ_B are given in Eqs. (27a) and (27d), respectively. We perform a partial integration on the term containing χ_B to obtain

$$\int_0^1 \chi_B \, d\epsilon = \frac{B}{4}\left(1 - \int_0^1 \frac{f(-\epsilon-\epsilon_0) - f(\epsilon-\epsilon_0)}{\epsilon}d\epsilon\right).\quad\text{(B3)}$$

We approximate

$$f(-\epsilon-\epsilon_0) - f(\epsilon-\epsilon_0) \simeq \begin{cases} \tanh(\epsilon/\tau), & \epsilon > \epsilon_0 \quad\text{(B4a)} \\[2mm] \dfrac{\sinh(\epsilon/\tau)}{\cosh(\epsilon_0/\tau)}, & \epsilon < \epsilon_0. \quad\text{(B4b)} \end{cases}$$

Furthermore, we approximate the right-hand side of Eq. (B4a) as 1 for $\epsilon > \tau$ and ϵ/τ for $\epsilon < \tau$. With these approximations, we obtain Eq. (27b) and (27c) for the integral of χ_B. A numerical check of these approximations shows an error of $\leq 4\%$ in the region where the contribution of this term is significant.

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[21] We note that our $c_0 = c_L/2$ where c_L of Ref. 15 is given by $c_L = 6.74$ Å.