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Theory of magnetic susceptibility in acceptor and donor graphite intercalation compounds

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Résumé. — Le calcul de la susceptibilité magnétique orbitale des composés d'insertion du graphite est réexaminé pour rendre compte du comportement différent des composés donneurs et accepteurs. Le modèle bidimensionnel de la liaison forte, traitant symétriquement les bandes de valence et de conduction, ne permet pas d'expliquer les résultats expérimentaux. L'introduction des interactions intraplanaires entre seconds voisins induit une faible dissymétrie entre les bandes de valence et de conduction. Cette dissymétrie a pour conséquence l'existence de différences importantes dans les valeurs de la susceptibilité orbitale des composés donneurs et accepteurs, en bon accord avec les résultats expérimentaux.

Abstract. — The tight binding calculation of the orbital magnetic susceptibility in Graphite Intercalation Compounds is reexamined to account for the different behaviour of Donor and Acceptor Compounds. The two dimensional tight binding model for π electrons treating symmetrically valence and conduction bands cannot explain experimental data. The inclusion of the second neighbour in-plane interaction, inducing a weak asymmetry between the valence and conduction bands, leads to a large difference in the orbital susceptibility of donor and acceptor GIC in agreement with the experimental results for first stage compounds.

1. Introduction.

Magnetic susceptibilities of graphite intercalation compounds (GIC) with nonmagnetic intercalants differ considerably from the susceptibility of pure graphite [1]. Intrinsic graphite exhibits the large, diamagnetic, highly anisotropic susceptibility with $\chi_\parallel \gtrsim 50 \chi_\perp$ ($\chi_\parallel$ and $\chi_\perp$ denote the susceptibilities for magnetic field parallel and perpendicular to the c-axis, respectively). The susceptibility measurements in GIC are usually made on powder samples, so that in most cases only average susceptibilities $\chi = 1/3(\chi_\parallel + 2 \chi_\perp)$ are known. The intercalation is always accompanied by an important reduction of $|\chi|$, but donor and acceptor compounds behave differently: the latter remain diamagnetic, while the former become paramagnetic. In all cases $|\chi|$ per one mole of carbon in GIC is one order of magnitude smaller than in pure graphite; for almost all compounds and stages, $|\chi|$ falls in the range $5 - 11 \times 10^{-6}$ emu/1 C mole (see Table I).

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Table I. — Magnetic susceptibilities of GIC per 1 mole of carbon (in units emu).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stage</th>
<th>$\chi_d$</th>
<th>$\chi_a$</th>
<th>$\chi_{core}$</th>
<th>$\chi_{exp}$</th>
<th>$\chi_{core}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>-253</td>
<td>-5.2</td>
<td>-8.8</td>
<td>-4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Donors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsI</td>
<td>1</td>
<td>15.4</td>
<td>5.0</td>
<td>8.6</td>
<td>-4.8</td>
<td></td>
</tr>
<tr>
<td>CsBr</td>
<td>2</td>
<td>10.4</td>
<td></td>
<td></td>
<td>-4.8</td>
<td></td>
</tr>
<tr>
<td>CsF</td>
<td>3</td>
<td>22.9</td>
<td>-0.3</td>
<td>7.4</td>
<td>-5.2</td>
<td></td>
</tr>
<tr>
<td>CsI</td>
<td>4</td>
<td>24.0</td>
<td>-0.8</td>
<td>7.5</td>
<td>-5.1</td>
<td></td>
</tr>
<tr>
<td>CsBr</td>
<td>5</td>
<td>15.0</td>
<td>1.1</td>
<td>5.7</td>
<td>-7.4</td>
<td></td>
</tr>
<tr>
<td>CsF</td>
<td>6</td>
<td>2.3</td>
<td>6.4</td>
<td>-5.7</td>
<td>-18.3</td>
<td></td>
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<tr>
<td>CsI</td>
<td>7</td>
<td>5.6</td>
<td></td>
<td>-5.4</td>
<td></td>
<td></td>
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<tr>
<td>CsBr</td>
<td>8</td>
<td>6.0</td>
<td></td>
<td>-3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsF</td>
<td>9</td>
<td>13.7</td>
<td>4.6</td>
<td>3.7</td>
<td>-9.7</td>
<td></td>
</tr>
<tr>
<td>CsI</td>
<td>10</td>
<td>6.8</td>
<td></td>
<td>-6.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* [2], b [3], c [4], d [5], e [6], f [7], g [8], h [9], i [10], j [11], k [12], l [13], m [14], o [26].

The difference between donor and acceptor compounds should originate from the orbital magnetism.

The applicability of the two-dimensional models is even more justified for acceptor than for alkali metal GIC. It is therefore interesting to apply the theory of [19] to the case of acceptors. It can be easily verified that the calculated orbital susceptibility is independent of the sign of $E_F$. With typical values of the charge transfer 2-3 times smaller than in donor GIC, one should expect in acceptor GIC an orbital paramagnetism, even stronger than for donor compounds. It is quite puzzling that the theory, based on the model a priori applicable for both families, gives satisfactory results for donor compounds and fails completely for acceptor compounds.

In this paper, we explain the different magnetic behaviour of acceptor and donor compounds as originating from the asymmetry between valence and conduction $\pi$-bands. We consider slightly more complex than in [19], but still tractable two-dimensional tight-binding model, including both first- and second-neighbour intralayer interactions. By applying the Fukuyama formalism, we derive the general expression in the integral form for the orbital susceptibility (section 2) which reduces to the corresponding expression in [19] when neglecting the second-neighbour interactions. Our final analytical results, presented in section 3 and in appendix, do not confirm however the strong decrease of $\chi_{orb}$ vs. $E_F$ obtained in [19] with the use of a numerical integration procedure. Our results show that the second-neighbour interactions induce important difference between the orbital susceptibilities of donor and acceptor GIC and explain qualitatively the experimental observations.

The formalism of Fukuyama [18] to calculate the orbital susceptibility within the Slonczewski-Weiss model completed by trigonal warping. The magnitude of the orbital terms was proved to be a rapidly decreasing function of the excess carrier concentration. For concentrations large enough, the theory predicted a paramagnetic orbital susceptibility for both donor and acceptor compounds. These conclusions however are not directly applicable to GIC as the rigid band structure model of pure graphite is inadequate for these compounds.

The simple two-dimensional tight-binding model covering the entire Brillouin zone was used by Safran and Di Salvo [19] to determine theoretically the orbital magnetic susceptibility $\chi_{orb}$ of alkali metal GIC.

In the physically interesting domain of Fermi energies $E_F$, $\chi_{orb}$ for a system of noninteracting equivalent graphite layers was found to be paramagnetic and decreasing with increasing $E_F$. This decrease was used to explain the stage dependence of the orbital susceptibility of donor compounds — higher stages were treated as systems of noninteracting layers with different charge densities (and Fermi energies) to account for the nonuniform charge distribution along the $c$-axis.

Up to now, the theoretical effort has been directed towards an interpretation of the paramagnetism of donor compounds, little attention has been paid to the diamagnetism of acceptor compounds. The striking difference between both families of GIC cannot be attributed to the core diamagnetism, as the estimated values of the core contribution in second stage halogen- and alkali metal-graphite compounds are very much the same, as shown in Table 1. The differences in the Pauli paramagnetism cannot be invoked either as it is rather weak [2] already in donor compounds.
2. Orbital susceptibility for the tight binding Wallace model.

Single-layer band-structure models prove to be very useful for qualitative interpretation of many properties of graphite GIC and offer a convenient starting point for the development of more realistic models accounting for the interlayer interactions. The single-layer models are particularly well suited for first stage acceptor GIC, where the separations between graphite layers are much larger than in pure graphite and the hybridization of graphite orbitals with orbitals of intercalated molecules seems to be negligible. Our primary concern is to explain the difference between acceptor and donor GIC, rather than to construct a quantitative theory accounting for stage and temperature dependence of the magnetic susceptibility, therefore we limit our considerations to the single-layer tight-binding model of Wallace [20] with first- and second-neighbour interactions. Following Sharma et al. [17] and [19], we employ the Fukuyama formalism to calculate the orbital magnetic susceptibility $\chi_{or}$ for magnetic fields parallel to the c-axis. We found most convenient to use the Bloch representation diagonalizing the tight-binding Hamiltonian. In this representation $\chi_{or}$ per 1 mole of carbon, for a system of equivalent noninteracting graphite layers is given by the formula [18]

$$\chi_{or} = \frac{2 \mu_B^2 N_A \Omega}{m^2} \kappa_B T \sum_{n} \frac{1}{(2\pi)^2} \int d^2 \kappa \times$$

$$\times \text{Tr} \{ G_j^{x} G_j^{y} G_j^{x} G_j^{y} \}$$

(1)

where the spin degeneracy is already included. $\mu_B$ is the Bohr magneton, $N_A$ : the Avogadro number, $\Omega$ : the surface of the elementary 2D lattice cell containing 2 carbon atoms, $\kappa_B$ : the Boltzmann constant.

$$\Omega = 3 \sqrt{3} b^2 / 2,$$

where $b$ is the distance between nearest neighbours. The summation over $n$ runs from $-\infty$ to $+\infty$ and the integration is over 2D Brillouin zone. Trace is taken over the band index $l = 1, 2, j_z$ and $j_x$ are the $2 \times 2$ matrices of the current operators, the explicit form of the matrices will be specified below. $G$ is the diagonal matrix of the temperature Green's function in the Bloch representation :

$$G_n = [\varepsilon_n - E_l(\kappa)]^{-1}, \quad l = 1, 2$$

(2)

where $\varepsilon_n = (2 n + 1) \pi \kappa_B T + E_F$.

In the Wallace model (with the overlaps neglected) [20], the conduction ($l = 1$) and valence ($l = 2$) $\pi$-bands dispersion laws are:

$$E_1(\kappa) = E_0 + \gamma_0 E(\kappa) - \gamma_0 [E(\kappa)^2 - 3],$$

$$E_2(\kappa) = E_0 - \gamma_0 E(\kappa) - \gamma_0 [E(\kappa)^2 - 3],$$

(3)

where $\gamma_0 > 0$ and $\gamma_0 > 0$ ($\gamma_0 \gg \gamma_0$) are the resonance integrals characterizing the strengths of first- and second-neighbour interactions. $E(\kappa) = |H(\kappa)|$ where $H(\kappa)$ is defined as:

$$H(\kappa) = \sum_{j=1}^{3} e^{ik \cdot b_j}, \quad 0 \leq |H(\kappa)| \leq 3;$$

(4)

$$E(\kappa)^2 - 3 = \sum_{j=1}^{6} e^{ik \cdot a_j} = 2[\cos (k \cdot a_1) + \cos (k, C_3 a_1) + \cos (k, C_3^{-1} a_1)],$$

(5)

where $b_j$ and $a_j$ are the position vectors of the first and second nearest neighbours of the atom at the origin of the coordinate system (see Fig. 1). $|b_j| = b$ and $|a_j| = \sqrt{3} b$. $C_3$ and $C_3^{-1}$ are the rotations of 2 $\pi$/3 and 4 $\pi$/3, respectively. One can see from (3) that the second neighbour interactions introduce the asymmetry between the valence and the conduction bands (with respect to the energy at the corner of the hexagonal 2D Brillouin zone, where $E(\kappa) = 0$) (Fig. 2).

To simplify the formulae, in the following we put $E^2 = A$, $\gamma_0 = \gamma_0 \gamma_0$, $E_0 - 3 \gamma_0 = 0$ and $\gamma_0 = 1$. The last two equations define the origin and the units of the energy scale. In the Bloch representation, the current matrices $j_x (\alpha = x, y)$ have the form

$$j_{s11} = \frac{m}{\hbar} \frac{\partial E_1(\kappa)}{\partial \kappa_x} = \frac{m}{\hbar} \left( \frac{1}{E} - 2 \gamma \right) \text{Re} (H_x H^*)$$

$$- \frac{m}{2 \hbar} \left( \frac{1}{E} - 2 \gamma \right) A_x,$$

$$j_{s22} = \frac{m}{\hbar} \frac{\partial E_2(\kappa)}{\partial \kappa_x} = - \frac{m}{\hbar} \left( \frac{1}{E} + 2 \gamma \right) \text{Re} (H_x H^*)$$

$$- \frac{m}{2 \hbar} \left( \frac{1}{E} + 2 \gamma \right) A_x,$$

$$j_{s12} = j_{s11}^* = \frac{i m}{\hbar} \frac{1}{E} \text{Im} (H_x H^*),$$

(6)

where $H_x = \frac{\partial H(\kappa)}{\partial \kappa_x}$ and $A_x = \frac{\partial A}{\partial \kappa_x} = \frac{\partial |H(\kappa)|^2}{\partial \kappa_x}$. 


The evaluation of the trace in (1) gives:

\[
\frac{\hbar^4}{m^4} \text{Tr} \left\{ G_{ij} G_{ij} G_{ij} G_{ij} \right\} = \frac{D_x^2 D_y^2}{D^4} + 4 \frac{D_x D_y}{D^3} (\text{Re}(H_x H_y^*) - \gamma^2 A_x A_y) + \\
\quad + \frac{2}{D^2} \left\{ (\text{Re}(H_x H_y^*) - \gamma^2 A_x A_y)^2 - (1 - 4 \gamma^2 E^2) (\text{Im}(H_x H_y^*)^2) \right\},
\]

(7)

where \( D = (E_n - E_1(\mathbf{k})) (E_n - E_2(\mathbf{k})) \) and \( D_x = \partial D/\partial \kappa_x \). We substitute (7) in (1) and perform two partial integrations to eliminate \( D^4 \) and \( D^3 \) in denominators. Then the summation over \( n \) is separated from the Brillouin zone integrations by introducing the additional dummy integration over the variable \( \varepsilon = E(\mathbf{k}) \), \( 0 \leq \varepsilon \leq 3 \). The result is:

\[
\chi_{or} = \frac{e}{\hbar c} N_A Q \gamma_0 \frac{b^2}{8 \pi^2} \left\{ \int_0^3 d\varepsilon \left( \kappa_x T \sum_n \frac{1}{D^2} \right) h_1(\varepsilon) + \gamma \int_0^3 d\varepsilon \left( \kappa_y T \sum_n \frac{(\varepsilon_n + \gamma \varepsilon^2)}{D^2} \right) h_2(\varepsilon) + \\
\quad + \gamma^2 \int_0^3 d\varepsilon \left( \kappa_x T \sum_n \frac{(\varepsilon_n + \gamma \varepsilon^2)}{D^2} \right) h_3(\varepsilon) + \gamma^2 \int_0^3 d\varepsilon \left( \kappa_y T \sum_n \frac{(\varepsilon_n + \gamma \varepsilon^2)}{D^2} \right) h_4(\varepsilon) + \gamma^3 \int_0^3 d\varepsilon \left( \kappa_x T \sum_n \frac{(\varepsilon_n + \gamma \varepsilon^2)}{D^2} \right) h_5(\varepsilon) \right\}.
\]

(8)

The functions \( h_i(\varepsilon) \), independent of \( \gamma \), are defined by the following formulae:

\[
h_1(\varepsilon) = \frac{1}{b^2} \int d^2\kappa \delta(\varepsilon - E(\mathbf{k})) \left\{ 2(\text{Re}(H_x H_y^*))^2 - 2(\text{Im}(H_x H_y^*))^2 + \\
\quad + \frac{1}{2}(A_{xy}^2 - A_{xx} A_{yy}) + \frac{1}{2}(A_{xx} A_{yy} - 2A_y \text{Re}(H_x H_y^*))_x \right\}.
\]

(9)

\[
h_2(\varepsilon) = -\frac{4}{b^2} \int d^2\kappa \delta(\varepsilon - E(\mathbf{k})) \left\{ \frac{1}{2}(A_{xy}^2 - A_{xx} A_{yy}) + \frac{1}{2}(A_{xx} A_{yy} - (A_y \text{Re}(H_x H_y^*))_x \right\}.
\]

(10)

\[
h_3(\varepsilon) = \frac{4}{b^2} \int d^2\kappa \delta(\varepsilon - E(\mathbf{k})) \left\{ \frac{1}{2}(A_{xy}^2 - A_{xx} A_{yy}) + \frac{1}{2}(A_{xx} A_{yy})_y \right\}.
\]

(11)

\[
h_4(\varepsilon) = \frac{1}{b^2} \int d^2\kappa \delta(\varepsilon - E(\mathbf{k})) \left\{ 8 A \text{(Im}(H_x H_y^*))^2 + \frac{1}{2}(A_x^2 A_y)_y \right\}.
\]

(12)

\[
h_5(\varepsilon) = -\frac{2}{3 b^2} \int d^2\kappa \delta(\varepsilon - E(\mathbf{k})) (A_x^2 A_y)_y.
\]

(13)

The subscripts \( x \) and \( y \) denote the derivatives with respect to \( \kappa_x \) and \( \kappa_y \). Inspite of the apparent asymmetry of equations (9)-(13), all the functions \( h_i(\varepsilon) \) are in fact symmetric with respect to the interchange of the subscripts \( x \) and \( y \).
The factors in brackets in (8) can be decomposed in simple fractions and the summation over \( n \) can be performed with the use of the formulae

\[
\sum_{n} \frac{\kappa_n T}{E_n - E_i} = f(E_i - E_F), \quad l = 1, 2, \quad (14)
\]

\[
\sum_{n} \frac{\kappa_n T}{(E_n - E_i)^2} = \frac{\partial f(E_i - E_F)}{\partial E_i}, \quad l = 1, 2, \quad (15)
\]

where \( E_i(e) = e - \gamma e^2 \) and \( E_2(e) = -e - \gamma e^2 \). The final expression for the orbital susceptibility as a function of the Fermi energy is:

\[
\chi_{\text{or}} = \left( \frac{e^2}{\hbar c} \right) \frac{N_{\nu} \Omega_{\nu} b^2}{32 \pi^2} \left\{ \int_{0}^{\infty} \frac{d\varepsilon}{\varepsilon^3} \left( f(E_2 - E_F) - f(E_1 - E_F) \right) \left( h_1(e) - \gamma^2 \varepsilon^2 h_3(e) + \gamma^2 h_4(e) \right) + \right. \\
\left. \int_{0}^{\infty} \frac{d\varepsilon}{\varepsilon^2} \left( h_1(e) + \gamma \varepsilon h_2(e) + \gamma^2 \varepsilon^2 h_3(e) + \gamma^2 h_4(e) + \gamma^3 \varepsilon h_5(e) \right) \frac{\partial f(E_i - E_F)}{\partial E_i} \right. \\
\left. \int_{0}^{\infty} \frac{d\varepsilon}{\varepsilon^2} \left( h_1(e) - \gamma \varepsilon h_2(e) + \gamma^2 \varepsilon^2 h_3(e) + \gamma^2 h_4(e) - \gamma^3 \varepsilon h_5(e) \right) \frac{\partial f(E_2 - E_F)}{\partial E_2} \right\}. \quad (16)
\]

All the Brillouin zone integrals are calculated analytically in appendix. The last integration over \( \varepsilon \) in (16) can be performed numerically without much difficulty for any temperature. One can note however, that the Fermi factors and their derivatives change rapidly in a narrow energy region of a few \( \kappa_n T \) centred at \( e \) corresponding to the Fermi energy \( E_F \). Thus most terms in (16) can be calculated in zero-temperature approximation which introduce considerable simplifications.

3. Results and discussions.

We consider first the case \( \gamma = 0 \), when the orbital susceptibility can be put in the form:

\[
\chi_{\text{or}}^0 = \left( \frac{e^2}{\hbar c} \right) \frac{N_{\nu} \Omega_{\nu} b^2}{32 \pi^2} \int_{0}^{\infty} \frac{d\varepsilon}{\varepsilon^3} \left( \frac{1}{\varepsilon} \frac{\partial}{\partial \varepsilon} \left[ f(e - E_F) - f(-e - E_F) \right] \right), \quad (17)
\]

where \( E_F \) and \( \kappa_n T \) in the Fermi factors are in units of \( \gamma_0 \). The superscript zero in \( \chi_{\text{or}}^0 \) is introduced to distinguish (17) and (16). The function \( h_1(e) \) is given by the formula (see appendix)

\[
h_1(e) = \frac{8}{3 \sqrt{3} M + 2} \frac{e^4 - 18 e - 27}{M + 1} K(m) + e^3 (e + 1)^3 (3 - \varepsilon) K(m) - E(m) + 4 \sqrt{3} \varepsilon K(m) Z(\psi/\alpha)
\]

for \( 0 \leq \varepsilon < 1 \), and

\[
h_1(e) = \frac{\sqrt{3} \varepsilon}{9} (2 e^4 + 9 e^2 - 18 e - 81) K(m^{-1}) + 4 \sqrt{3} \varepsilon^{3/2} (K(m^{-1}) - E(m^{-1})) + 4 \sqrt{3} \varepsilon K(m^{-1}) Z(\psi/\beta)
\]

for \( 1 < \varepsilon \leq 3 \), where \( m = \frac{16 e}{(e + 1)^3 (3 - \varepsilon)} = \sin^2 \alpha = \sin^2 \beta \),

\[
\sin \phi = \sin^{-1} \psi = \frac{e + 1}{2}.
\]

\( K(m) \) and \( E(m) \) are the complete elliptic integrals of the first and second kind, respectively; \( Z(\psi/\alpha) \) is the Jacobi's zeta function [21].

In figure 3, we plot the functions \( h_1(e)/\varepsilon \) and \( \rho^0(e)/\varepsilon \) for \( 0 \leq \varepsilon < 1 \), where \( \rho^0(e) \) is the density of states per unit energy for \( \pi \)-bands in 2D graphite, calculated in the appendix (Eq. (A.17)). The values of both functions at \( \varepsilon = 0 \) agree exactly with the results of the linear approximation for \( \pi \)-bands considered by McClure [15]. In the present tight-binding model (with \( \gamma = 0 \)), the \( \pi \)-bands are strongly nonlinear, as evidenced by the increase of \( \rho^0(e)/\varepsilon \). It is somewhat unexpected that in spite of this nonlinearity and the resulting complexity of the integrand in (A.2) for \( h_1(e) \), the function \( h_1(e)/\varepsilon \) is practically constant up to \( \varepsilon \approx 0.6 \). Even at \( \varepsilon = 0.8 \), its deviation from the value at \( \varepsilon = 0 \) does not exceed 5%. In fact, one can rigorously prove, using asymptotic expressions for
Fig. 3. — Left scale : relative variations of $- h_1(e)/e$ calculated analytically in this paper (upper solid curve) and from fitting formula in [19] (lower solid curve). Right scale : broken curve represents the relative variations of $\rho^0(e)/e$ where $\rho^0(e)$ is the energetic density of states.

elliptic integrals, that at $\varepsilon \ll 1$ the power series for the function $h_1(e)/e$ has the form

$$h_1(e)/e = -12\pi\left(1 + \frac{7\sqrt{3}}{324}e^4 + 0(e^6)\right);$$

the terms proportional to $e^1, e^2, e^3$ and $e^5$ vanish identically. Using (19), we express (17) in the form

$$\chi_0^2 = \left(\frac{e}{\hbar c}\right)^2 \frac{N_A \Omega \gamma_0 b^2}{32 \pi^2} \left\{ -\frac{6\pi \gamma_0}{\kappa_B T} \text{sech}^2 (E_F/2 \kappa_B T) - 12\pi f(\gamma_0 - E_F) - f(-\gamma_0 - E_F) \right\} +$$

$$+ \int_0^1 \frac{d\varepsilon}{\varepsilon} (12\pi + h_1(e)/e) \frac{\partial}{\partial \varepsilon} \left(\frac{f(\varepsilon \gamma_0 - E_F) - f(-\varepsilon \gamma_0 - E_F)}{\varepsilon}\right) \right.$$ 

$$\left. + \int_1^3 \frac{d\varepsilon}{\varepsilon} h_1(e)/e \frac{\partial}{\partial \varepsilon} \left(\frac{f(\varepsilon \gamma_0 - E_F) - f(-\varepsilon \gamma_0 - E_F)}{\varepsilon}\right) \right\}. \quad (20)$$

where the standard energy units have been restored.

In the physically interesting region of Fermi energies, the inequality $\gamma_0 - |E_F| \gg \kappa_B T$ is always satisfied. ($|E_F| = \gamma_0$ corresponds exactly to the case of one excess carrier per four carbon atoms, whereas in C$_6$Li, which seems to be GIC with the largest charge transfer, there is at most one excess carrier per six carbon atoms.) Both integrals in (20) can be calculated with a good accuracy in the zero-temperature approximation, the region of rapid variations of the Fermi factors being situated either outside the integration limits, or in the domain of the smooth behaviour of the remaining factors in the integrand. We obtain therefore

$$\chi_0^2 = \left(\frac{e}{\hbar c}\right)^2 \frac{N_A \Omega \gamma_0 b^2}{32 \pi^2} \left\{ -\frac{6\pi \gamma_0}{\kappa_B T} \text{sech}^2 (E_F/2 \kappa_B T) + 12\pi - K - \right.$$ 

$$\left. \frac{\gamma_0^2}{E_F^2} \left(\frac{\gamma_0}{E_F} + h_1(\gamma_0)\right) - \int_{E_F/\gamma_0}^{\gamma_0} \frac{d\varepsilon}{\varepsilon} \frac{12\pi \varepsilon + h_1(e)}{\varepsilon^3} \right\}. \quad (21)$$

The positive constant $K$ is defined as

$$K = -\int_0^1 \frac{d\varepsilon}{\varepsilon} \frac{12\pi \varepsilon + h_1(e)}{\varepsilon^3} - \int_1^3 \frac{d\varepsilon}{\varepsilon} \frac{h_1(e)}{\varepsilon^3}; \quad (22)$$

the numerical integration gives $K \approx 7.1$.

Bearing in mind that the function $12\pi \varepsilon + h_1(e)$ is negative and monotonic for $0 \leq \varepsilon < 1$, one can see from (21) that $\chi_0^2$ is a monotonic, increasing function of $|E_F|$. It is large and diamagnetic for $|E_F|$ of the order of $\kappa_B T$, then reaches a temperature independent paramagnetic plateau and finally increases rapidly when the Fermi level approaches the saddle point energy in $\pi$-bands. In figure 4, we plot for room temperature the Fermi level dependence of $\chi_0^2$ per 1 C mole resulting from numerical calculation of the integral in (21) (curve (a)). The curve corresponds to the experimentally established value of $\gamma_0 = 2.62$ eV, appropriate for first stage GIC [22]. One can see from figure 4 that for $0.1 \gamma_0 \leq |E_F| \leq 0.8 \gamma_0$ (i.e. for all Fermi energies of physical interest) the orbital susceptibility of GIC resulting from the tight-binding model with $\gamma = 0$ depends very little on the
Fermi energy. For first stage donor compounds, the experimental values of orbital susceptibility $\chi_{\text{or}}$ per 1 C mole are equal to 13-14 \times 10^{-6} \text{ emu/1 C mole} [2]. For acceptor compounds, the data for average susceptibility indicate that the orbital susceptibility $\chi_{\text{or}}$ is close to zero (see also [26]). The present theory with $\gamma = 0$ predicts the same value of about 6 \times 10^{-6} \text{ emu/1 C mole} for both families of GIC. The agreement of the theory with the experiment is therefore not satisfactory for the donor nor for the acceptor compounds.

These conclusions are quite different from the results of [19] obtained for the same band structure model. In [19], $\chi_{\text{or}}^0$ reaches high paramagnetic values at $E_F \simeq 8 \kappa_B T$ and then decreases with increasing $E_F$ as long as $E_F \leq 0.8 \gamma_0$. At room temperature, the peak-to-minimum ratio of about 4 is predicted.

It has to be noticed that, in contrast to our calculations, the Brillouin zone integration in [19] was not performed analytically but numerically. The numerical results were approximated by the fitting formula

$$h(\varepsilon) = - (A \varepsilon + B \varepsilon^2 + C \varepsilon^3) \ln (1 - \varepsilon))$$

with $A = 3.47$, $B = -4.19$, $C = 0.79$. It is easy to prove that the function $h(\varepsilon)$ as defined by (17)-(19) in [19] should coincide with our function $h_1(\varepsilon)$ up to a constant multiplicative factor $C = (3\sqrt{3} b^4 \gamma_0^2 m^2)/(4 \pi^2 t^4)$. The comparison of the function $-Ch(\varepsilon)/\varepsilon$ calculated from (23) with the analytical results for $-h_1(\varepsilon)/\varepsilon$ presented in figure 3 shows that the numerical Brillouin zone integration in [19] introduced considerable errors. In particular, the term $-B \varepsilon^2$ in (23) resulted entirely from the inaccuracies of numerical integrations, as it can be seen from (19). It is this spurious term which accounts for the essential differences between the results obtained in the present paper and in [19]. The present results clearly show that the simple tight-binding model with $\gamma = 0$ does not explain the stage dependence of the orbital susceptibility of alkali metal GIC, contrarily to the conclusions of Di Salvo et al. [2]. In particular, there is no hope to use the susceptibility measurements as the tests for the charge density distribution as suggested in [19].

Let us consider now the case $\gamma \neq 0$. We denote by $\varepsilon_0$ the value of $\varepsilon$ corresponding to the Fermi energy in donor GIC

$$\varepsilon_D - \gamma \varepsilon_0^2 = E_F/\gamma_0 > 0, \quad \varepsilon_D \simeq E_F/\gamma_0 (1 + \gamma E_F/\gamma_0) \quad (24)$$

$\varepsilon_A$ denotes the corresponding quantity in the case of acceptor compounds

$$-\varepsilon_A - \gamma \varepsilon_A^2 = E_F/\gamma_0 < 0, \quad \varepsilon_A \simeq - E_F/\gamma_0 (1 + \gamma E_F/\gamma_0) \quad (25)$$

In all cases of physical interest, the inequality $\kappa_B T/\gamma_0 \ll \varepsilon_0 \leq 0.8$ or $\kappa_B T/\gamma_0 \leq \varepsilon_A \leq 0.8$ is satisfied. (When compared to the case $\gamma = 0$, the density of states per unit energy is changed, but the density of states per unit $\varepsilon$ remains the same. The cases $\varepsilon_0 = 1$ and $\varepsilon_A = 1$ still correspond to one excess carrier per four carbon atoms).

This allows to evaluate (16) by the same method as used for (17) in the case $\gamma = 0$. It can be proved (see appendix) that the functions $h_5(\varepsilon)$ and $h_4(\varepsilon)$ are linear in $\varepsilon$ for $\varepsilon \to 0$ whereas the functions $h_1(\varepsilon)$ and $h_2(\varepsilon)$ behave like $\varepsilon^3$. We separate the term linear in $\varepsilon$ from $h_1(\varepsilon)$ in the first integral in (16) and we adopt zero-temperature approximation for the remaining integrals with integrands finite at $\varepsilon = 0$. The final result for the case of donor com-
pounds \((E_F > 0)\) is

\[
\chi_\omega^D(\gamma_0 \epsilon_D) = \frac{e^2 N_A Q \gamma_0 b^2}{32 \pi^2} \left\{ \gamma^2 \int_{E_D} d\epsilon \frac{h_4(\epsilon) - e^2 h_3(\epsilon)}{\epsilon^3} - \frac{\gamma}{\epsilon_D(1 - 2 \gamma \epsilon_D)} \left( 2 h_1(\epsilon_D) + h_2(\epsilon_D) + \gamma \epsilon_D h_3(\epsilon_D) + \gamma \epsilon_D^{-1} h_4(\epsilon_D) + \gamma^2 h_5(\epsilon_D) \right) \right\}
\]

(26)

and for acceptor compounds \((E_F < 0)\):

\[
\chi_\omega^A(\gamma_0 \epsilon_A) = \frac{e^2 N_A Q \gamma_0 b^2}{32 \pi^2} \left\{ \gamma^2 \int_{E_A} d\epsilon \frac{h_4(\epsilon) - e^2 h_3(\epsilon)}{\epsilon^3} + \frac{\gamma}{\epsilon_A(1 + 2 \gamma \epsilon_A)} \left( 2 h_1(\epsilon_A) + h_2(\epsilon_A) - \gamma \epsilon_A h_3(\epsilon_A) - \gamma \epsilon_A^{-1} h_4(\epsilon_A) + \gamma^2 h_5(\epsilon_A) \right) \right\}
\]

(27)

To get the results of (26) and (27) in the relatively simple form, we introduced minor changes in the arguments of the function \(\text{sech}^2(\frac{E_F}{2 \kappa_B T})\) present in the rigorous expressions for \(\chi_\omega^D\) and \(\chi_\omega^A\). We put \(E_F \approx \gamma_0 \epsilon_D\) for \(E_F > 0\) and \(E_F \approx -\gamma_0 \epsilon_A\) for \(E_F < 0\). One can see from (24) and (25) that these approximations are well justified for all \(\Delta p / \rho_T\) of the order of 2 \(x_B T\) when the function \(\text{sech}^2(\frac{E_F}{2 \kappa_B T})\) is significantly different from zero. In order to estimate the magnitude of the terms originating from second-neighbour interactions, one can use the approximation

\[\gamma = \gamma_0 / \gamma_0 \approx S(a)/S(b)\]

proposed by Mullikan and employed in the tight-binding calculations of the band structure of graphite due to Johnston [23]. \(S(b)\) and \(S(a)\) are the overlap integrals between 2pz atomic orbitals of carbon for nearest and second nearest neighbours, respectively. With \(\psi_{2p_z} \sim ze^{-1.5 r_{nn}}\) [24] one gets \(\gamma \approx 0.14\).

In figure 4, we plot the orbital susceptibilities \(\chi_\omega^D\) of donor (curve b) and \(\chi_\omega^A\) of acceptor (curve c) compounds as given by (26) and (27) and the orbital susceptibility \(\chi_{\omega_2}\). The choice of different arguments \((\epsilon_D, \epsilon_A\) and \(| E_F | / \gamma_0\) allows for direct comparison of the values of the three functions corresponding to the same excess charge concentration. One can see from figure 4 that the second-neighbour interactions strongly affect the orbital susceptibility, introducing important difference between the donor and the acceptor compounds of the order of the difference observed experimentally. For both families, the estimated theoretical susceptibilities are comparable with the values resulting from experiments for low stage compounds (13-14 \(\times 10^{-6}\) emu/1 C mole for donor GIC and about zero for acceptor GIC). It seems therefore that, inspite of its obvious oversimplifications, the single-layer tight-binding model with the first and second-neighbour interactions accounts qualitatively for both the paramagnetism of the donor GIC and the diamagnetism of the acceptor GIC. The striking difference between the magnetic properties of both families may be attributed to the band-shape and wave-function differences between the valence and the conduction \(\pi\)-bands. The present results show however that in the region of physical interest the calculated susceptibilities depend only weakly on the carrier concentration. Therefore, contrary to the previous statements the single-layer model (with or without the band asymmetry) cannot explain the stage dependence of the susceptibility observed for donor compounds.

The most general conclusion from the present calculation is that the orbital susceptibility of GIC proved to be a very sensitive function of the band structure details and has to be calculated very carefully. Because of this sensitivity, it is difficult to expect that the simplified models, neglecting the interlayer interactions, trigonal warping and the details of the excess charge distribution, can explain correctly the stage dependence of the orbital magnetic susceptibility of GIC. The conclusive quantitative theory should be based on a very precise band structure model. The amount of labour required for the calculations of orbital susceptibility already for simple models leaves little hope that such theory will be worked out.

Appendix.

BRILLOUIN ZONE INTEGRATIONS. — The integrands in (8)-(11) are rather complicated functions of sines and cosines of the arguments \(\theta_1 = \mathbf{k} \cdot \mathbf{a}_1, \theta_2 = \mathbf{k} \cdot \mathbf{C}_3 \mathbf{a}_1, \) and \(\theta_3 = \mathbf{k} \cdot \mathbf{C}_3^{-1} \mathbf{a}_1\). For example, the integral \(h_1(\epsilon)\) has the form

\[
h_1(\epsilon) = \frac{3 b^2}{4} \int_{\mathbb{R}^2} d^2 \kappa \delta(\epsilon - E(\kappa)) (-3 + \cos^2 \theta_1 + \cos^2 \theta_3 + 2 \cos^2 \theta_2 + 6 \cos \theta_1 \cos \theta_2 + \\
+ 6 \cos \theta_2 \cos \theta_3 + 5 \cos \theta_3 \cos \theta_1 - 7 \sin \theta_1 \sin \theta_2 - 7 \sin \theta_2 \sin \theta_3 - \sin \theta_3 \sin \theta_1).
\]
The integrands in (8)-(11) can be very much simplified by symmetry arguments. As both, the Brillouin zone and the function \(E(\mathbf{k})\), (Eq. (5)), are invariant with respect to the rotations \(C_3\) and \(C_3^{-1}\) in the \(\kappa\)-space, we have

\[
\int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \, F(\theta_1, \theta_2, \theta_3) = \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \, F(\theta_2, \theta_3, \theta_1) = \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \, F(\theta_3, \theta_1, \theta_2),
\]

where \(F(\theta_1, \theta_2, \theta_3)\) is an arbitrary function.

Using (A.1), (4) and (5), one can express (8)-(11) in the form

\[
h_1(e) = \frac{b^2}{4} \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \left( e^4 + 9 e^2 - 18 - 18 z - 18 z^{-1} \left( \frac{e^2 - 1}{4} \right)^2 \right)
\]

\[
h_2(e) = \frac{b^2}{2} \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \left( -3 e^4 + 36 e^2 - 9 - 36 z - 36 z^{-1} \left( \frac{e^2 - 1}{4} \right)^2 \right)
\]

\[
h_3(e) = \frac{3b^2}{2} \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \left( 3 e^4 - 6 e^2 + 27 - 36 z - 36 z^{-1} \left( \frac{e^2 - 1}{4} \right)^2 \right)
\]

\[
h_4(e) = \frac{3b^2}{8} \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \left( - e^6 - 69 e^4 + 69 e^2 - 135 - 144 z^2 + \right.
\]

\[
(30 e^2 + 522) z + (138 e^2 + 54) z^{-1} \left( \frac{e^2 - 1}{4} \right)^2 \right)
\]

\[
h_5(e) = \frac{9b^2}{4} \int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \left( - e^6 - e^4 - 19 e^2 + 45 + 48 z^2 + (54 e^2 - 174) z + 72 z^{-1} \left( \frac{e^2 - 1}{4} \right)^3 \right)
\]

where

\[
z = \cos^2 \left( \frac{\theta}{2} \right) = \cos^2 \left( \frac{\sqrt{3} \kappa_x}{2} \right) \neq 0 \quad \text{for} \quad e \neq 1.
\]

All the integrands in (A.2)-(A.6) are periodic functions in the \(\kappa\)-space. Instead of integrating over the standard hexagonal Brillouin zone, we can therefore integrate over the rhomboidal Brillouin zone shown in figure 2. Then we note that the integrands are even functions of the variables \(\kappa_x\) and \(\kappa'_x = \kappa_x - 2 \pi/3 b\), because in these variables, the function \(E(\mathbf{k})\) has the form

\[
E(\kappa_x, \kappa_y) = \left( 1 + 4 \cos^2 \left( \frac{\sqrt{3} \kappa_x}{2} \right) - 4 \cos \left( \frac{3 \kappa_x}{2} \right) \cos \left( \frac{\sqrt{3} \kappa_x}{2} \right) \right).
\]

Thus, the integration over the Brillouin zone reduces to the integration over the rectangular triangle

\[
0 \leq \kappa'_x < \frac{2 \pi}{3 b} - \frac{\kappa_x}{\sqrt{3}}, \quad 0 \leq \kappa_x \leq \frac{2 \pi}{\sqrt{3} b}.
\]

After a straightforward integration over \(\kappa'_x\) and the change of variables from \(\kappa_x\) to the variable \(z\) defined by (A.7), one obtains

\[
\int_{\text{Br}z} d^2\kappa \, \delta(e - E(\mathbf{k})) \, z^l = \frac{4 e}{3 \sqrt{3} b^2} I_l(e)
\]

where \(l = -1, 0, 1, 2\) and \(I_l(e)\) are elliptic integrals of the form

\[
I_l(e) = \int_0^{e(1)} \frac{z^l \, dz}{\sqrt{z(1 - z)} \left( z - \left( \frac{e - 1}{2} \right)^2 \right)} \left( \frac{e + 1}{2} \right)^2 - z
\]
where
\[
g(\varepsilon) = \begin{cases} 
\frac{(\varepsilon + 1)}{2} & \text{for } 0 \leq \varepsilon < 1, \\
1 & \text{for } 1 < \varepsilon \leq 3.
\end{cases}
\]

By standard procedures, one can relate the integrals \( I_i \) to the complete elliptic integrals of the first and second kind and to the Jacobi zeta function, denoted respectively by \( K(m) \), \( E(m) \), \( Z(\phi \setminus \alpha) \) [21, 25]. The results are the following: for \( 0 \leq \varepsilon \leq 3 \),
\[
I_2(\varepsilon) = \frac{3 + \varepsilon^2}{4} I_1(\varepsilon) - \frac{1}{2} I_{-1}(\varepsilon) \cdot \left( \frac{\varepsilon^2 - 1}{4} \right)^2
\]
(A.10)

for \( 0 \leq \varepsilon < 1 \)
\[
I_0(\varepsilon) = \frac{8}{\sqrt{(3 - \varepsilon)(\varepsilon + 1)^3}} K(m)
\]
(A.11)

\[
I_{-1}(\varepsilon) = I_0(\varepsilon) + \frac{8}{(\varepsilon - 1)^2} \frac{3 - \varepsilon}{\varepsilon + 1} E(m)
\]
(A.12)

\[
I_1(\varepsilon) = \frac{(\varepsilon + 1)^2}{4} I_0(\varepsilon) - 2 Z(\phi \setminus \alpha) K(m)
\]
(A.13)

for \( 1 < \varepsilon \leq 3 \)
\[
I_0(\varepsilon) = \frac{2}{\sqrt{\varepsilon}} K(m^{-1})
\]
(A.14)

\[
I_{-1}(\varepsilon) = \left( \frac{2}{\varepsilon + 1} \right)^2 \left( I_0(\varepsilon) + 2\sqrt{\varepsilon} \left( \frac{2}{\varepsilon - 1} \right)^2 E(m^{-1}) \right)
\]
(A.15)

\[
I_1(\varepsilon) = I_0(\varepsilon) - 2 Z(\psi \setminus \beta) K(m^{-1})
\]
(A.16)

where
\[
m = \frac{16 \varepsilon}{(3 - \varepsilon)(\varepsilon + 1)^2}, \quad \sin \phi = \left( \frac{\varepsilon + 1}{2} \right),
\]
\[
\sin^2 \alpha = m, \quad \sin^2 \beta = m^{-1}, \quad \sin \psi = \left( \frac{2}{\varepsilon + 1} \right).
\]

The functions \( K, E \) and \( Z \) can be calculated with a very high accuracy by standard algorithms.

Making use of the properties of \( K(m), E(m) \) and \( Z(\phi \setminus \alpha) \) for \( m \to 0 \), one can easily establish the following properties of the functions \( h_i(\varepsilon) \) for \( \varepsilon \to 0 \).
\[
h_1(\varepsilon) = -12 \pi \varepsilon \left( 1 + \frac{7}{108\sqrt{3}} \varepsilon^4 + 0_4(\varepsilon^6) \right),
\]
\[
h_2(\varepsilon) = -24 \pi \varepsilon \left( 1 - \varepsilon^2 + 0_2(\varepsilon^4) \right),
\]
\[
h_3(\varepsilon) = +24 \pi \varepsilon \left( 1 + 0_2(\varepsilon^2) \right),
\]
\[
h_4(\varepsilon) = +84 \pi \varepsilon^3 \left( 1 + 0_4(\varepsilon^2) \right),
\]
\[
h_5(\varepsilon) = -24 \pi \varepsilon^3 \left( 1 + 0_4(\varepsilon^2) \right).
\]

It is to be noted that, in the case \( \gamma = 0 \), the density of states per unit energy \( \rho(\varepsilon) \) is given directly by the integral \( I_0(\varepsilon) \). The density of states normalized by the condition \( \int_0^\infty \rho(\varepsilon) \, d\varepsilon = 2 \) is given by the formula
\[
\rho^0(\varepsilon) = \frac{3\sqrt{3}}{(2\pi)^2} b^2 \int_{B_2} \frac{d^2k}{\delta \varepsilon} \delta(\varepsilon - E(\mathbf{k})) = \frac{e}{\pi^2} I_0(\varepsilon)
\]
(A.17)

for \( \varepsilon \to 0 \),
\[
\rho^0(\varepsilon) = \frac{4\varepsilon}{\pi \sqrt{3}} \left( 1 + \frac{\varepsilon^2}{3} + 0(\varepsilon^4) \right).
\]
(A.18)
It is easy to show that, for the case $\gamma \neq 0$, the density of states function for both valence and conduction bands are simply related to the function $\rho^0(\epsilon)$. For the conduction band, we have

$$\rho_c(E_1) = \rho^0(\epsilon_1)$$

where $\epsilon_1 - \gamma \epsilon_1^2 = E_1$ and $\int_0^\infty \rho_c(E_1) \, dE_1 = 2$ whereas, for the valence band,

$$\rho_v(E_2) = \rho^0(\epsilon_2)$$

where $-\epsilon_2 - \gamma \epsilon_2^2 = E_2$ and $\int_0^\infty \rho_v(E_2) \, dE_2 = 2$. 

References