

## Electrical conductivity of a graphite layer

L. Pietronero, S. Strässler, and H. R. Zeller

*Brown Boveri Research Center, CH-5405 Baden, Switzerland*

M. J. Rice

*Xerox Webster Research Center, Webster, New York 14580  
and NORDITA, Copenhagen, Denmark*

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The electrical conductivity of a charged layer of graphite is calculated from first principles within a tight-binding framework. The Fermi surface consists of circles around the  $P$  points in the Brillouin zone. In the neighborhood of these points we obtain analytical expressions for the electron-phonon coupling  $g_{\vec{k}\vec{v}}$ . The longitudinal and transverse phonons are shown to give exactly the same average contribution to scattering (contrary to the case of simple metals). In the high-temperature limit we obtain a conductivity (at  $T = 300$  K) that is about thrice that of copper. The significance of this result with respect to graphite intercalation compounds is discussed.

### I. INTRODUCTION

The long-standing interest in graphite intercalation compounds has been spurred by recent reports of electrical conductivities exceeding that of copper.<sup>1-3</sup>

Although detailed experimental information about the Fermi surface is becoming increasingly available,<sup>4,5</sup> further progress in this field is hampered by the fact that elementary questions concerning the electronic structure of such compounds are not yet settled. It is the purpose of this paper to resolve some of the problems by asking the following question: What is the conductivity of a single layer of graphite as a function of the electronic chemical potential? This question is of direct relevance for intercalation compounds in which the shift of the chemical potential of the graphite layers adjacent to the intercalate is sufficient to make the Fermi surface essentially two dimensional and for which an ionic picture is appropriate. The conductivity in the graphite layers may then be calculated from the carbon electron-phonon coupling constant as a function of the chemical potential.

We describe the electron-phonon coupling starting from a tight-binding Hamiltonian<sup>6-9</sup> which is known to be appropriate for the  $\pi$  bonds of graphite.<sup>9</sup> The maximum charge transfer per carbon atom due to intercalation is of the order of a few percent of an electron,<sup>4,5</sup> and it is easy to estimate that even in this case the scattering due to the modulation of the tight-binding matrix element is much larger than the one due to charge fluctuations. From this point of view these systems are more similar to strongly doped semiconductors than to metals.

### II. ELECTRON-PHONON COUPLING FOR A TIGHT-BINDING HAMILTONIAN

In this section we derive the general expressions for the electron-phonon coupling corresponding to a tight-binding Hamiltonian. This is done under the assumption that when the lattice is deformed by displacing an atom on the site  $(n, s)$  ( $n$  indicates the unit cell and  $s$  the position within a unit cell) at the position  $\vec{R}_{n,s} = \vec{R}_n + \vec{d}_s$  to the displaced position  $\vec{R}_{n,s} + \vec{u}_{n,s}$ , the orbitals follow the atoms without appreciable deformation.<sup>8</sup>

Introducing the operator  $a_{n,s}^\dagger$  that creates an electron in the orbital  $(\vec{r} - \vec{R}_{n,s} - \vec{u}_{n,s})$ , we can write the tight-binding Hamiltonian for a general distorted state as

$$H = \sum_{n,n',s,s'} a_{n,s}^\dagger J(n, s; n', s') a_{n',s'}, \quad (2.1)$$

where

$$J(n, s; n', s') = \int \phi^*(\vec{r} + \vec{R}_{n,s} - \vec{R}_{n',s'} + \vec{u}_{n,s} - \vec{u}_{n',s'}) \times V(\vec{r}) \phi(\vec{r}) d\vec{r} \quad (2.2)$$

is the matrix element between orbitals belonging to nearest-neighboring atoms and  $V(\vec{r})$  is the atomic potential.

The electron-phonon coupling constant is obtained by expanding Eq. (2.1) to first order in  $\vec{u}_{n,s} - \vec{u}_{n',s'} = \vec{\delta}(n, s; n', s')$ . We have

$$J = J_0 + \sum_{\alpha} \delta_{\alpha} [\nabla_{\alpha} J]_0, \quad (2.3)$$

where  $\alpha$  indicates a direction  $(x, y, z)$  and  $J_0$  refers to the undistorted case. The Hamiltonian is then given by

$$H = H_0 + H_{\text{int}}, \quad (2.4)$$

where

$$H_0 = \sum_{n, n', s, s'} a_{n, s}^\dagger J_0(n, s; n', s') a_{n', s} \quad (2.5)$$

and

$$H_{\text{int}} = \sum_{n, n', s, s'} \sum_{\alpha} a_{n, s}^\dagger \delta_{\alpha}(n, s; n', s') \times [\nabla_{\alpha} J(n, s; n', s')]_0 a_{n', s}. \quad (2.6)$$

We express now the components of the displacements in terms of the phonon field:

$$u_{n, s, \alpha} = \frac{1}{\sqrt{N}} \sum_{\vec{q}, v} e^{i \vec{q} \cdot \vec{R}_n} S_{s, \alpha}^v(\vec{q}) \frac{1}{\omega_{\vec{q}, v} \sqrt{m_s}} \phi_{\vec{q}, v}, \quad (2.7)$$

where  $\vec{q}$  is the wave vector,  $v$  is the phonon branch,  $m$  is the mass,  $\omega$  is the frequency, and  $S_{s, \alpha}^v(\vec{q})$  is the polarization vector. The phonon field  $\phi_{\vec{q}, v}$  is

given by

$$\phi_{\vec{q}, v} = (\frac{1}{2} \hbar \omega_{\vec{q}, v})^{1/2} (b_{-\vec{q}, v}^\dagger + b_{\vec{q}, v}), \quad (2.8)$$

where  $b$  and  $b^\dagger$  are the usual phonon operators. We also write

$$a_{n, s} = \frac{1}{\sqrt{N}} \sum_{\vec{k}, p} e^{i \vec{k} \cdot \vec{R}_n} U_{s, p}(\vec{k}) c_{\vec{k}, p}^\dagger, \quad (2.9)$$

where  $c_{\vec{k}, p}^\dagger$  is the creation operator for an electron in the state  $\vec{k}$  of the band  $p$  and  $U$  is the matrix that diagonalizes the electronic Hamiltonian after Fourier decomposition. Using Eq. (2.9) we can rewrite  $H_0$  as

$$H_0 = \sum_{\vec{k}, p} (\epsilon_{\vec{k}, p} - \mu) c_{\vec{k}, p}^\dagger c_{\vec{k}, p}, \quad (2.10)$$

where  $\epsilon$  is the band energy and  $\mu$  is the chemical potential. Inserting Eqs. (2.7) and (2.9) into Eq. (2.6) we have

$$H_{\text{int}} = \frac{1}{N} \sum_{\alpha, v} \sum_{n, n', s, s'} \sum_{\alpha, p, p'} \sum_{\vec{k}, \vec{k}'} e^{i \vec{k} \cdot \vec{R}_n} e^{i \vec{k}' \cdot \vec{R}_{n'}} U_{s, p}^*(\vec{k}) U_{s', p'}(\vec{k}') c_{\vec{k}, p}^\dagger c_{\vec{k}', p'} \frac{1}{\omega_{\vec{q}, v} (Nm_s)^{1/2}} \phi_{\vec{q}, v} \times [e^{i \vec{q} \cdot \vec{R}_n} S_{s, \alpha}^v(\vec{q}) - e^{i \vec{q} \cdot \vec{R}_{n'}} S_{s', \alpha}^v(\vec{q})] [\nabla_{\alpha} J(n, s; n', s')]_0. \quad (2.11)$$

After some algebra we can rewrite Eq. (2.11) as

$$H_{\text{int}} = \sum_{v, \alpha} \sum_{n', s', s'} \sum_{\vec{k}, \vec{k}', p, p'} \frac{1}{\omega_{\vec{k} - \vec{k}', v} (Nm_s)^{1/2}} \phi_{\vec{k} - \vec{k}', v} U_{s, p}^*(\vec{k}) U_{s', p'}(\vec{k}') a_{\vec{k}, p}^\dagger a_{\vec{k}', p'} [\nabla_{\alpha} J(0, s; n', s')]_0 \times [e^{i \vec{k}' \cdot \vec{R}_{n'}} S_{s', \alpha}^v(\vec{k} - \vec{k}') - e^{i \vec{k} \cdot \vec{R}_{n'}} S_{s, \alpha}^v(\vec{k} - \vec{k}')], \quad (2.12)$$

and, since the electron-phonon coupling  $g$  is defined by the relation<sup>10</sup>

$$H_{\text{int}} = \frac{1}{\sqrt{V}} \sum_{\vec{k}, \vec{k}', v, p, p'} g_{\vec{k}, p; \vec{k}', p'}^v a_{\vec{k}, p}^\dagger a_{\vec{k}', p'} \phi_{\vec{k} - \vec{k}', v}, \quad (2.13)$$

we have

$$g_{\vec{k}, p; \vec{k}', p'}^v = \left(\frac{V}{N}\right)^{1/2} \sum_{n', \alpha, s, s'} \frac{1}{\omega_{\vec{k} - \vec{k}', v} \sqrt{m_s}} [\nabla_{\alpha} J(0, s; n', s')]_0 \times [e^{i \vec{k}' \cdot \vec{R}_{n'}} S_{s', \alpha}^v(\vec{k} - \vec{k}') - e^{i \vec{k} \cdot \vec{R}_{n'}} S_{s, \alpha}^v(\vec{k} - \vec{k}')] U_{s, p}^*(\vec{k}) U_{s', p'}(\vec{k}'), \quad (2.14)$$

which is the final expression for the electron-phonon coupling corresponding to a tight-binding Hamiltonian. The present result is a generalization of the case described by Barisic *et al.*<sup>7</sup>

### III. APPLICATION TO TWO-DIMENSIONAL GRAPHITE

In this section we derive the electron-phonon coupling as given by Eq. (2.14) for the case of a single graphite layer. We treat the phonons of the layer as those of an elastic continuum and consider only the modes with polarization vector parallel to the plane. Phonons with out-of-plane

displacements do not contribute to the linear coupling.

The polarization vector for longitudinal modes is

$$S_s^l(\vec{q}) = \frac{1}{\sqrt{2}} \frac{\vec{q}}{|\vec{q}|} e^{i \vec{q} \cdot \vec{d}_s} \quad (3.1)$$

and for transverse modes

$$S_s^t(\vec{q}) = \frac{1}{\sqrt{2}} \frac{\vec{q}^\perp}{|\vec{q}|} e^{i \vec{q} \cdot \vec{d}_s}, \quad (3.2)$$

where  $\vec{q}^\perp = (-q_y, q_x)$  is a vector perpendicular to  $\vec{q}$ . Here and in the following we will give a full

derivation of the longitudinal modes, while for the transverse modes we only report the results that can be obtained in an analogous way.

The term in the square bracket of Eq. (2.14) becomes, using Eq. (3.1),

$$\frac{1}{\sqrt{2}} \frac{(\vec{k} - \vec{k}')_\alpha}{|\vec{k} - \vec{k}'|} (e^{i\vec{k} \cdot \vec{R}_{n'}} e^{i(\vec{k} - \vec{k}') \cdot \vec{d}_s} - e^{i\vec{k} \cdot \vec{R}_{n'}} e^{i(\vec{k} - \vec{k}') \cdot \vec{d}_s}). \quad (3.3)$$

As we shall see in the following, the Fermi surface in a charged graphite layer is small with respect to the Brillouin zone so that  $(\vec{k} - \vec{k}') \cdot \vec{d}_s \ll 1$  and we can expand with respect to this term. Equation (3.3) then becomes

$$\frac{i}{\sqrt{2}} \frac{(\vec{k} - \vec{k}')_\alpha}{|\vec{k} - \vec{k}'|} (\vec{k} - \vec{k}') (\vec{R}_{0,s} - \vec{R}_{n',s'}) e^{i\vec{k} \cdot \vec{R}_{n'}}. \quad (3.4)$$

If the matrix element  $J$  defined by Eq. (2.2) depends only on the distance we can write

$$[\nabla_\alpha J(\vec{R}_{0,s} - \vec{R}_{n',s'})]_0 = \frac{(\vec{R}_{0,s} - \vec{R}_{n',s'})_\alpha}{|\vec{R}_{0,s} - \vec{R}_{n',s'}|} q_0 J_0 \quad (3.5)$$

having defined  $q_0$  as

$$q_0 = \frac{1}{J_0} \left( \frac{\partial J(\vec{r})}{\partial |\vec{r}|} \right)_0. \quad (3.6)$$

For our graphite layer we can write the phonon frequencies as

$$\omega^t \simeq \omega^l \simeq c |\vec{k} - \vec{k}'|, \quad (3.7)$$

where  $c$  is an average speed of sound for in plane modes.<sup>11</sup> By making use of Eqs. (3.4) and (3.5) into Eq. (2.14) and considering only one band ( $p = p'$ ) we obtain

$$g_{\vec{k}, \vec{k}'}^i = i \frac{q_0 J_0}{c \sqrt{\rho_c}} \sum_{s, s', n} \left[ \frac{(\vec{k} - \vec{k}') \cdot (\vec{R}_{0,s} - \vec{R}_{n',s'})}{|\vec{k} - \vec{k}'|} \right]^2 \times e^{i\vec{k} \cdot \vec{R}_{n'}} U_s^*(\vec{k}) U_{s'}(\vec{k}'), \quad (3.8)$$

where  $\rho_c = 2Nm_c/V$  is the carbon mass density.

In order to evaluate Eq. (3.8) explicitly for the case of a graphite layer it is necessary to undertake a mathematical, or better trigonometrical "tour de force." The reader who does not want to refresh his ability in such a game can go directly to the final result given by Eqs. (3.47) and (3.48).

It is convenient to introduce the unimodular vectors

$$\vec{m} = (\vec{k} - \vec{k}') / |\vec{k} - \vec{k}'| \quad (3.9)$$

and

$$\vec{e}(0, s; n', s') = \frac{\vec{R}_{0,s} - \vec{R}_{n',s'}}{|\vec{R}_{0,s} - \vec{R}_{n',s'}|}. \quad (3.10)$$

Since in two-dimensional graphite the distance between two nearest carbon atoms is  $a = 1.42 \text{ \AA}$ ,

we always have  $|\vec{R}_{0,s} - \vec{R}_{n',s'}| = a$ , that, together with Eqs. (3.9) and (3.10), allows us to rewrite Eq. (3.8) as

$$g_{\vec{k}, \vec{k}'}^i = \left( \frac{iaq_0 J_0}{c \sqrt{\rho_c}} \right) \sum_{s, s'} F_{s, s'}^i(\vec{m}) f_{s, s'}^*(\vec{k}, \vec{k}'), \quad (3.11)$$

where we have introduced

$$F_{s, s'}^i = \sum_{n'} [\vec{m} \cdot \vec{e}(0, s; n', s')]^2 e^{i\vec{k} \cdot \vec{R}_{n'}} \quad (3.12)$$

and

$$f_{s, s'}^*(\vec{k}, \vec{k}') = U_s^*(\vec{k}) U_{s'}(\vec{k}'). \quad (3.13)$$

For the transverse modes Eq. (3.12) has to be replaced by

$$F_{s, s'}^i = \sum_{n'} [\vec{m} \cdot \vec{e}(0, s; n', s')] \times [\vec{m}^\perp \cdot \vec{e}(0, s; n', s')] e^{i\vec{k} \cdot \vec{R}_{n'}}, \quad (3.14)$$

where  $\vec{m}^\perp \equiv (-m_y, m_x)$  is a vector perpendicular to  $\vec{m}$ .

We have now to specify a coordinate system for our graphite plane. We choose as primitive lattice vectors ( $\vec{n}_1$  and  $\vec{n}_2$  are defined as the corresponding unimodular vectors)

$$\vec{a}_1 = \sqrt{3} \vec{n}_1 \equiv a(0; \sqrt{3}), \quad (3.15)$$

$$\vec{a}_2 = \sqrt{3} \vec{n}_2 \equiv a(\frac{3}{2}; \sqrt{3}/2).$$

The two atoms ( $s = 1, 2$ ) in the unit cell are, respectively, at positions  $\frac{1}{3}(\vec{a}_1 + \vec{a}_2) \equiv a(\frac{1}{2}; \sqrt{3}/2)$  and  $\frac{2}{3}(\vec{a}_1 + \vec{a}_2) \equiv a(1; \sqrt{3})$ .

The primitive vectors of the reciprocal lattice are

$$\vec{k}_1 = (2\pi/3a)(-1; \sqrt{3}), \quad (3.16)$$

$$\vec{k}_2 = (2\pi/3a)a(2; 0).$$

The Fermi surface of two-dimensional charged graphite consists of small circles around the  $P$  points in the Brillouin zone.<sup>9</sup> Because of symmetry it is only necessary to consider one of these points that we choose to be the one corresponding to the vector

$$\vec{k}_p = (2\pi/3a)(1; 1/\sqrt{3}). \quad (3.17)$$

The unimodular vectors connecting the nearest-neighboring atoms to the atom  $s = 1$  (bond vectors) are

$$\vec{e}_1 \equiv (-\frac{1}{2}; -\frac{1}{2}\sqrt{3}),$$

$$\vec{e}_2 \equiv (1; 0), \quad (3.18)$$

$$\vec{e}_3 \equiv (-\frac{1}{2}; \frac{1}{2}\sqrt{3}).$$

The atomic orbitals of interest are the  $\pi$  orbitals of carbon atoms, one orbital per atom. The matrix elements of the tight-binding Hamiltonian

(2.1) between the Bloch states corresponding to these orbitals are given by

$$A = J_0 \begin{bmatrix} 0 & \alpha(\vec{k}) \\ \alpha^*(\vec{k}) & 0 \end{bmatrix}, \quad (3.19)$$

where

$$\alpha(\vec{k}) = 1 + e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2}. \quad (3.20)$$

The matrix that diagonalizes  $A$  is

$$U = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & u(\vec{k}) \\ -u^*(\vec{k}) & 1 \end{bmatrix} \quad (3.21)$$

with

$$u(\vec{k}) = \alpha(\vec{k}) / |\alpha(\vec{k})|. \quad (3.22)$$

Since the electronic states of interest are those in the vicinity of  $\vec{k}_p$ , it is convenient to introduce  $\vec{Q}(\vec{Q}')$  ( $Q = |\vec{Q}|$ ) such that

$$\vec{k} = \vec{k}_p + \vec{Q} \quad (\vec{k}' = \vec{k}_p + \vec{Q}'). \quad (3.23)$$

We then have, expanding around  $k_p$  (small  $\vec{Q}$ ),

$$\alpha^* \alpha = 3 + 2 \cos \vec{k} \cdot \vec{a}_1 + 2 \cos \vec{k} \cdot \vec{a}_2 + 2 \cos \vec{k} \cdot (\vec{a}_1 - \vec{a}_2) = (\frac{3}{2} Q a)^2. \quad (3.24)$$

Expanding also  $\alpha$  as given by Eq. (3.20) and inserting it into Eq. (3.22) we obtain

$$u = \alpha / |\alpha| = (2/\sqrt{3}) [e^{i\vec{k}_p \cdot \vec{a}_1} i(\vec{n} \cdot \vec{n}_1) + e^{i\vec{k}_p \cdot \vec{a}_2} i(\vec{n} \cdot \vec{n}_2)], \quad (3.25)$$

where we have introduced

$$\vec{n} = \vec{Q} / |\vec{Q}| \quad (\vec{n}' = \vec{Q}' / |\vec{Q}'|) \quad (3.26)$$

and the vectors  $\vec{n}_i$  are defined by Eq. (3.15).

We notice now that in the summation over  $s$  and  $s'$  in Eq. (3.11) only the off-diagonal terms are nonzero. This is due to the fact that the nearest-neighbor atoms of an atom of type  $s=1$  are only of type  $s'=2$  and vice versa. The diagonal terms of Eq. (3.12) are therefore zero and so we are only interested in the off-diagonal terms also for Eq. (3.13).

These terms are

$$f_{12}^*(\vec{n}, \vec{n}') = U_1^*(\vec{n}) U_2(\vec{n}') = -\frac{1}{2} u^*(\vec{n}') = -(1/\sqrt{3}) [e^{-i\vec{k}_p \cdot \vec{a}_1} i(\vec{n}' \cdot \vec{n}_1) + e^{-i\vec{k}_p \cdot \vec{a}_2} i(\vec{n}' \cdot \vec{n}_2)] \quad (3.27)$$

and

$$f_{21}^*(\vec{n}, \vec{n}') = U_2^*(\vec{n}) U_1(\vec{n}') = -\frac{1}{2} u(\vec{n}) = f_{12}(\vec{n}', \vec{n}). \quad (3.28)$$

We can now explicitly evaluate Eqs. (3.27) and (3.28). In fact

$$\begin{aligned} \vec{n} &\equiv (n_x, n_y), \\ (\vec{n} \cdot \vec{n}_1) &= n_y, \\ (\vec{n} \cdot \vec{n}_2) &= (\sqrt{3}/2)n_x + \frac{1}{2}n_y, \end{aligned} \quad (3.29)$$

and introducing

$$\phi = \cos^{-1} n_x, \quad \phi' = \cos^{-1} n'_x \quad (3.30)$$

we obtain, after some algebra,

$$f_{12}^*(\vec{n}') = B^* e^{i\phi'}, \quad (3.31)$$

$$f_{21}^*(\vec{n}) = f_{12}(\vec{n}) = B e^{-i\phi}, \quad (3.32)$$

where

$$\begin{aligned} B &= (\sqrt{3}/4) [1 + i(1/\sqrt{3})], \\ B^* &= (\sqrt{3}/4) [1 - i(1/\sqrt{3})]. \end{aligned} \quad (3.33)$$

Turning now to the terms given by Eq. (3.12) we notice that the expansion of the terms (3.13) does not produce zero-order terms but only linear terms in  $\vec{Q}$ . This implies that to have linear terms in the product [Eq. (3.11)], we have to take only the zero-order terms in Eq. (3.12). These are

$$\begin{aligned} F_{12}^l(\vec{m}) &= (\vec{m} \cdot \vec{e}_1)^2 + (\vec{m} \cdot \vec{e}_2)^2 e^{-i\vec{k}_p \cdot \vec{a}_2} \\ &\quad + (\vec{m} \cdot \vec{e}_2)^2 e^{i\vec{k}_p \cdot \vec{a}_1}, \\ F_{21}^l(\vec{m}) &= F_{12}^l(\vec{m})^*. \end{aligned} \quad (3.34)$$

Diagonal terms are zero as discussed before.

Having now

$$\begin{aligned} \vec{m} \cdot \vec{e}_1 &= -\frac{1}{2} m_x - (\sqrt{3}/2) m_y, \\ \vec{m} \cdot \vec{e}_2 &= m_x, \\ \vec{m} \cdot \vec{e}_3 &= -\frac{1}{2} m_x + (\sqrt{3}/2) m_y, \end{aligned} \quad (3.35)$$

we obtain, after some algebra,

$$F_{12}^l = A (m_x + i m_y)^2 \quad (3.36)$$

with

$$A = -\frac{3}{8} (1 + i\sqrt{3}). \quad (3.37)$$

Inserting Eqs. (3.23) and (3.26) into Eq. (3.9) we have

$$\vec{m} = (\vec{n} - \vec{n}') / |\vec{n} - \vec{n}'| \quad (3.38)$$

and therefore we can rewrite Eq. (3.36) as

$$F_{12}^l = A (e^{i\phi} - e^{i\phi'})^2 / |e^{i\phi} - e^{i\phi'}|^2. \quad (3.39)$$

With Eqs. (3.27), (3.28), and (3.39) we can now explicitly evaluate Eq. (3.11). In particular we are interested in the square modulus of the electron-phonon coupling. This is

$$|g_{\vec{k}, \vec{k}'}^l|^2 = (a q_0 J_0 / c \sqrt{\rho_c})^2 |G|^2, \quad (3.40)$$

where

$$\begin{aligned}
|G|^2 &= |[F_{12}^i(\vec{m})f_{12}^*(\vec{n}') + F_{12}^{i*}(\vec{m})f_{12}(\vec{n})]|^2 \\
&= \left| \left( A \frac{(e^{i\phi} - e^{i\phi'})^2}{|e^{i\phi} - e^{i\phi'}|^2} B^* e^{i\phi'} \right. \right. \\
&\quad \left. \left. + A^* \frac{(e^{-i\phi} - e^{-i\phi'})^2}{|e^{-i\phi} - e^{-i\phi'}|^2} B e^{-i\phi} \right) \right|^2. \quad (3.41)
\end{aligned}$$

From Eqs. (3.33) and (3.37) we have

$$AA^*BB^* = \frac{9}{64} \quad (3.42)$$

and

$$AAB^*B^* = A^*A^*BB = -\frac{9}{64}. \quad (3.43)$$

Also, we have

$$|e^{i\phi} - e^{i\phi'}|^2 = 2 - 2\cos(\phi - \phi'), \quad (3.44)$$

and Eq. (3.11) gives

$$|G|^2 = \frac{9}{64} \frac{1}{[2 - 2\cos(\phi - \phi')]^2} \{2[2 - 2\cos(\phi - \phi')]^2 - (e^{i\phi} - e^{i\phi'})^4 e^{i(\phi + \phi')} - (e^{-i\phi} - e^{-i\phi'})^4 e^{-i(\phi + \phi')}\}. \quad (3.45)$$

We leave it as an exercise to show that Eq. (3.45) reduces to the simple result

$$|G|^2 = \frac{9}{32} [1 - \cos 3(\phi + \phi')] \quad (3.46)$$

and therefore

$$|g_{\vec{k}, \vec{k}'}^l|^2 = \frac{1}{2} \left( \frac{3}{4} a q_0 J_0 / c \sqrt{\rho_c} \right)^2 [1 - \cos 3(\phi + \phi')]. \quad (3.47)$$

Repeating the calculation for the transverse modes, one obtains

$$|g_{\vec{k}, \vec{k}'}^t|^2 = \frac{1}{2} \left( \frac{3}{4} a q_0 J_0 / c \sqrt{\rho_c} \right)^2 [1 + \cos 3(\phi + \phi')]. \quad (3.48)$$

Equations (3.47) and (3.48) represent the central result of this paper. In the following we will exploit the consequences of this result. Before concluding this section we would like to point out the important fact that while in simple metals (quasi-free electrons) the electron-phonon coupling due to transverse modes is negligible, here (tight binding) it gives a contribution as large as that of the longitudinal phonons.

#### IV. CONDUCTIVITY

In the relaxation time ( $\tau$ ) approximation the conductivity is given by<sup>12,13</sup>

$$\sigma_0 = e^2 N(\mu) \langle v_x(\mu)^2 \rangle \tau, \quad (4.1)$$

where  $\mu$  is the shift of chemical potential with respect to the neutral layer.  $N(\mu)$  is the density of states at the Fermi surface (two full circles per unit cell). The Fermi velocity in  $x$  direction is  $v_x(\mu)$  and the average  $\langle \dots \rangle$  is over the Brillouin zone. In order to obtain Eq. (4.1) we have also replaced the derivative of the Fermi function with a delta function. At (and below) room temperature this approximation is valid.

In the neighborhood of the point  $P$  in the Brillouin zone of two-dimensional graphite the band

has the linear dispersion [see Eqs. (3.19) and (3.24)]:

$$\epsilon(Q) = \frac{3}{2} J_0 a Q. \quad (4.2)$$

This gives

$$\langle v_x^2 \rangle = \frac{1}{2} \langle v^2 \rangle = \frac{1}{2} \left( \frac{3}{2} J_0 a \right)^2 \hbar^{-2} \quad (4.3)$$

independent of  $\mu$ .

The relaxation time  $\tau$  is computed from the electron-phonon scattering. The electron-electron scattering can be neglected because, as in  $\text{TiS}_2$ ,<sup>14</sup> the carrier pockets are too small (for reasonable values of  $\mu$ ) to allow for the umklapp electron-electron process. We obtain then in the high-temperature limit, and including only scattering within the same circular Fermi surface,

$$\tau = \frac{2}{\pi} \frac{\hbar}{N(\mu) k_B T} \frac{1}{\langle |g|^2 \rangle_{\text{tr}}}, \quad (4.4)$$

where  $|g|^2$  is the sum of all the terms that contribute to electron-phonon scattering. The average  $\langle \dots \rangle_{\text{tr}}$  is the transport average over the Fermi surface:

$$\langle A \rangle_{\text{tr}} = \langle A [1 - \cos(\phi - \phi')] \rangle. \quad (4.5)$$

From Eqs. (3.47) and (3.48) we have

$$\begin{aligned}
\langle |g|^2 \rangle_{\text{tr}} &= \langle |g_{\vec{k}, \vec{k}'}^l|^2 \rangle_{\text{tr}} + \langle |g_{\vec{k}, \vec{k}'}^t|^2 \rangle_{\text{tr}} \\
&= \left( \frac{3}{4} a q_0 J_0 / c \sqrt{\rho_c} \right)^2 \quad (4.6)
\end{aligned}$$

and therefore

$$\sigma_0 = \frac{4}{\pi} \frac{e^2}{\hbar} \frac{\rho_c c^2}{q_0^2 k_B T}. \quad (4.7)$$

As is evident from Eq. (4.7), the conductivity does not depend on the Fermi level and therefore on the carrier concentration. This is due to the fact that, contrary to the case of free electron, the band energy given by Eq. (4.2) is linear in  $Q$ .

For the carbon mass density  $\rho_c$  we take the

three-dimensional value of graphite  $\rho_c = m_c 1.14 \times 10^{23} \text{ cm}^{-3}$  so that our conductivity refers to a three-dimensional crystal made out of independent layers. The average speed of sound for in-plane modes can be estimated to be  $c \approx 2.1 \times 10^8 \text{ cm sec}^{-1}$ .<sup>11</sup> In order to determine explicitly  $\sigma_0$  we only have to determine  $q_0$  as defined from Eq. (3.6). We need therefore an analytical expression for  $J(r)$ . The carbon  $\pi$  orbitals and the atomic potential are constructed from Slater orbitals whose exponent is fixed to give  $J_0 = 2.2 \text{ eV}$  as obtained from optical experiments.<sup>15</sup> The value of the exponent that produces the correct  $J_0$  is  $\xi \approx 1.5$  (in a. u.). The corresponding value for  $q_0$  is  $q_0 \approx 2.5 \text{ \AA}^{-1}$ . One should notice that this estimate does not include the fact that the  $\pi$  orbitals in the solid have a partial hybridization (deviation from circular symmetry). The inclusion of this effect would reduce  $q_0$ . A completely independent estimate for  $q_0$  can be obtained by interpreting the optical spectrum of polyacetylene in terms of a Peierls transition.<sup>16</sup> In this case we obtain<sup>17</sup>  $q_0 \approx 2.0 \text{ \AA}^{-1}$ , which is reasonably consistent with the previous estimate. With  $q_0 = 2.5 \text{ \AA}^{-1}$  we obtain at  $T = 300 \text{ K}$ ; in  $(\Omega \text{ cm})^{-1}$ ,

$$\sigma_0 \approx 13 \times 10^5, \quad (4.8)$$

which is more than twice the conductivity of copper at the same temperature. This result corresponds to the asymptotic ( $T \rightarrow \infty$ ) expression for conductivity. The inclusion of the effects due to the finiteness of temperature (phonon freezing) would increase  $\sigma_0$ .

## V. SUMMARY AND DISCUSSION

In this paper we have computed by first principles the electron-phonon coupling for a graphite layer. The calculation is performed within the tight-binding framework.<sup>6-8</sup> This implies that when an ion is displaced by a phonon the orbitals rigidly follow the ion. This is different than the standard approach for normal metals where the displaced ion is assumed to produce a Coulomb potential that is then screened by the electrons.<sup>24</sup>

In the tight-binding case the coupling comes from the modulation of the tight-binding matrix elements arising from the change in the overlap between orbitals placed on different atoms and not from a Coulomb potential. In this respect the tight binding corresponds to the limit of total screening. In graphite the electrons are quite localized on the carbon orbitals and the tight-binding picture is quite appropriate.<sup>9</sup> Of course, the assumption that the orbitals rigidly follow the displaced ions might be too drastic and the effect of partial "orbital relaxation" should be consider-

ed.<sup>8</sup> This is not included in the present calculation that in this respect provides an upper limit for the electron-phonon coupling. Orbital relaxation would in fact decrease the change in electronic energy due to the distortion and therefore it would reduce  $g$ .

Our calculation refers in particular to the neighborhood of the point  $P$  of the Brillouin zone where a circular Fermi surface appears when charge is added or taken from the graphite layer. The analytical result we derive is based on a linear expansion for small deviation from the  $P$  point. For this case we find that the longitudinal and transverse (in-plane) modes give exactly the same total contribution to the scattering. This is quite different from the scattering by charge fluctuations where the transverse modes give zero or negligible contributions.<sup>12</sup>

In the case of a large shift of the Fermi level ( $|\mu| \geq 1 \text{ eV}$ ) the linear expansion used here becomes inappropriate and higher-order terms provide an increase of  $|g^2|$  with a term proportional to  $Q^2$ .<sup>17</sup> It is interesting to note that for this additional term the longitudinal modes give a much larger contribution than the transverse ones.

Also, for  $|\mu| \geq 1 \text{ eV}$  the high-temperature limit that we use for the conductivity [Eq. (4.4) and following] might be inappropriate even at room temperature. This is because the population of the phonons responsible for scattering is reduced by the Bose function. This effect enhances  $\sigma_0$  and produces deviations from the  $T^{-1}$  behavior that are larger at lower temperatures.<sup>17</sup> This behavior is in agreement with recent experiments on intercalation compounds.<sup>18</sup>

Before discussing the relevance of the results of this calculation with respect to intercalation compounds we should explicitly point out that the present model does not apply to pure three-dimensional graphite. The reason is that in pure graphite the Fermi surface is drastically modified by the coupling between layers and so is the electron-phonon coupling.<sup>19</sup> An additional consequence of this is that phonons with displacements perpendicular to the planes are also important for scattering.<sup>11</sup> By sufficiently shifting the chemical potential ( $|\mu| \geq 0.1 \text{ eV}$ ), as is the case when charge transfer occurs (due to intercalation), one actually reaches a region in which the band structure has essentially a *two-dimensional character*.<sup>3</sup> In this region the coupling between graphite layers becomes negligible with respect to the electrical properties. For the application of the present calculation to intercalation compounds there is also an upper limit to the shift of the chemical potential in the graphite layers,  $|\mu| \leq 1.5 \text{ eV}$ . Above this value there are deviations

from the simple band structure given by Eq. (4.2).<sup>9</sup> In some materials, mainly donor intercalation compounds,<sup>1-3</sup> there is also an appreciable coupling between the intercalated and the graphite layers. This effect, not included in our model, can give rise to a new three-dimensional conduction band that decreases the conductivity anisotropy with respect to pure graphite. On the opposite, the best conductors are of acceptor type and show an increase of the conductivity anisotropy with respect to pure graphite. This indicates a small coupling between intercalated and graphite layers and supports the hypothesis of independently conducting graphite layers. The condition on the shift of the chemical potential ( $0.1 \lesssim |\mu| \lesssim 1.5$  eV) for the validity of our model seems to be satisfied in the best-known materials.<sup>4,5</sup>

On the basis of our results we therefore conclude

that the theoretical conductivity for intercalation compounds, including the geometrical factors due to the presence of the intercalate, is not expected to reach values much larger than that of copper.

Finally, we would like to point out that an additional scattering mechanism exists in these systems and it is related to the potential exerted on the carriers (in the graphite layers) by the ionized intercalated molecules. This mechanism is responsible for the different conductivities observed for various compounds<sup>1-3</sup> and depends on the state of order of the intercalate molecules.<sup>17</sup>

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