

ELECTRON-PHONON INTERACTION AND CONDUCTIVITY
OF A CHARGED GRAPHITE LAYER

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The microscopic origin of the high electrical conductivity of graphite intercalation compounds is discussed. The electron-phonon coupling is shown to be due to modulations of the tight binding matrix elements more than to charge fluctuations as in normal metals. This coupling is used to compute the conductivity as well as other properties and an overall good agreement with available experiments is obtained.

I. Introduction

Recently there have been reports according to which the conductivity of some graphite intercalation compounds can reach or exceed that of copper at room temperature [1]. These syntetic metals are compounds in which graphite layers alternate with intercalate layers [1-3]. The intercalate molecules can be of many different types and they can either give (donors) or take (acceptors) charge from the graphite layers. Of particular interest are the acceptors in which the intercalate layers contain strong acids like AsF_5 and SbF_5 [4]. These systems show the highest conductivities with a very large anisotropy. Conduction takes places essentially in the charged graphite layers.

Since these compounds are very different from simple metals the question whether the reported conductivity is intrinsic or it could be improved significantly (by improving the sample preparation or the chemistry of the compounds) is of both practical and fundamental importance. In the following we will study the problem of the calculation by first principles of the conductivity of a charged graphite layer. In particular the question of what is the theoretical maximum conductivity for these compounds will be considered.

II. Variational Solution of Boltzmann Equation

The variational solution of Boltzmann equation has been discussed by various authors [5]. Here we will write it in a form that is specially simple for a physical interpretation of the various terms [6]. The resistivity (along the x-axis) is given by

$$\rho(T) = \left[e^2 N(\mu) \langle v_x^2(\mu) \rangle \tau(\mu, T) \right]^{-1} \quad (1)$$

where v_x is the x component of the electron band velocity, τ is the "transport" relaxation time [5,6], μ is the Fermi level, N is the density of states and $\langle \dots \rangle$ is the average over the Fermi surface.

For the electron-phonon scattering it is convenient to write the relaxation time τ as the product of the asymptotic high temperature expression $\tilde{\tau}(\propto T^{-1})$ divided a correction function $F(T)$ that takes care of the fact that the temperature is actually finite and not all phonon states are populated.

$$\tau(\mu, T) = \tilde{\tau}/F(T), \quad (2)$$

where

$$\tilde{\tau} = \left[\frac{2\pi}{\hbar} k_B T \langle |g_{\underline{k}, \underline{k}'}|^2 (1 - \cos\theta) \rangle N(\mu) \right]^{-1} \quad (3)$$

is given by the variational solution of Boltzmann equation [5]. Here $g_{\underline{k}\underline{k}'}$ is the el-ph coupling in the notations of Ref. [7] and θ is the scattering angle between $\underline{k}$ and $\underline{k}'$. The correction function $F(T)$ is [6]

$$F(T) = \left(\frac{\hbar}{k_B T} \right)^2 \langle q^2 (1 - \cos\theta) G^{-1} \rangle / \langle q^2 (1 - \cos\theta) [\omega(q)]^{-2} \rangle, \quad (4)$$

$$G = \left\{ \exp [\hbar\omega(q)/k_B T] - 1 \right\} \cdot \left\{ 1 - \exp[-\hbar\omega(q)/k_B T] \right\}, \quad (5)$$

where $\underline{q} = \underline{k} - \underline{k}'$ and ω is the phonon frequency. Of course for $T \rightarrow \infty$ we have $F(T) \rightarrow 1$.

For a single graphite layer the Fermi surface consists of circles around the P (or K) points of the hexagonal Brillouin zone and the band dispersion in the vicinity of these points is linear [8]. The band energy is [9]

$$\varepsilon(k) = \frac{3}{2} J_0 a \hbar k, \quad (6)$$

where $a = 1.42\text{\AA}$ is the distance between nearest carbon atoms and $J_0 \approx 2.4\text{ eV}$ is the tight binding matrix element [10]. We only consider the scattering within the same circle (around a P point) [6,9] and, of course, between states with the same spin. Since the density of states N refers to two circles and two spins an extra factor of four goes into Eq. (3) when applied to this case. Specifying the formulas for the case of the compound C_8AsF_5 [4] (one graphite layer per intercalate layer) and defining an asymptotic $\tilde{\rho}$ as for $\tilde{\tau}$ we have

$$\tilde{\rho} = \rho/F(T) = \frac{4}{9} \frac{(d+d')\pi k_B T \hbar}{e^2 (J_0 a)^2} \langle |g_{\underline{k}, \underline{k}'}|^2 (1 - \cos\theta) \rangle, \quad (7)$$

where $d = 3.35\text{\AA}$ and $d' = 4.95\text{\AA}$ are the thickness of a graphite and an intercalate (AsF_5) layer respectively. The problem is reduced now to the evaluation of the electron-phonon coupling.

III. The Electron-Phonon Coupling in the Tight Binding Scheme

In this section we sketch the derivation of the electron-phonon coupling within the tight binding framework. A more complete derivation can be found in [9]. The reason for using a tight binding description instead of the rigid ion model [11] is the following: The rigid ion model arises from a description of a metal in terms of a lattice of charged ions plus a gas of quasi free electrons. A

phonon produces a distortion of the ionic lattice that gives rise to a fluctuation in the charge density. This charge fluctuation, eventually screened by the quasi-free electrons, is the source of scattering in the rigid ion model. The situation is quite different in graphite because the π orbitals corresponding to the conduction band are tightly bound to the carbon atoms [8]. A lattice distortion is therefore expected to produce mainly a change in the overlap between localized states and only to higher order the orbital relaxation gives rise to a charge fluctuation. This naturally leads to a tight binding approach as the correct starting point for the electron-phonon coupling. Of course, as in band structure calculations, the difference between the two methods (tight binding and rigid ion) should be large when they are applied to lowest order and disappear if a large basis set is used and orbital relaxation is fully included.

The tight binding hamiltonian is written as

$$H = \sum_{\substack{n,n' \\ s,s'}} a_{n,s}^+ J(n,s; n',s') a_{n',s'} \quad , \quad (8)$$

where n refers to the unit cell, s to the atom within the cell and J is the tight binding matrix element between orbitals belonging to nearest neighboring atoms. Expanding J to first order in the distortion $u_{n,s} - u_{n',s'} \equiv \underline{\delta}(n,s; n',s')$ we have

$$J = J_0 + \sum_{\alpha} \delta_{\alpha} [\nabla_{\alpha} J]_0 \quad , \quad (9)$$

where α indicates a direction (x, y, z) and J_0 refers to the undistorted case. Writing then the distortion in terms of the phonon coordinates and using the transformations that diagonalize the unperturbed electronic hamiltonian one can obtain a general expression for the electron-phonon coupling $g_{\underline{k}, \underline{k}'}$, that we do not report here for simplicity [9]. Specifying this expression for a graphite layer and expanding in the vicinity of the P points we obtain [9]

$$|g_{\underline{k}, \underline{k}'}^{\ell(t)}|^2 = \frac{9}{32\rho_c} \left(\frac{a q_0 J_0}{c} \right)^2 [1(\pm) \cos 3(\phi + \phi')] \quad (10)$$

for long wavelength longitudinal (ℓ) and transverse (t) phonons respectively ($c = 2.1 \times 10^6$ cm/s is the average speed of sound). Here ρ_c is the 2-d mass density of graphite ($\rho_c = m_c \cdot 3.82 \times 10^{15}$ cm $^{-2}$) and $\phi(\phi')$ is the angle corresponding to $\underline{k}(\underline{k}')$. The term $q_0 = [dJ(r)/dr] \cdot J_0^{-1}$ can be computed by writing $J(r)$ in terms of Slater orbitals. This gives $q_0 \approx 2.5 \text{\AA}^{-1}$ [9]. Other methods to compute q_0 (or to fit it from other experiments) can also be used and give values between 2 and $3 \text{\AA}^{-1}$. We have then

$$\langle |g_{\underline{k}, \underline{k}'}^{\ell}|^2 (1 - \cos \theta) \rangle = \langle |g_{\underline{k}, \underline{k}'}^t|^2 (1 - \cos \theta) \rangle = \frac{9}{32\rho_c} \left(\frac{a q_0 J_0}{c} \right)^2 \quad (11)$$

From eqs. (4, 5, 7, 11) we obtain at $T = 300^\circ\text{K}$, $F(T = 300^\circ\text{K}) \approx 1.5$ [6] and for the conductivity

$$\sigma(T = 300^\circ\text{K}) = \rho^{-1} \simeq 7.5 \cdot 10^5 (\Omega\text{cm})^{-1} \quad (12)$$

This value, in good agreement with experiments [1,4,6], shows that the observed conductivities are already intrinsic and close to the theoretical maximum for this class of systems. A more detailed analysis of theory and experiments can be found in [6].

In addition to the conductivity there are other properties that are affected by the electron-phonon interaction. One of these is the variation of the in plane distance between carbon atoms (a) as a function of the charge transfer. For this quantity we obtain the following expression [12]

$$a = a_0 + \delta a \quad (a_0 = 1.42\text{\AA}) \quad (13)$$

$$\delta a = \frac{2\pi}{3} \left(\frac{a_0 J_0 q_0}{\eta} \right) f_c^{3/2} \sqrt{\tilde{\rho}_c} \quad (14)$$

where f_c is the charge transfer per carbon atom, $\tilde{\rho}_c = \rho_c/m = 3.82 \times 10^{15} \text{ cm}^{-2}$ is the 2-d density of carbon atoms and $\eta = 3.62 \times 10^5 \text{ dyn/cm}$ is the carbon-carbon bond-stretching force constant [13]. For $f_c \sim .1$ Eqs. (13,14) give $\delta a \sim .008\text{\AA}$ in good agreement with observations [14].

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