

Conductivity in quasi-one-dimensional organic metals. A new approach

I. A. Misurkin and A. L. Tchougreff

Karpov Institute of Physical Chemistry, 103064, Vorontsovo pole, 10, Moscow, Russia

(Received 15 April 1993; accepted 5 August 1993)

A new model for the electric conductivity in quasi-one-dimensional organic metals is proposed. The conductivity is attributed to electron hopping between the separate segments of the one-dimensional donor stacks. The metalliclike behavior of the conductivity at the room temperature as well the low temperature conductivity maximum are explained. The relation of the model with the Anderson's confinement hypothesis is briefly discussed.

I. INTRODUCTION

In recent years there has been considerable progress in preparation of organic and organometallic highly conducting materials (for reference see Refs. 1–3). Most of the materials of that type have as their precursors either large planar molecules forming long stacks or long polymer molecules with conjugated π system.^{1–4} These precursor materials are partially oxidized in order to obtain the desired conducting material. The electric properties of these materials allow one to describe the whole class of the compounds as “organic metals” or “molecular metals.” The band theory (often the lower dimensional tight binding model) is widely used as a theoretical framework for the analysis of the properties of organic metals.

There are, however, strong objections against this picture, both experimental and theoretical ones. Careful analysis of experimental data reveal that the actual behavior of the said materials noticeably deviates from that of normal metals. At low temperatures most of organic metals experience phase transitions of different type which (now it is generally accepted) do not fit in the tight-binding picture. The magnetic susceptibility is remarkably enhanced over its Pauli value^{1,4–6} and sometimes strongly depends on temperature,^{1,5,6} the feature absolutely inappropriate for a normal metal.

The main theoretical objection comes from the paper by Anderson,⁷ where he proposed that the Coulomb repulsion of electrons in the quasi-one-dimensional materials completely changes the electronic states and makes impossible the coherent motion of electrons (the band formation) in the transverse direction (“confinement”). He suggested to reinterpret all the body of the data on conductivity in organic metals from this point of view.

Recently Tchougreff and Misurkin^{8,9} have noticed that, since the structure defects like the Coulomb repulsion also cause the electronic states in quasi-one-dimensional systems to be absolutely different from the Bloch states of the conventional tight-binding model^{10–13} the description of conductivity in “organic metals” normally given in terms of the Fermi velocities and relaxation times^{14–17} generally should not apply.

In this paper we present a model designed to resolve the above-mentioned contradictions and to incorporate diverse experimental facts concerning transport properties of “organic metals.” The paper is organized as follows: In

Sec. II we briefly outline the current state of the problem and present basic ideas of the model. In Sec. III we present a derivation of the formula for the dc conductivity adapted to pick up the specific features of our model. There we also study an important specific case and make some numerical estimates for the conductivity. Some discussions and remarks are given in Sec. IV. The derivations of the cumbersome general formulas are given in Appendices A and B.

II. STATE OF THE PROBLEM AND BASIC IDEAS

A. Review of the problem

All the highly conducting “organic metals” are actually salts (in the chemical sense) formed by their organic or organometallic precursors (Fig. 1) and small molecules of inorganic oxidants. Thus the “organic metals” present a specific case of a broader class of materials known as charge-transfer molecular crystals. When a charge-transfer crystal is formed electrons are transferred from the organic or organometallic (donor) precursors to the acceptor component (in our case to an inorganic molecule). In the crystal of an “organic metal” the flat organic molecules are partially oxidized and form stacked arrays whereas small inorganic anions occupy the cavities between the bulky organic molecules [see Figs. 2(a) and 2(b)].

The most studied materials of this type are probably the derivatives of tetramethyltetraselenafulvalene (TMTSF) better known as Bechgaard salts (TMTSF)₂X, where X is an inorganic anion like PF₆⁻, AsF₆⁻, or SbF₆⁻, or closely related to them derivatives of bisethylenedithia-tetrathiafulvalene (BEDT-TTF),^{1–3} or metallaphthalocyanineiodides MPcI, where M is a divalent metal; M=Ni, Co, Cu, and H₂, other metallophthalocyanine derivatives like NiPc(BF₄)_y or NiPc(ClO₄)_y, and similar compounds with chelating ligands other than phthalocyanine⁴ (see Fig. 1).

The view upon these materials and many other similar systems as upon metals is substantiated by the optical and conductivity measurements performed on these compounds. The presence of the plasma-edge-like features in the reflectance spectra, high room-temperature conductivity along the stacks (σ_{\parallel} ca. $10^3 \div 10^4 \Omega^{-1} \text{cm}^{-1}$), metallic type of the temperature dependence of the conductivity ($d\sigma_{\parallel}/dT < 0$), and the positive and linearly increase with the temperature Seebeck coefficient ($S \sim T$) strongly support the general trend to fit all the data concerning “or-

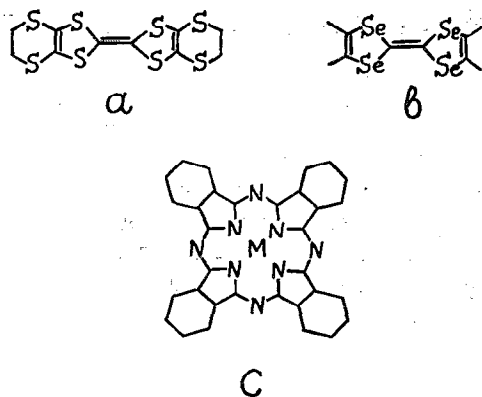


FIG. 1. Building blocks for the stacked quasi-one-dimensional materials.

ganic metals" to the simple tight-binding theory with organic/organometallic units considered as sites. (It is worthwhile to note that the alternative approximation treating the organic stacks as continuous one-dimensional wires and leading to the Ginzburg-Landau-type descriptions of organic metals^{1,13,18} with all its power nevertheless is not able to successfully take into account the structural data.)

In the one-dimensional tight-binding picture each donor molecule supplies its highest occupied molecular orbital (HOMO) to form a one-dimensional band and the parameter of one-electron hopping between the HOMOs of the two adjacent molecules in the stack t_{\parallel} is directly related to the bandwidth $W=4t_{\parallel}$. Before the crystal is formed the HOMOs of all the donor molecules are doubly occupied. In the process of crystal formation some part of electrons (consistent with the overall stoichiometry and the actual structure of the inorganic anions to be formed) moves to the acceptor molecules and each donor unit acquires the average positive charge qe (where e is the unit charge). The average charge q is related to the density of electrons $\rho=2-q$, to the band occupancy $\rho/2$ and to the

Fermi wave number $2k_F=\pi\rho/d$, where d is the intermolecular separation along the stack.

In the case of Bechgaard salts with the stoichiometry $(\text{TMTSF})_2\text{X}$ each inorganic molecule X captures one electron from the donor stack of TMTSF molecules. The average charge of TMTSF unit is $1/2$, $\rho=3/2$, and the band occupancy is $3/4$. In the compounds of the MPcI family iodine atoms form the linear I_3^- anions in the channels between the MPC stacks. Each I_3^- unit captures one electron from the donor stack and the average charge is $1/3$, $\rho=5/3$, and the band occupancy is $5/6$.

The conventional tight-binding model allows one to have simple expressions for the basic experimental quantities through W , ρ , and other parameters of the model (see Refs. 4, 17, 19, and references therein),

$$(\hbar\omega_p)^2 = \frac{W\rho}{4N_e e^2 d^2 \sin^2 \pi\rho/2}, \quad (1)$$

$$S = \frac{2\pi^2 k_B^2 T \cos \pi\rho/2}{3 e W \sin^2 \pi\rho/2}, \quad (2)$$

$$\chi_{\text{Pauli}} = \frac{N_A \mu_B^2 g_e^2}{\pi W \sin^2 \pi\rho/2}, \quad (3)$$

$$\sigma_{\parallel} = e^2 v_F^2 \tau_F \mathcal{N}(\epsilon_F),$$

$$v_F = (Wd/2\hbar) \sin \pi\rho/2; \quad (4)$$

$$\mathcal{N}(\epsilon_F) = (\pi \mathcal{V}_c t_{\parallel} \sin \pi\rho/2)^{-1}.$$

In the listed formulas ω_p is the plasma edge frequency, N_e is the carrier density, k_B is the Boltzmann constant, χ_{Pauli} is the mole paramagnetic susceptibility, N_A is the Avogadro number, μ_B is the Bohr magneton, g_e is the electronic g -factor, v_F is the electron velocity on the Fermi level, τ_F is the scattering time for an electron on the Fermi level, $\mathcal{N}(\epsilon_F)$ is the density of electron states at the Fermi energy per unit volume, and \mathcal{V}_c is the volume of the unit cell. The characteristic time τ_F describes all the possible mechanisms of electron scattering (for example, due to phonons) and contains different types of the temperature dependence of the conductivity.

The first three formulas [Eqs. (1)–(3)] are particularly important because they enable one to relate the measurable quantities to the parameters of the tight-binding model and to check its consistency. The results of that comparison are, however, contradictory. Though the Seebeck coefficient is linear with temperature above ~ 20 K for both Bechgaard salts¹ and H_2PcI (Ref. 4) and the values of the bandwidths obtained from the thermoelectric power (TEP) measurements are in perfect agreement with those derived from the reflectance spectra the measured paramagnetic susceptibility is two or three times enhanced over its Pauli value Eq. (3) and in the case of the Bechgaard salts remarkably depends on temperature. It increases by a factor 1.8 while the temperature increases from 100 to 300 K.^{5,6} The susceptibility enhancement is frequently attributed to the electron-electron repulsion (see, for example, Ref. 20), which must be rather strong as compared to the bandwidth ($\gamma/W \sim 1/2$) to account for the observed factor

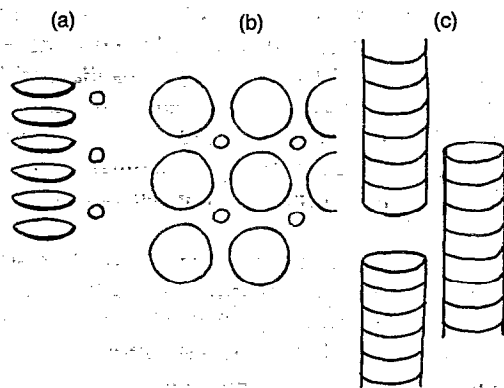


FIG. 2. Structural mode for the typical spatial arrangement of the donor (large circles) and acceptor (small balls) moieties in organic metals; (a) the most typical packing mode; (b) view along the stack direction; (c) arrangement of the adjacent segments of the neighbor stacks.

$\sim (1 - \gamma/W)^{-1}$, which is probably beyond the area where the theory²⁰ applies. Moreover, the electron repulsion does not explain the temperature dependence of the susceptibility in the Bechgaard salts (for more details see Ref. 9).

Additional problems arise when one tries to incorporate into the tight-binding picture the results of the conductivity measurements. Experimentally the longitudinal resistivity $\rho = (\sigma_{\parallel})^{-1}$ of organic metals is characterized as proportional to T^{α} , where α ranges from 1 to 2 for the temperatures above $\sim 15 \div 20$ K. This type of temperature dependence is attributed¹⁵⁻¹⁷ to a cooperative action of two scattering mechanisms—the one-phonon scattering with $\tau_{1p}^{-1} \sim k_B T$ and the two-libron scattering with $\tau_{2l}^{-1} \sim (k_B T)^2$. According to Ref. 17 the one-phonon contribution to the total resistivity dominates at low temperatures whereas at the room temperature the two are approximately equal. The model,¹⁷ however, fails to describe the low-temperature drop of the conductivity of organic metals which happens at the temperatures $\sim 15 \div 20$ K. In the Bechgaard salts this drop is attributed to the transitions of different nature (antiferromagnetic or structural, depending on the type of the inorganic anion X) which actually take place in these compounds. However, the same low-temperature drop is observed in H_2PcI and $NiPcI$ where no phase transition has been found. In the $CuPcI$ compound, having $1/2$ -spins localized in the copper sites, that interact with the itinerant π electrons of the stacked Pc rings, the conductivity drop takes place far above the temperature of the magnetic transition whose precise nature and relation to the conductivity remains unclear until now.²¹

Another group of problems arises when one makes an attempt to incorporate in the one-dimensional tight-binding picture the data on the electric conductivity and other properties obtained on the irradiated samples of organic metals.²²⁻²⁶

It is known that electronic states in the infinite one-dimensional stack are delocalized. Any defects change the electronic structure of a one-dimensional system drastically. Even a small concentration of defects leads to the complete localization of the electronic states (for review see Refs. 10 and 13) and, respectively, even small irradiation damage (or small concentration of substituents in the case of alloying) has to result in sharp changes in the transport and other electronic properties of organic metals. The quasi-one-dimensionality (i.e., the presence of the weak transverse hopping of the strength t_{\perp}) slightly modifies the above conclusion derived for purely one-dimensional systems. The electronic states in a quasi-one-dimensional system localize when $t_{\perp}/t_{\parallel} < (k_F l)^{-1}$, where l is the mean free path, the average separation between the defects.^{10,13} The critical defect concentration n_c above which the mentioned drastic changes in the transport properties are expected to happen is then estimated $n_c = \pi \rho t_{\perp} / 2t_{\parallel}$. In contrast with this prediction all the characteristics (with the only exception, the superconducting T_c) of the irradiated samples of Bechgaard salts vary smoothly with the irradiation dose (or with the fraction of the alloying molecules). No sharp transition from the neat to the irra-

diated crystal is observed. At the same time it is clear²⁷ that for the high irradiation doses the electronic states of the quasi-one-dimensional systems are localized. That suggests that the irradiation merely provides the defects additional to those which persisted in the crystal before and arose during its preparation. The zero irradiation dose corresponds not to zero but to some finite defect concentration n_0 which in its turn is larger than the critical concentration n_c . The very existence of the finite defect concentration in the neat crystals of "organic metals" does not seem surprising in view of the way these materials are obtained. The Bechgaard salts are synthesized by means of electrochemical precipitation from the solution at the room temperature; the metallophthalocyanine iodides are obtained by cosublimation of the metallophthalocyanine and iodine at an elevated temperature. Under the cited conditions either vacancies or dislocations of the organic molecules or other structure defects may well appear. So both the methods mentioned above (and may be any other) are to give a considerable defect concentration, which, we believe, satisfies the condition $n_0 > n_c$.

We arrive to a certain contradiction; the high-temperature conductivity, TEP, and optical data fit nicely into the one-dimensional tight-binding theory, whereas the low-temperature conductivity, magnetic susceptibility, and the data obtained on the irradiated samples do not fit into it at all. The problem is to describe all these data within a single model. Recently an approach alternative to the one-dimensional tight-binding theory to the magnetic properties of the "organic metals" has been proposed.^{8,9} Within that approach the authors succeeded in the uniform description of the magnetic susceptibility data in the neat and irradiated samples of Bechgaard salts by introducing incidentally an alternative description for the electronic structure of the material. In the present paper we apply the same ideas (see below) concerning the electronic structure to the transport properties of "organic metals."

B. Basic ideas and assumptions

Any satisfactory theory should organize into a single picture the following facts briefly reviewed just above: (i) The temperature dependence of the longitudinal conductivity is metalliclike in the high-temperature region. (ii) One electron states are perfectly localized (the system is in the highly doped regime $n > n_c$).

As we have mentioned in the previous section the quasi-one-dimensional materials are usually considered as assemblies of one-dimensional infinite stacks. The stacks are formed by the flat donor (organic or organometallic) molecules. Each molecule supplies its HOMO (most commonly of the π type with respect to the molecular plane) for the delocalized Bloch states would be possibly formed. We accept this description of the local structure of the separate stack but supply it with (i) the structure defects occurring randomly in the stacks; (ii) the intersite electron hopping in the transverse (interstack) direction; and (iii) with an equilibrium phonon heat bath. According to Refs. 8 and 9 we consider only such structure defects which are the unsurmountable barriers for the one-dimensional (lon-

gitudinal) motion of electrons. One electron states are thus extended only over the separate segment rather than over the entire stack as the Bloch states were. The wave function of the system is then an antisymmetrized product of the segment functions.

The segments segregated by the defects on the same stack do not interact. On the other hand the transverse electron hopping results in the interaction between the adjacent segments on the neighbor stacks [Fig. 2(c)]. The transverse intersite hopping leads to transitions between the one-electron states of the adjacent fragments and allows one to introduce the electric current operator. The conductivity is then determined by the rate of the decay of the corresponding elements of the total density matrix of the system and the electron-phonon interactions are included in order to provide the necessary relaxation terms.

To find the relaxation rates we must make certain assumptions concerning the phonon spectrum of the organic metal. It seems reasonable to assume that the vacancies in the donor stacks do not affect the phonon spectrum significantly. This assumption can be substantiated if we treat the vacancy as a molecule with zero mass. In this case the local modes emerging from the acoustic bands have the frequencies higher than all the frequencies in the bands.²⁸ The number of the local modes is proportional to the number of the vacancies n and thus it is small. The long-wave acoustic modes remain unaffected. This allows us to take the phonon Hamiltonian of organic metal as the lattice Hamiltonian of the ideal charge-transfer molecular crystal. We also assume that the matrix elements of the one electron Hamiltonian between the electronic states are linear in the lattice deformations.

III. THEORY

A. One-electron states of a separate segment

In the previous section we assumed that the simplest approximate wave function of the ground state of the crystal of an "organic metal" is the antisymmetrized product of electron functions confined to the segments. We consider the one electron states of the segments (see Refs. 8, 9, 29, and 30). For the sake of simplicity we assume that the planar donor molecules form a rhombohedral lattice with parameters a , b , and c containing one donor molecule per unit cell having the volume $\mathcal{V}_c = abc$. We also assume that the donors are stacked along the a direction and thus this parameter is the intermolecular spacing d within the donor stack [Eqs. (1)–(4)]. For the sake of definiteness we assume that the defects in our case are simple vacancies in the donor stacks.

Let the subscripts α number the vacancies. Then the sites with radius-vectors r_α are vacant. The segments of the stacks are bound by the randomly distributed vacancies. For a given configuration of the defects the radius-vector of the middle of the α th segment is $R_\alpha = (r_\alpha + r_{\alpha+1})/2$ and the segment length $aN_\alpha = r_{\alpha+1} - r_\alpha$. [We assume here that the α th and $(\alpha+1)$ st vacancy occur in the same stack so only their a coordinates are different.] The number of sites in the α th segment is N_α . If the mole fraction of vacancies

is n the average number of the sites (donor molecules) in a segment $\langle N \rangle$ is n^{-1} .

In the tight-binding approximation the one-electron (Hückel) Hamiltonian of the separate fragment coincides with that of the linear polyene of the same length.³¹ If the number of sites in the segment is N the one-electron energies are given by

$$\epsilon(j) = -2t_{\parallel} \cdot \cos \frac{\pi j}{N+1}, \quad j=1 \div N \quad (5)$$

and the coefficients in the expansion of the j th state over the site states are given by

$$A_{jk} = \left(\frac{2}{N+1} \right)^{1/2} \sin \frac{\pi k j}{N+1}. \quad (6)$$

The one electron states of the segment are either symmetric or antisymmetric with respect to its center. For that reason the mean value of the radius vector of an electron in any one of one-electron states of the α th segment is R_α and coincides with the middle of the segment.

If the density of electrons is ρ , the number j_H of the occupied one-electron level in the segment of the length N is $N\rho/2$. The energy gap between the highest occupied (j_H) level and the lowest empty ($j_L = j_H + 1$) one is

$$\Delta = 4\pi t_{\parallel} \cdot \sin(\pi\rho/2)/N. \quad (7)$$

The many-electron states of the system are the products of the local states. The ground state Ψ_g of the system of the segments is the product of the segment ground states $\Psi_g^{(\alpha)}$,

$$\Psi_g = \prod_{\alpha} \Psi_g^{(\alpha)}.$$

The many electron states of the segments $\Psi_g^{(\alpha)}$ are in their turn the Slater determinants of the occupied one-electron states with $j < j_H$,

$$\Psi_g^{(\alpha)} = \prod_{\substack{j < j_H \\ \sigma}} a_{\alpha j \sigma}^+ |0\rangle,$$

where $a_{\alpha j \sigma}^+$ are the operators of creation of an electron with the spin projection σ in the respective one-electron states.

The excited states of the system can be obtained by transfers of electrons from the occupied states to the empty ones. The low energy states correspond to the transfer of one electron. The excited state $|m\rangle$, $m = (i\alpha \rightarrow j\beta)$, is obtained by transfer of an electron from the i th state in the α th segment to the j th state in the β th segment (β may equal to α). The states of the lowest energy are those where an electron is transferred from the highest occupied (j_H^α) state to the lowest unoccupied state (j_H^β). The energies of the states of this type are $(\Delta_\alpha + \Delta_\beta)/2$, where Δ_α and Δ_β are given by Eq. (7) with N equal to N_α and N_β , respectively.

B. The velocity operator in the system of segments

Specific properties of organic metals are reflected in the theory through the electron velocity operator having the form characteristic for this system.

As we mentioned in Sec. III A, the one electron states in organic metals are localized and confined to the segments and the donor stacks are broken in by the vacancies. The mean value of the spatial coordinate of an electron in any one-electron state localized in the α th segment equals that of the middle of the segment R_α . For that reason the electronic transitions between the one-electron states confined to the same segment do not contribute to the velocity. On the other hand the transitions between the segments contribute to the velocity. So we can write

$$i\hbar v = i\hbar \dot{r} = [r, H] \quad (8)$$

$$v = -i/\hbar \sum_{\alpha, \beta} (R_\alpha - R_\beta) \sum_{i, j} T_{ij}^{(\alpha\beta)} (\alpha_{i\sigma}^+ \alpha_{\beta j \sigma} - \alpha_{\beta j \sigma}^+ \alpha_{i\sigma}),$$

where R_α and R_β are the vectors of the middles of the α th and β th segments; $T_{ij}^{(\alpha\beta)} \sim t_1$ is the matrix element of the electron hopping between the i th one-electron state of the α th segment and the j th state of the β th segment,

In the above definition of the electron velocity the summation is formally extended to all pairs of the fragments existing in the sample. The hopping matrix elements $T_{ij}^{(\alpha\beta)}$ reduce the number of the terms in the sum, because the nonvanishing hopping elements occur only between the segments of the adjacent donor stacks which in addition must satisfy the following geometrical condition:

$$2(R_\alpha - R_\beta) < a(N_\alpha + N_\beta),$$

which means that the a th component of the separation vector between the middle of fragments α and β are shorter than half of the sum of the segment lengths. This condition ensures that two segments α and β contain donor sites which are immediate neighbors of each other in the transverse direction. Then the matrix element of the transverse electron hopping between the one-electron states of two fragments reads

$$T_{ij}^{(\alpha\beta)} = -t_1 \sum' A_{ik_\alpha}^{(\alpha)} A_{jk_\beta}^{(\beta)}, \quad (9)$$

where the donor sites with numbers k_α and k_β in the respective segments are the immediate neighbors of each other in the transverse direction and the prime at the summation sign indicates that the sum is extended to such pairs of neighbor sites. $A^{(\alpha)}$ and $A^{(\beta)}$ are given by Eq. (6) with $N = N_\alpha$ or N_β , respectively.

C. The dc conductivity in the system of segments

Now an estimate for the dc conductivity in the system of the segments can be obtained from the general Greenwood-Kubo formula³²⁻³⁴ (for the details of the derivation see Appendix A). The conductivity at the frequency ω is given by [Eq. (A9)]

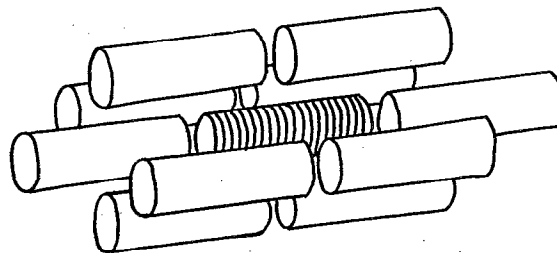


FIG. 3. Regular body centered tetragonal lattice built of the equivalent stack segments.

$$\sigma(\omega) = \frac{e^2}{\hbar \omega \mathcal{V}} \sum_m w_m \sum_{m'} \frac{|v_{mm'}|^2 [1 - \exp(-\hbar \beta \omega_{m'm})] \gamma_{m'm}}{(\omega - \omega_{m'm})^2 + (\gamma_{m'm})^2}. \quad (10)$$

The main contribution to $\sigma(\omega)$ comes from the terms with $\omega_{m'm} = \omega$ in the sum over m' . If $\hbar \omega \ll k_B T$ we have (see Appendix B)

$$\begin{aligned} \sigma(0) &= \frac{e^2}{\hbar} \frac{\hbar}{k_B T \mathcal{V}} \sum_m w_m \sum_{m'} \frac{|v_{mm'}|^2}{\gamma_{m'm}} \\ &= \frac{e^2}{\hbar} \frac{\hbar^2}{2(k_B T)^2 \mathcal{V}} \sum_m w_m \sum_{m'}' D_{m'm} |v_{mm'}|^2, \end{aligned} \quad (11)$$

where the prime at the sum over m' means that the summation is extended to the states with $E_{m'} = E_m$.

The formula for the dc conductivity Eq. (11) can be evaluated in some model situations and the conclusions concerning electric conductivity of organic metals can be derived.

We assume that the vacancies are regularly distributed in the sample. This means that all the segments between two consequent vacancies have the same number of donor sites N and thus the same length Na . Following Ref. 8 we assume that the segments in the adjacent stacks are shifted with respect to each other by one-half of their length so that each segment has eight other segments adjacent to it and the body centered tetragonal lattice is formed where the segments themselves take part of the sites (see Fig. 3).

In this model the energies of the one-electron states do not depend on α , the number of the segment. If we accept the simple Hückel approximation (see Sec. III A) for the electron structure of the segments the estimate for the energies of the lowest excited states $|m\rangle$, $m = (j_H \alpha \rightarrow j_L \beta)$, is Δ and this energy does not depend on α and β . If the energy gap is large as compared to $k_B T$ we can be sure that the excited states involving the electron transfers from the deeper one-electron levels to the higher ones do not contribute to transport effects and we can restrict ourselves with the states of the type $(j_H \alpha \rightarrow j_L \beta)$. The statistical weight of all the states $m = (j_H \alpha \rightarrow j_L \beta)$ is $w_m \sim \exp(-\Delta/k_B T)$.

The intersegment hopping matrix elements between the j_L -states also can be estimated

$$T_{ij}^{(\alpha\beta)} = -t_1 \sum_{k=1}^{N/2} A_{j_L k} A_{j_L k + N/2} \approx -t_1 / 2.$$

With these estimates we have for the matrix element of the electron velocity

$$v_{mm'} = -(i/2)(t_1/\hbar)(R_{\beta'} - R_{\beta}),$$

where $m = (j_H\alpha \rightarrow j_L\beta)$ and $m' = (j_H\alpha \rightarrow j_L\beta')$ and the fragments β and β' are the adjacent ones.

Now we are ready to employ all the estimates made for the system with the regularly displaced defects in order to find the dc conductivity of this system with use of Eq. (11). It is easy to perform the summation over m' first. For any given state $m = (j_H\alpha \rightarrow j_L\beta)$ the only accessible states m' are those $m' = (j_H\alpha \rightarrow j_L\beta')$, where β' runs over eight segments adjacent to the segment β in the bcc lattice of the segments (see above). For the symmetry reasons the relaxation factors $D_{m'm}$ do not depend on the mutual displacement of the segments α , β , and β' so they can be factorized from the sum over m' . Inserting the velocity matrix element one can see that the squares of the hopping vectors $(R_{\beta'}^\mu - R_{\beta}^\mu)^2$ are the same for all allowed pairs of the states m and m' and for the dc conductivity tensor one obtains

$$\sigma_{\mu\nu}(0) = \delta_{\mu\nu} \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T)^2 \mathcal{V}} (R_{\beta'}^\mu - R_{\beta}^\mu)^2 \left(\sum_m w_m \right) \quad (12)$$

or

$$\sigma_{aa}(0) = \sigma_{\parallel}(0) = \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T)^2 \mathcal{V}} (aN)^2 \left(\sum_m w_m \right) \quad (13)$$

$$\sigma_{bb}(0) = \sigma_{\perp b}(0) = \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T)^2 \mathcal{V}} b^2 \left(\sum_m w_m \right) \quad (14)$$

and the conductivity anisotropy becomes

$$\sigma_{\parallel} / \sigma_{\perp b} = (aN)^2 / 4b^2.$$

To estimate the last sum in the brackets we recall that only the excited states of the lowest energy Δ contribute to the sum over m . This sum is equal to $g \cdot \exp(-\Delta/k_B T)$, where g is the number of the excited states with energy Δ in the sample of the volume \mathcal{V} . Each of $\mathcal{V}/N\mathcal{V}_c$ segments can be ionized, however it is unrealistic to think that the extracted electron can go far away from the parent segment (α). The Coulomb forces trap it in certain proximity of the latter so that the extracted electron can be placed only on the segments (β) which environ the parent segment α . The number of the allowed segments β is $\mathcal{N}_{\text{Coul}}$. The number of the excited states g is then $\mathcal{V} \mathcal{N}_{\text{Coul}} / \mathcal{V}_c N$ and the conductivity becomes

$$\sigma_{\parallel} = \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T)^2} \frac{aN}{bc} \mathcal{N}_{\text{Coul}} \exp(-\Delta/k_B T). \quad (15)$$

At the high temperatures, $\exp(-\Delta/k_B T) \approx 1 - \Delta/k_B T$, the longitudinal conductivity becomes

$$\sigma_{\parallel} = \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T)^2} \frac{aN}{bc} \mathcal{N}_{\text{Coul}} (1 - \Delta/k_B T). \quad (16)$$

The longitudinal conductivity reaches its maximum at the temperature $k_B T_m = \Delta/2$,

$$\sigma_{\parallel \text{ max}} = \frac{e^2}{\hbar} \frac{t_1^2 D}{4(k_B T_m)^2} \frac{aN}{bc} \mathcal{N}_{\text{Coul}} e^{-2}. \quad (17)$$

Below T_m the conductivity rapidly drops to zero whereas above T_m there is a long tail $\sim T^{-2}$ mimicking the normal metallic behavior.

The numerical estimates of the parameters entering the theory can be done by fitting the experimental data on the longitudinal conductivity and the conductivity anisotropy. For the H_2PcI the intermolecular separation along the stack $a = 3.25 \text{ \AA}$, and that in the transverse direction $b = c = 14 \text{ \AA}$. With these data the experimental conductivity anisotropy^{4,35} $\sigma_{\parallel} / \sigma_{\perp} \approx 500$ is reproduced if $N \approx 200$. In H_2PcI the conductivity maximum is observed at $T_m = 15 \text{ K}$ and $\sigma_{\parallel \text{ max}} \approx 3800 \Omega^{-1} \text{ cm}^{-1}$.^{4,35} There is no universally adopted values of the transversal hopping parameter t_1 . For the salts $(\text{TMTSF})_2\text{X}$ two types of values are known, $t_1 = 30 \text{ K}$ (Ref. 8) and $t_1 = 300 \text{ K}$ (Ref. 36). Both values seem to be reasonable for the H_2PcI compound as well. Then the experimental $\sigma_{\parallel \text{ max}}$ can be reproduced with $D \mathcal{N}_{\text{Coul}}$ equal, respectively, to either 15 or 0.15. The value of $\mathcal{N}_{\text{Coul}}$ estimated for the Coulomb trap in polyacetylene³⁷ is ~ 10 , so that D is either 1.5 or 1.5×10^{-2} , and both values seem to be reasonable.

The room-temperature conductivity $\sigma_{\parallel}(300)$ of H_2PcI is $\sim 700 \Omega^{-1} \text{ cm}^{-1}$ (Refs. 4 and 35) so that $\sigma_{\parallel}(300) / \sigma_{\parallel \text{ max}}$ is 0.2. The calculation with our parameters gives an order of magnitude lower estimate 0.02, which indicates certain problems within the proposed approach. Another problem arises when we try to estimate independently the characteristic energy Δ . Taking $t_1 = 1.3 \text{ eV}$ from the reflectance measurements^{4,35} and $N = 200$ (see above) we get $\Delta \approx 100 \text{ K}$. Since Δ appears in the exponent the discrepancy with the value of Δ obtained from T_m is significant. It should be noted, however, that the summation over the excited states in the sample leading to the exponential expression in Eq. (15) is very approximate. It is probably correct at low temperatures $T \approx T_m$. At room temperature, when $k_B T \gg \Delta$, multiply excited states may well be important. It suggests that the summation over m in Eqs. (12)–(14) are to be performed more carefully. This work is in progress now.

IV. COMMENTS

In the present paper we develop a model for the hopping conductivity in the system of finite segments each of those is described within the simple tight-binding approximation. The proposed model is applied to the electric conductivity in a quasi-one-dimensional "organic metal," which, we think, can be considered as a system of such segments bound by the structure defects.

The electric properties of materials of this type are usually considered within a standard one-dimensional tight-binding model, which was successful in the description of the metalliclike temperature dependence of the conductivity. We, however, managed to show, that the conductivity increase with the temperature decrease is not the feature characteristic for the normal metals only. The hopping conductivity may also increase with temperature de-

crease (see also Refs. 38, 39, and references therein) and thus the property $d\sigma/dT < 0$ is not an unequivocal indicator of the metallic behavior.

We also describe the conductivity maximum on organic metals occurring at low temperature within our model. These maxima are normally attributed to the metal-insulator phase transitions of different nature (magnetic or structural) taking place in one-dimensional stacks. There are, however, at least several examples (H_2PcI , $NiPcI$) when the conductivity maxima are not related to any phase transition, which simply do not exist in these materials^{40,41} (see also the Introduction). We believe that our approach explains the conductivity maximum without evoking the phase transitions but does not contradict to their possibility (for more detail see Ref. 8).

It is interesting to discuss the relation between our analysis of the conductivity in quasi-one-dimensional organic metals and the proposal due to Anderson⁷ to re-examine the transport properties of these systems from the point of view of his hypothesis of "confinement." Anderson's reasoning is based on the fact that the point $\gamma=0$ (γ is the electron-electron interaction) is a singular point for the one-dimensional system of electrons. At $\gamma=0$ the delocalized Bloch states present the exact answer of the many-electron problem. At any $\gamma \neq 0$ the one-electron states in the one-dimensional system are localized. This singular behavior strongly affects the perturbational treatment of anisotropic two-dimensional systems with $t_{\perp} < t_{\parallel}$. According to Ref. 7 the parameter space (t_{\perp}, γ) falls into two areas. In the area where $t_{\perp} > \gamma$ the correct description can be obtained perturbatively from the delocalized description by turning on first t_{\perp} and then γ . In the area where $t_{\perp} < \gamma$ the confined regime occurs. In this regime the correct description cannot be got if one starts from the delocalized states and turns on t_{\perp} . In this area the interaction should be taken into account first, which leads to the localization in one dimensional system. The quasi-one-dimensional systems, where $t_{\perp} \ll t_{\parallel}$ and $t_{\parallel} \approx \gamma$, seem to fall in the confined regime so that the response in these systems must come entirely from the virtual hopping between the stacks, not from the real transitions.

To reveal the relation between the work by Anderson⁷ and ours one should note that there is at least one more relevant variable with respect to which the one-dimensional many electron problem is singular. That is the defect concentration. If the defects and interaction are absent ($\gamma, n=0$) the delocalized description using the Bloch states is the precise answer. Any nonvanishing concentration of defects destroys this picture, and all one electron states in one dimension become localized. It is easy to see that there is a certain analogy between the effect of the electron-electron interaction and that of defects upon the electronic states of a one-dimensional system. In that concern a question arises if the Bloch description of a separate stack without defects applies as a zero approximation for the anisotropic system with defects. It is obviously so for the modest values of the anisotropy parameter t_{\parallel}/t_{\perp} , and the defects can be treated as a perturbation. By contrast the quasi-one-dimensional organic metals are characterized by

very strong anisotropy $t_{\parallel}/t_{\perp} \sim 10^2$. For such an anisotropy first the defects must be taken into consideration, and then the interstack hopping can be included perturbatively. The analogy with the approach by Anderson is obvious. We have taken into account the defects from very beginning, considering the one-electron states of the separate segments. As a result we have got the response function (the conductivity) entirely due to the virtual hopping.

ACKNOWLEDGMENTS

We thank Professors B. M. Hoffman, M. A. Ratner, and W. P. Halperin for the stimulating discussions during the visit of one of us (A.L.T.) to the Northwestern University. We also thankful to Dr. A. M. Berezkhowski for his instructive comments.

APPENDIX A: THE KUBO-GREENWOOD FORMULA WITH RELAXATION

Here we derive the Kubo-Greenwood formula for the electric conductivity in the system of segments. We follow here the general scheme of the derivation of the Kubo-Greenwood formula given in Ref. 28, but retain the relaxation terms explicitly like in Refs. 34 and 42. We use the technique of the Liouville superoperator presented, for example, in Ref. 42.

The density matrix of the electronic subsystem ρ obeys the equation of motion in the Liouville representation

$$d\rho/dt = \dot{\rho} = -i\hat{L}\rho + \hat{R}\rho, \quad (A1)$$

where the Liouville superoperator \hat{L} is defined by

$$\hbar\hat{L}\rho = H\rho - \rho H.$$

Here H is the Hamiltonian of electrons only. The superoperator \hat{R} describes the relaxation effects due to interactions with the phonon heat bath.

Now let the electronic Hamiltonian H be a sum $H_0 + H'(t)$, where a weak external perturbation $H'(t) \sim \exp(-i\omega t)$. The density matrix then becomes $\rho = \rho_0 + \rho'$. The total density matrix ρ obeys the following equation of motion:

$$\dot{\rho} = -i(\hat{L}_0 + \hat{L}')\rho + \hat{R}\rho, \quad (A2)$$

where

$$\hbar\hat{L}_0 = H_0\rho - \rho H_0;$$

$$\hbar\hat{L}'\rho = H'\rho - \rho H'.$$

We insert the above expansion for ρ in the equation of motion and take into account that the matrix ρ_0 obeys the equation of motion with the Liouville operator \hat{L}_0 . Then, retaining only the terms linear in \hat{L}' we get for the first order correction to the density matrix

$$\dot{\rho}' = -i\hat{L}'\rho_0 - i\hat{L}_0\rho' + \hat{R}\rho'. \quad (A3)$$

The time dependence of the first order correction ρ' to the density matrix coincides with that of the perturbation itself; $\rho' \sim \exp(-i\omega t)$ so taking of the time derivative gives the multiplier $-i\omega$,

$$-i\omega\rho' = -i\hat{L}'\rho_0 - i\hat{L}_0\rho' + \hat{R}\rho'. \quad (\text{A4})$$

The solution of the latter equation with respect to ρ' can be formally written as

$$\rho' = (\omega\hat{I} - \hat{L}_0 - i\hat{R})^{-1}\hat{L}'\rho_0, \quad (\text{A5})$$

where \hat{I} is the superoperator unity.

To find the inverse of the superoperator in the brackets we consider the equation of motion for ρ in the representation of the eigenstates of the electronic Hamiltonian H_0 ,

$$\dot{\rho}_{m'm} = -i\omega_{m'm}\rho_{m'm} + \sum_{n'n} R_{m'mn'n}\rho_{n'n}, \quad (\text{A6})$$

where $\omega_{m'm} = (E_{m'} - E_m)/\hbar$ and E_m is the energy of the electronic eigenstate $|m\rangle$ of the unperturbed Hamiltonian H_0 . For the relaxation superoperator \hat{R} we accept the secular approximation (see Ref. 42),

$$R_{m'mn'n} = \delta_{m'm}\delta_{n'n}(1 - \delta_{mn})W_{mn} - \delta_{m'n}\delta_{mn}\gamma_{m'm}.$$

In this approximation the off-diagonal (in the above representation) elements of the density matrix become the eigenvectors of both the time evolution superoperator $-i\hat{L}_0 + \hat{R}$ with the eigenvalues $-i\omega_{m'm} - \gamma_{m'm}$ and of the inverse superoperator with the eigenvalues $(\omega - \omega_{m'm} + i\gamma_{m'm})^{-1}$. Since the unperturbed density matrix ρ_0 is diagonal in the basis of the eigenstates of the Hamiltonian H_0 and its matrix elements are w_m the perturbation Liouville operator \hat{L}' gives $(\hbar\hat{L}'\rho_0)_{m'm} = H'_{m'm}(w_m - w_{m'})$. Finally we have for the off-diagonal correction to the density matrix

$$\hbar\rho'_{m'm} = \frac{H'_{m'm}(w_m - w_{m'})}{\omega - \omega_{m'm} + i\gamma_{m'm}}. \quad (\text{A7})$$

To find the electric conductivity we introduce the perturbation through the electric vector potential $-iEe^{-i\omega t}/\omega$ and the electric current operator $J = -ev$, where v is the operator of the velocity of electrons.²⁸ The perturbation operator reads

$$H' = -ievEe^{-i\omega t}/\omega$$

so that the amplitude of the external field is E and the electronic operator is $-iev/\omega$. The average current density in the sample is $j = -ev/\mathcal{V}$, where \mathcal{V} is the volume of the sample. For its mean value we have

$$\begin{aligned} \langle j \rangle &= \text{tr}(\rho j) \\ &= \text{tr}(\rho' j) \\ &= \frac{ie^2}{\hbar\omega\mathcal{V}} \sum_{m'm} \frac{v_{mm'}v_{m'm}(w_m - w_{m'})}{\omega - \omega_{m'm} + i\gamma_{m'm}} Ee^{-i\omega t} \end{aligned} \quad (\text{A8})$$

and the real part of the conductivity reads

$$\begin{aligned} \sigma(\omega) &= \frac{e^2}{\hbar\omega\mathcal{V}} \sum_{m'm} \frac{|v_{mm'}|^2 (w_m - w_{m'}) \gamma'_{m'm}}{(\omega - \omega_{m'm} - \gamma''_{m'm})^2 + (\gamma'_{m'm})^2} \\ &= \frac{e^2}{\hbar\omega\mathcal{V}} \sum_m w_m \\ &\quad \times \sum_{m'} \frac{|v_{mm'}|^2 [1 - \exp(-\hbar\beta\omega_{m'm})] \gamma'_{m'm}}{(\omega - \omega_{m'm} - \gamma''_{m'm})^2 + (\gamma'_{m'm})^2}, \end{aligned} \quad (\text{A9})$$

where the complex relaxation rate reads $\gamma_{m'm} = \gamma'_{m'm} + i\gamma''_{m'm}$ and we accepted the relation $w_{m'}/w_m = \exp(-\hbar\beta\omega_{m'm})$ for the statistical weights [as usual $\beta = (k_B T)^{-1}$].

APPENDIX B

Here we (following Ref. 42) derive the estimates for the relaxation rates of the off-diagonal elements $\rho_{m'm}$ of the electronic density matrix. Assume that the interaction operator responsible for the relaxation processes in the system has the form

$$V = \sum_p Q_p F_p,$$

where the operators Q_p act on the variables of the system and the operators F_p on the variables of the heat bath. According to Ref. 42 then the relaxation rates $\gamma_{m'm}$ can be expressed in terms of the quantities $\Gamma_{mkl'n}^{\pm}$

$$\begin{aligned} \Gamma_{mkl'n}^+ &= \hbar^{-2} \sum_{p,q} \langle m | Q_p | k \rangle \langle l | Q_q | n \rangle \\ &\quad \times \int_0^\infty dt \exp(-i\omega_{ln}t) \langle F_p(t) F_q \rangle, \end{aligned}$$

$$\begin{aligned} \Gamma_{mkl'n}^- &= \hbar^{-2} \sum_{p,q} \langle m | Q_p | k \rangle \langle l | Q_p | n \rangle \\ &\quad \times \int_0^\infty dt \exp(-i\omega_{mkt}) \langle F_q F_p(t) \rangle, \end{aligned}$$

$$\gamma_{m'm} = \sum_k (\Gamma_{m'kkm'}^+ + \Gamma_{m'kkm'}^-) - \Gamma_{mmmm'm'}^+ - \Gamma_{mmmm'm'}^-.$$

We assumed (see Sec. II B) that the relaxation in our case appears because of the electron-phonon interaction, so that the operators Q_p act on the electron variables and operators F_p on the phonon ones. The phonon Hamiltonian can be taken in the model form

$$H_{\text{ph}} = \sum_{s,q} \hbar\omega_{sq} (b_{sq}^+ b_{sq} + 1/2), \quad (\text{B1})$$

where ω_{sq} are the phonon frequencies of the mode with the wave vector q and the polarization s ; b_{sq}^+ (b_{sq}) are the creation (annihilation) operators of the corresponding phonons. The linear in lattice deformation matrix element of electron-phonon interaction has the form

$$H_{m'm}^{\text{e-ph}} = \sum_{s,q} Q_{sq}^{mm'} (b_{s-q}^+ + b_{sq}), \quad (\text{B2})$$

The electron-phonon operator Eq. (B2) has the desired form of the interaction operator V . We assume that the phonon correlation functions $\langle F_p(t)F_q \rangle$ have the form

$$\tau_{\text{ph}}\delta(t)(n_{sq}+n_{s-q}),$$

where n_{sq} is the number of phonons, and τ_{ph} is the correlation time for the interaction between electrons and the heat bath.⁴² In this case the integral multipliers simplify to $\tau_{\text{ph}}(n_{sq}+n_{s-q})$ and the quantities $\Gamma_{mkl n}^{\pm}$ become

$$\Gamma_{mkl n}^{+} = (\tau_{\text{ph}}/\hbar) \sum_{s,q} Q_{sq}^{mk} Q_{s-q}^{ln} (n_{sq}+n_{s-q}), \quad (\text{B3})$$

$$\Gamma_{mkl n}^{-} = (\tau_{\text{ph}}/\hbar^2) \sum_{s,q} Q_{s-q}^{mk} Q_{sq}^{ln} (n_{sq}+n_{s-q}).$$

For $\gamma_{m'm}$ we have

$$\begin{aligned} \gamma_{m'm} = & \tau_{\text{ph}}/\hbar^2 \sum_{s,q} (n_{sq}+n_{s-q}) \left[\sum_k (Q_{sq}^{m'k} Q_{s-q}^{km'} + Q_{s-q}^{mk} Q_{sq}^{km}) \right. \\ & \left. - (Q_{sq}^{mm} Q_{s-q}^{m'm'} + Q_{s-q}^{mm} Q_{sq}^{m'm'}) \right] \quad (\text{B4}) \end{aligned}$$

and the relaxation rates $\gamma_{m'm}$ are real ($\gamma_{m'm}'' = 0$).

The temperature dependence of $\gamma_{m'm}$ immediately follows from Eq. (B4). It is determined by that of the number of phonons. The main contribution comes from the low-energy phonons with $\hbar\omega_{sq} \ll k_B T$ and $n_{sq} = k_B T/\hbar\omega_{sq}$. Performing formally the summations over sq and k and factorizing $k_B T/\hbar$ we get

$$\gamma_{m'm} = 2(k_B T/\hbar) D_{m'm}^{-1} \quad (\text{B5})$$

where the dimensionless relaxation factors $D_{m'm}^{-1}$ are given by

$$\begin{aligned} D_{m'm}^{-1} = & \tau_{\text{ph}}/\hbar^2 \sum_{s,q} \omega_{sq}^{-1} \left[\sum_k (Q_{sq}^{m'k} Q_{s-q}^{km'} + Q_{s-q}^{mk} Q_{sq}^{km}) \right. \\ & \left. - (Q_{sq}^{mm} Q_{s-q}^{m'm'} + Q_{s-q}^{mm} Q_{sq}^{m'm'}) \right]. \end{aligned}$$

¹D. Jerome and H. J. Schulz, *Adv. Phys.* **31**, 299 (1982).

²*Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1982), Vol. 1-3.

³*Low Dimensional Conductors and Superconductors*, edited by D. Jerome and L. G. Caron (Plenum, New York, 1987).

⁴T. J. Marks, *Angew. Chem. Int. Ed. Engl.* **29**, 857 (1990).

⁵J. C. Scott, H. J. Pedersen, and K. Bechgaard, *Phys. Rev. Lett.* **45**, 2125 (1980).

⁶L. Forro, J. R. Cooper, B. Rothamel, J. S. Schilling, M. Weger, D. Schweitzer, H. J. Keller, and K. Bechgaard, *Synth. Met.* **19**, 339 (1987).

⁷P. W. Anderson, *Phys. Rev. Lett.* **67**, 3844 (1991).

⁸A. L. Tchougreff and I. A. Misurkin, *Fiz. Tverd. Tela* **30**, 1043 (1988) (in Russian); *Sov. Phys. Solid State* **30**, 605 (1988) (in English).

⁹A. L. Tchougreff and I. A. Misurkin, *Il Nuovo Cimento D* **14**, 833 (1992).

¹⁰N. F. Mott and W. D. Twose, *Adv. Phys.* **10**, 107 (1961).

¹¹N. F. Mott, *Metal-Insulator transitions* (Taylor & Francis, London, 1974).

¹²P. W. Anderson, D. J. Thouless, E. Abrahams, and D. S. Fisher, *Phys. Rev. B* **22**, 3519 (1980).

¹³Yu. A. Firsov, V. N. Prigodin, and C. Seidel, *Phys. Rep.* **126**, 245 (1985).

¹⁴H. Gutfreund, C. Hartstein, and M. Weger, *Solid State Commun.* **36**, 647 (1980).

¹⁵M. Weger, M. Kaveh, and H. Gutfreund, *Solid State Commun.* **37**, 421 (1981).

¹⁶E. M. Conwell, *Phys. Rev. B* **22**, 1761 (1980).

¹⁷P. D. Hale and M. A. Ratner, *J. Chem. Phys.* **83**, 5277 (1985).

¹⁸J. Solyom, *Adv. Phys.* **28**, 201 (1979).

¹⁹J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1972).

²⁰J. B. Torrance, Y. Tomkiewicz, and D. B. Silverman, *Phys. Rev. B* **15**, 4738 (1977).

²¹M. Y. Ogawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Green, B. M. Hoffman, and J. A. Ibers, *J. Am. Chem. Soc.* **109**, 1115 (1987); M. Y. Ogawa, B. M. Hoffman, S. Lee, M. Yudkowsky, and W. P. Halperin, *Phys. Rev. Lett.* **57**, 1177 (1986); G. Quirion, M. Poirier, K. K. Liou, and B. M. Hoffman, *Phys. Rev. B* **43**, 860 (1991); W. P. Halperin (private communication).

²²L. Zuppiroli, *Ber. Bunsenges. Phys. Chem.* **88**, 304 (1984).

²³L. Forro, *Mol. Cryst. Liquid Cryst.* **85**, 315 (1982).

²⁴L. Zuppiroli, S. Bouffard, K. Bechgaard, B. Hilti, and C. W. Mayer, *Phys. Rev. B* **22**, 6035 (1980).

²⁵B. Korin-Hamzic, L. Forro, J. R. Cooper, and K. Bechgaard, *Phys. Rev. B* **38**, 11 177 (1988).

²⁶L. Zuppiroli, *Radiat. Eff.* **62**, 53 (1982).

²⁷L. Zuppiroli, H. Mutka, and S. Bouffard, *Mol. Cryst. Liquid Cryst.* **85**, 1 (1982).

²⁸W. A. Harrison, *Solid State Theory* (McGraw-Hill, New York, 1970).

²⁹D. Kuze and H. R. Zeller, *Phys. Rev. Lett.* **27**, 1060 (1971).

³⁰M. J. Rice and J. Bernasconi, *J. Phys. F* **3**, 55 (1973).

³¹C. A. Coulson and A. Streitwieser, *Dictionary of π Electron Calculations* (Pergamon, New York, 1965).

³²R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).

³³D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

³⁴C. H. Wang, *Spectroscopy of Condensed Media* (Academic, New York, 1985).

³⁵T. Inabe, T. J. Marks, R. L. Burton, J. W. Lyding, W. J. MacCarthy, C. R. Kannewurf, G. M. Reisner, and F. H. Herbstein, *Solid State Commun.* **54**, 501 (1985).

³⁶K. Yamaji, *J. Phys. Soc. Jpn.* **51**, 2787 (1982).

³⁷I. A. Misurkin and A. Yu. Cohn, *Europhys. Lett.* **11**, 145 (1990).

³⁸H. Sumi, *J. Chem. Phys.* **70**, 3775 (1979).

³⁹H. Böttger and V. V. Bryksin, *Hopping Conduction in Solids* (VCH, Berlin, 1985).

⁴⁰C. S. Schramm, R. P. Scarige, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, *J. Am. Chem. Soc.* **102**, 6702 (1982).

⁴¹T. Inabe, S. Nakamura, W.-B. Liang, T. J. Marks, R. L. Burton, C. R. Kannewurf, and K.-I. Imaeda, *J. Am. Chem. Soc.* **107**, 7224 (1985).

⁴²K. Blum, *Density Matrix. Theory and Applications* (Plenum, New York, 1981).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/jcpo/jcpcr/jsp>
Copyright of Journal of Chemical Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.