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Low-temperature transport in charge-density-wave or spin-density-wave distorted quasi-one-dimensional conductors: Low electric fields

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We study transport in low electric fields below T_{MS}, the metal-to-semiconductor transition temperature, for materials such as TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) and $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (*bis*-tetramethyltetraselenafulvalene hexafluorophosphate). For the charge-density-wave (CDW) case we start from a site Hamiltonian including terms for the elastic energy due to lattice distortion arising from internal as well as external modes. From the Hamiltonian in the momentum representation we obtain, for an arbitrary degree of band filling, expressions for the gap (including in the CDW case the contributions of all lattice modes), wave functions, densities of states, etc. Using the wave functions so derived, we show that the matrix element for acoustic-mode scattering below T_{MS} may be taken equal to that above T_{MS} provided we are dealing with thermal (i.e., not hot) electrons. For this matrix element a relaxation time exists, and the mobility μ is obtained by solving the Boltzmann equation. It is shown that, for the large mass anisotropy characterizing these materials, μ along the chain axis obtained by a one-dimensional calculation should be in excellent agreement with the actual μ. The mobility values calculated for acoustic-mode scattering are quite high, 10^4–10^6 cm^2/V sec for the materials concerned, but nevertheless in order-of-magnitude agreement with μ's deduced from experimental data. The significance of the remaining differences between theory and experiment for $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is discussed.

I. INTRODUCTION

Large changes in conductivity with electric field have been found for a number of quasi-one-dimensional (quasi-1D) organic conductors below T_{MS}. Two materials in which these changes have been studied extensively are tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) below the Peierls [charge-density-wave (CDW)] transition temperature[1,2] and bis-tetramethyltetraselenafulvalene hexafluorophosphate $[(\mathrm{TMTSF})_2\mathrm{PF}_6]$ below the spin-density-wave (SDW) transition temperature.[3–5] A prerequisite to studying nonlinear transport is the understanding of linear, or low electric field, transport. This paper is devoted to the theory of low-field transport in the CDW or SDW regime of the family of quasi-one-dimensional organics of which TTF-TCNQ and $(\mathrm{TMTSF})_2\mathrm{PF}_6$ are members.[6] A subsequent paper is planned to take up high-field transport.

To study transport we need wave functions, energy as a function of wave vector k, effective masses, densities of states, etc. for the materials concerned. Wave functions and energies in the Peierls-distorted state have been determined for the case of the half-filled band, starting from the Fröhlich Hamiltonian with acoustic modes only.[7] Essentially the same approach was used for a band of arbitrary filling,[8] although in a free-electron approximation more suitable to wide-band metals than to the organic crystals, which have fairly narrow bands. Recently a treatment of the half-filled-band case which relates the gap more accurately to the deformation due to acoustic modes has been carried out by Su, Schrieffer, and Heeger[9] (SSH) starting from a site representation. The Hamiltonian for the electrons is in the usual tight-binding or hopping form and to this SSH have added a term for the elastic energy due to lattice distortion. Since there is no case of a half-filled band in the family of materials with which we are concerned, it is clear that the theory must be carried out for the case of arbitrary band filling. It must also be extended to take into account the contribution of other modes—librons[10,11] and internal vibrations[12]—to the Peierls gap. These things are done in Sec. II, and expressions for effective masses and densities of states derived. In Sec. III we calculate the carrier concentration from the density of states and use it, together with the known gap, to calculate the mobility in the intrinsic range of TTF- and TSeF- (tetraselenafulvalene-) TCNQ. The reasons for the very high μ's found in these materials, and more directly (through measurement of the Hall effect[5]) in $(\mathrm{TMTSF})_2\mathrm{PF}_6$, are discussed. Since the high μ's suggest dominant phonon scattering, we proceed to calculate μ_{ac}, the mobility due to phonon scattering. We first show that, despite the different wave functions below the transition, the matrix element for acoustic-mode scattering may be taken the same as that above the transition unless the carriers are hot. The matrix element is used to obtain a relaxation time for scattering which, inserted into the Boltzmann equation, leads to an expression for μ_{ac} along the chain direction. We show that, due to the very large mass anisotropy, μ_{ac} should not be much affected by the actual three-dimensional (3D) nature of the crystals. Finally we compare μ_{ac} with the electron and hole μ's deduced from experiment, particularly for $(\mathrm{TMTSF})_2\mathrm{PF}_6$, where the separate μ's have been deduced from Hall effect and magnetoresistance, and consider the implications for the materials.

II. WAVE FUNCTIONS, ENERGIES, AND THE GAP EQUATION

A. The electronic Hamiltonian

We consider first the case of the Peierls transition. As indicated above, for the electronic part of the Hamiltonian, H_{el}, we start with the usual tight-binding form for noninteracting electrons on a chain of N identical molecules

$$H_{\mathrm{el}}=\sum_{j=1}^{N}\sum_{\sigma}\left[\epsilon_j c_{j\sigma}^{\dagger}c_{j\sigma}-t_{j+1,j}\left(c_{j+1,\sigma}^{\dagger}c_{j\sigma}+\mathrm{H.c.}\right)\right] , \tag{2.1}$$

where ϵ_j is the energy, and $c_{j\sigma}^{\dagger}$ and $c_{j\sigma}$ are the creation and annihilation operators, respectively, for an electron on the jth site with spin σ. The coupling between the electrons and the lattice distortion arises through the hopping or transfer integral $t_{j+1,j}$, whose value depends on the relative spacing and orientation of neighboring molecules. Thus the value of $t_{j+1,j}$ is affected both by translational motion and librations. In an idealized case with no mode mixing,[13] we may write

$$-t_{j+1,j}=-t_0+\sum_{i=1}^{3}\left[\frac{\partial t}{\partial u^{(i)}}\right]_0\left(u_{j+1}^{(i)}-u_j^{(i)}\right)+\sum_{i=1}^{3}\left[\frac{\partial t}{\partial \theta^{(i)}}\right]_0\left(\theta_{j+1}^{(i)}-\theta_j^{(i)}\right) , \tag{2.2}$$

t_0 being the transfer integral for the undistorted chain, and $u_j^{(i)}$ and $\theta_j^{(i)}$ the linear and angular displacements, respectively, of the jth molecule due to the ith mode of the type concerned. As a result of symmetry, some of the $(\partial t/\partial u^{(i)})_0$ and $(\partial t/\partial \theta^{(i)})_0$ may vanish.[11] For the modes with nonvanishing derivatives, distortions $u_j^{(i)}$ and $\theta_j^{(i)}$ are frozen in below the Peierls transition temperature with period $Q\equiv 2k_F$, k_F being the Fermi wave vector.[12] We may take these as

$$\begin{aligned} u_j^{(i)}&=A_{0t}^{(i)}\cos(Qx_j) , \\ \theta_j^{(i)}&=A_{0l}^{(i)}\cos(Qx_j) , \end{aligned} \tag{2.3}$$

where the A_0's are amplitudes to be determined to give minimum free energy, and x_j the position of the jth molecule in the undistorted lattice. Actually, as has been pointed out by many authors,[13] for an incommensurate case terms with harmonics of Q should be included in Eq. (2.3). It has been shown, however, that for Q either at or well away from commensurability the harmonic components of the lattice displacement are far smaller than the fundamental,[13,14] and we shall neglect them. Near-commensurate cases require special considerations, such as solitons, and will not be taken up in this paper.

The internal modes are coupled to the electrons through their effect on ϵ_j, the energy of an electron on the jth site. To terms linear in the (dimensionless) normal coordinate $Q_n(j)$ for the nth internal vibration on the jth site we may write[15]

$$\epsilon_j=\epsilon_{j0}+\sum_{n=1}^{G}\beta_n Q_n(j) , \tag{2.4}$$

where ϵ_{j0} is the site energy in the absence of excited vibrations, $\beta_n\equiv[\partial\epsilon_j/\partial Q_n(j)]_0$, and the summation includes only the modes, G in number, linearly coupled to the electrons.[16] For the modes that participate in the Peierls distortion,[12,17] we take

$$Q_n(j)=A_n\cos(Qx_j) , \tag{2.5}$$

the A_n being amplitudes to be determined also by the condition of minimum free energy.

Before using Eqs. (2.2)–(2.5) to write H_{el} in the momentum representation, we note that there is an important difference between the half-filled-band case and all others—there is more than one gap in the other cases. For a tight-binding Hamiltonian symmetric under nearest-neighbor interchange, as is (2.1), it has been shown that the density of states must have symmetry about the center of the band.[15,18(a)] Thus, when there is a gap at $\pm k_F$, there is also one at $\pm(\pi/a-k_F)$, where a is the lattice spacing. For the materials of interest here the gaps are separated by a sizable fraction of the bandwidth, $4t_0$, as a result of the band filling being $\sim\frac{1}{4}$ or $\frac{1}{3}$

and the gaps (2Δ) quite small compared to $4t_0$. Since, as will be seen, the wave functions are altered significantly only within an energy range of a few Δ about the gap, it is a good approximation for these materials to deal with only one gap, the one separating filled and empty subbands. With this in mind we transform H_{el} of (2.1) to the momentum representation, using Eqs. (2.2)–(2.5) and the Fourier transforms of $c_j, c_j^\dagger$. The result may be written

$$H_{\text{el}} = 2 \sum_{0\le k\le k_F} \sum_{\sigma} [\, \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \epsilon_{k-Q} c_{k-Q,\sigma}^\dagger c_{k-Q,\sigma} + (\Delta_k' c_{k\sigma}^\dagger c_{k-Q,\sigma} + \text{H.c.})] \;, \tag{2.6}$$

where ϵ_k, the energy in the undistorted band measured from the Fermi energy (not equal to ϵ_j in the present case) is given by

$$\epsilon_k = 2t_0[\cos(k_F a) - \cos(ka)] \;. \tag{2.7}$$

The gap parameter Δ_k' consists of two parts

$$\Delta_k' = \Delta' + i\Delta_k \;, \tag{2.8}$$

Δ_k incorporating the effects of translational and librational mode distortions and Δ' the effects of internal modes. From Eqs. (2.2) and (2.3)

$$\Delta_k = 4\alpha A_0 \sin(k_F a)\cos[(k-k_F)a] \;, \tag{2.9}$$

where

$$\alpha A_0 = \sum_{i=1}^{3} \left[\left[\frac{\partial t}{\partial u^{(i)}} \right]_0 A_{0t}^{(i)} + \left[\frac{\partial t}{\partial \theta^{(i)}} \right]_0 A_{0l}^{(i)} \right] . \tag{2.10}$$

It is seen that for the case of a half-filled band ($k_F = \pi/2a$) and one acoustic mode only Δ_k goes over to the gap parameter obtained by SSH for this case.[9] When there is mode mixing, αA_0 represents the sum over the mixed modes. The quantity Δ' is given by

$$\Delta' = \sum_{n=1}^{G} \beta_n A_n / 2 = \sum_{n=1}^{G} \Delta_n' \;, \tag{2.11}$$

the sum being over the contributions of the G internal modes coupled linearly to the electrons. The fact that the contributions to the Peierls gap of the external and internal modes are $\pi/2$ out of phase, as seen in Eq. (2.8), was first pointed out by Rice.[18(b)] As a result the gap parameter is the square root of the sum of Δ_k^2 and $(\Delta')^2$.

We have made the approximation in Eq. (2.6) of replacing the upper limit of the k summation for the upper subband, $\pi/a - k_F$, by $2k_F$. This is reasonable since our treatment is limited to the case where the widths of the subbands are large compared to $k_B T$, and we will be concerned only with Maxwell-Boltzmann distributions of electrons and holes.

The electronic part of the Hamiltonian for the SDW case may be written in a form similar to (2.6), with the gap parameter Δ_k' replaced by[19(a)]

$$\Delta_{\text{SDW}} = -\sigma M \;, \tag{2.12a}$$

where M is the sublattice magnetization of the SDW state, given by

$$M = (I/2) \sum_{k} \sum_{\sigma} \sigma \langle c_{k\sigma}^\dagger c_{k-Q,\sigma} \rangle \;, \tag{2.12b}$$

I being the exchange integral.

B. Wave functions and energies

To find the wave functions and energies in the CDW or SDW state we diagonalize H_{el} by introducing new operators according to

$$c_k = u_k \alpha_1 + v_k \alpha_2 \;, \tag{2.13a}$$

$$c_{k-Q} = v_k \alpha_1 - u_k \alpha_2 \;, \tag{2.13b}$$

where $\alpha_1, \alpha_1^\dagger$ and $\alpha_2, \alpha_2^\dagger$ operate on the upper and lower subbands, respectively. The coefficients are required to obey the normalization condition

$$u_k u_k^* + v_k v_k^* = 1 \;. \tag{2.14}$$

With (2.13) in Eq. (2.6) we find the eigenvalues for both CDW and SDW, measured from the Fermi energy in the metallic state, to be

$$E_{k,i}^{\pm} = [(\epsilon_k + \epsilon_{k-Q})/2] \pm \{[(\epsilon_k - \epsilon_{k-Q})^2/4] + |\Delta_i|^2\}^{1/2} \;, \tag{2.15}$$

where + refers to the upper band, − to the lower, and i refers to either CDW or SDW. For $i \to$CDW

$$\Delta_i = \Delta_k' \;, \tag{2.16}$$

the gap parameter defined in Eq. (2.8), while for $i \to$SDW

$$\Delta_i = -\sigma M \;. \tag{2.17}$$

Equation (2.15) was obtained previously[8] for the case of acoustic modes only, with $|\Delta_k'|$ replaced by Δ, a constant to be determined empirically or by the condition that the motion of the lattice ions must satisfy Newton's second law. For the half-filled band ($Q = \pi/a$) $\epsilon_k = -\epsilon_{k-Q}$ and, for acoustic modes only, $E_k^{\pm}$ goes over to $\pm(\epsilon_k^2 + \Delta_k^2)^{1/2}$, the SSH result.

The relation between u_k and v_k results from diagonalizing H_{el} subject to the normalization condition (2.14). For the upper band that relation is

$$(u_1/v_1) = \Delta_i/(E_k^+ - \epsilon_k) \;, \tag{2.18}$$

where the subscript k on u and v has been dropped for conciseness. Combining (2.18) with (2.15) we obtain

$$u_1 u_1^* = (E_k^+ - \epsilon_{k-Q})/(2E_k^+ - \epsilon_k - \epsilon_{k-Q}) \ , \tag{2.19a}$$

$$v_1 v_1^* = (E_k^+ - \epsilon_k)/(2E_k^+ - \epsilon_k - \epsilon_{k-Q}) \ . \tag{2.19b}$$

For the lower band $u_2 u_2^*$ is given by the right-hand side of (2.19b) and $v_2 v_2^*$ by that of (2.19a), with E_k^+ replaced by E_k^-, of course, in both cases. We note that, for $Q = \pi/a$ and no internal modes, u_1 and v_1 go over to the coefficients α_k and β_k of SSH.

C. The gap equation

To find the equilibrium value of the gap at $T=0$ for the CDW case we need an expression for the total energy at that temperature. The energy of the translational part of the lattice deformation is given by[9]

$$H_{\text{ac}} = \tfrac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{N} K^{(i)} (u_{j+1} - u_j)^2 \ , \tag{2.20}$$

where $K^{(i)}$ is an effective spring constant for the distortion due to the ith acoustic mode. Taking $x_j = ja$ we obtain using (2.3)

$$H_{\text{ac}} = 2 \sum_{i=1}^{3} K (A_{0t}^{(i)})^2 \sin^2(k_F a) \times \sum_{j=1}^{N} \sin^2[(2j+1)k_F a] \ . \tag{2.21}$$

With the notation $4k_F a = \alpha$ we may write

$$\sum_{j=1}^{N} \sin^2[(2j+1)k_F a] = (N/2)\{ 1 - \cos(\alpha/2)\cos[(N+1)\alpha/2]\sin(N\alpha/2)/N\sin(\alpha/2) + \sin[(N+1)\alpha/2]\sin(N\alpha/2)/N \} \ . \tag{2.22}$$

The term in curly brackets equals 2 for $\alpha = 2\pi$, the half-filled-band case. For α not an integer times 2π, however, the second and third terms in curly brackets are of order $1/N$ and can be neglected. Thus for the non-half-filled-band case the translational mode contribution to the lattice energy is

$$H_{\text{ac}} = \sum_{i=1}^{3} NK (A_{0t}^{(i)})^2 \sin^2(k_F a) \ , \quad k_F a \neq \pi/2 \tag{2.23}$$

less for each mode than half of that for the corresponding mode in the half-filled-band case, $2NK(A_{0t}^{(i)})^2$.[9] An expression similar to (2.23) may be obtained for the librational modes with $A_{0t}^{(i)}$ replaced by $A_{0l}^{(i)}$ and $K^{(i)}$ by the elastic constant appropriate to the motion concerned.

For the internal modes the contribution to the lattice energy is

$$H_{\text{int}} = \tfrac{1}{2} \sum_{n=1}^{G} \hbar\omega_n A_n^2 \cos^2(Q x_j) \ , \tag{2.24}$$

where A_n is the dimensionless amplitude introduced in Eq. (2.5). By arguments similar to those used for the acoustic energy we obtain for the band of arbitrary filling

$$H_{\text{int}} = (N/4) \sum_{n=1}^{G} \hbar\omega_n A_n^2 \ , \quad k_F a \neq \pi/2 \ . \tag{2.25}$$

For the half-filled band H_{int} is twice that given by (2.25). With the use of Eq. (2.11) Eq. (2.25) may be written

$$H_{\text{int}} = N \sum_{n=1}^{G} (\Delta'_n)^2/(\beta_n^2/\hbar\omega_n) \ , \quad k_F a \neq \pi/2 \tag{2.26}$$

where Δ'_n is the contribution to Δ' of the nth internal mode. This equation may be written in terms of Δ' by using a relation derived by Rice, Duke, and Lipari[12]:

$$\Delta'_n/(\beta_n^2/\hbar\omega_n) = \sum_{n=1}^{G} \Delta'_n \Big/ \sum_{n=1}^{G} (\beta_n^2/\hbar\omega_n) = \Delta'/4E_p \ , \tag{2.27}$$

where E_p is the so-called polaron binding energy. With the relation (2.27) Eq. (2.26) may be written

$$H_{\text{int}} = (N/4)(\Delta')^2/E_p \ , \quad k_F a \neq \pi/2 \ . \tag{2.28}$$

Thus, for the case of internal modes, since there is no k dependence of the gap parameter it is possible to express the contribution to the lattice energy in terms of the gap Δ'. This in turn makes it possible, when there are only internal modes present, to obtain a simple equation for the gap by minimizing the total energy with respect to Δ', as will now be shown.

Since the electrons are all in the lower band at $T=0$, the electronic part of the total energy, H_e, is given by the integral over the lower band of E_k^-. We may then write, using (2.15),

$$\left[\frac{dH_{\text{el}}}{d\Delta'}\right]=-(2N/\pi)\int_0^{k_Fa} d(ka)\Delta'[(\epsilon_k-\epsilon_{k-Q})^2/4+(\Delta')^2]^{-1/2}\ . \tag{2.29}$$

From Eqs. (2.28), (2.29), and (2.7), using the condition that the derivative with respect to Δ' of the total energy vanish, the gap equation is found to be

$$[\pi t_0\sin(k_Fa)/2E_p]=m_1^{1/2}\int_{\pi/2-k_Fa}^{\pi/2} d(\kappa a)[1-m_I\sin^2(\kappa a)]^{-1/2}\ ,\quad k_Fa\neq\pi/2 \tag{2.30}$$

where

$$m_I=[1+(\Delta')^2/4t_0^2\sin^2(k_Fa)]^{-1} \tag{2.31}$$

This can be expressed in terms of complete $[K(m_I)]$ and incomplete elliptic integrals of the first kind. For the half-filled band the right-hand side of Eq. (2.30) becomes $m_I^{1/2}K(m_I)$ while the left-hand side must be multiplied by a factor of 2 due to the larger lattice energy of the half-filled band. The result is then in agreement with the gap equation obtained earlier by Rice[19(b)] for the half-filled-band case with internal modes only.

When the contribution to the gap of external modes is also important, the k dependence of the gap parameter makes it impossible to obtain the gap equation by directly minimizing with respect to Δ. The total energy must be minimized with respect to all the $A_0^{(i)}$'s and the gap obtained from the $A_0^{(i)}$'s so determined through Eqs. (2.8)–(2.10). Such a program was carried out for polyacetylene where only one parameter, A_{0t} for longitudinal modes, is required. Actually, as pointed out in Ref. 12, Eq. (2.30), the gap equation for internal modes only, should provide a good approximation for the Peierls distortion on TCNQ chains since the large number of internal modes causes their contribution to the gap to be dominant.[19(c)] This should be true also for other quasi-1D crystals with large molecules.

C. Effective masses and densities of states

Below the transition temperature the electrons and holes responsible for transport are in the neighborhood of the band edges. For k close enough to k_F, $|\Delta_i|^2 \gg (\epsilon_k-\epsilon_{k-Q})^2/4$ and the quantity inside the radical in Eq. (2.15) may be expanded. To terms quadratic in $(k-k_F)^2$ the expansion gives

$$E_k=\pm[\Delta+\hbar^2(k-k_F)^2/2m^*]\ , \tag{2.32}$$

where

$$(m^*)^{-1}=(2ta^2/\hbar^2)[(2t/\Delta)\sin^2(k_Fa)\pm\cos(k_Fa)] \tag{2.33}$$

and $\Delta=[\Delta_{k_F}^2+(\Delta')^2]^{1/2}$ for the CDW case and αM for the SDW case, thus no longer a function of k in either case. Equation (2.33) is the same expression for m^* as was obtained previously with a Δ independent of k in Eq. (2.15); the additional k dependence arising from the introduction of Δ_k thus has a negligible effect on m^*. We note that the first factor on the right of Eq. (2.33) is the reciprocal of the mass at the bottom of the original, undistorted band. Thus, as discussed earlier,[20] in the distorted band m^* is essentially multiplied by a factor of the energy gap over the bandwidth, which makes it quite small for the materials of interest here. In that case Eq. (2.33) may be rewritten,[20]

$$m_{\substack{n\\p}}^*=\langle m\rangle(1\mp\alpha) \tag{2.34}$$

where $\langle m\rangle$ is the average of the electron mass m_n^* and the hole mass m_p^*, given by

$$\langle m\rangle=\hbar^2\Delta/4t^2a^2\sin^2(k_Fa) \tag{2.35}$$

and

$$\alpha=\Delta\cos(k_Fa)/2t\sin^2(k_Fa)\ . \tag{2.36}$$

The term α represents a small correction to the mass, being smaller by another factor Δ/t than $\langle m\rangle$. For a band less than half-filled $[\cos(k_Fa)>0]$ $m_n^* < m_p^*$, while the reverse is true for a band more than half-filled. Other things being equal, this would result in a larger mobility for the carriers with the same sign as the dominant carriers above the transition. Thus for a single-chain conductor one would predict the same sign of thermoelectric power below the transition as above, and this is generally found to be the case with the possible exception of very low temperatures.

The density of states per unit length, $\rho(E_k)$, for states of a given k and either spin, is obtained from

$$\rho(E_k)=1/2\pi(dE_k/dk)\ . \tag{2.37}$$

With E_k given by Eq. (2.15), $\rho(E_k)$ has a complicated form. For $k_BT \ll \Delta$, where E_k may be written in the form (2.32), it simplifies to

$$\rho(E_k)=m^*/2\pi\hbar^2|k-k_F|\ ,\quad \epsilon_k \ll \Delta \tag{2.38}$$

as is appropriate for a 1D parabolic band. In the opposite limit, $\epsilon_k \gg \Delta$, $\rho(E_k)$ goes over to the 1D density of states for the undistorted band, which is of course much larger.

III. MOBILITIES AT LOW TEMPERATURES

A. The high low-temperature mobilities

The low mobilities at room temperature, a few $\text{cm}^2/\text{V sec}$, in this family of quasi-1D conductors led many people to assume that the low-temperature mobilities would be correspondingly small. In almost all cases the small transverse mobility makes it difficult to measure the Hall effect, and it is necessary to deduce the mobility μ from the measured conductivity σ. This can be done by using the density of states and the known gap to calculate the carrier concentration. It is important, of course, that the calculation be carried out for the range of temperatures in which, as manifested by the slope of $\ln\sigma$ vs $1/T$, the carriers are produced by excitation across the gap, i.e., for the intrinsic range. For TTF-TCNQ samples for example, the intrinsic range is $\sim 25 \geq T \geq \sim 10$ K, on the evidence that $\ln\sigma$ vs $1/T$ in this range has a constant slope of ~ 200 K,[2,21] equal to half the gap found in photoconductivity[22] and infrared absorption.[23] Below 25 K we may use the approximations (2.32) and (2.38) for E_k and $\rho(E_k)$, respectively. The number of conduction electrons per unit length, n_l, may be obtained as the integral from k_F to ∞ (since $\Delta \gg k_B T$) of $\rho(E_k)f(E_k)$, $f(E_k)$ being taken as the Maxwell-Boltzmann distribution. It should be noted that, except for the case of the half-filled band, for $T \neq 0$ the Fermi energy E_F in the distorted state does not coincide with that in the undistorted state. This results from the unequal electron and hole masses in the distorted state. Taking the difference between E_F in the distorted state and that in the undistorted state as δ, we obtain the electron concentration

$$n_l = 2(2\pi m_n^* k_B T/h^2)^{1/2} e^{(\delta-\Delta)/k_B T} , \tag{3.1}$$

while the hole concentration is given by

$$p_l = 2(2\pi m_p^* k_B T/h^2)^{1/2} e^{-(\delta+\Delta)/k_B T} . \tag{3.2}$$

δ is determined by the condition $n_l = p_l$, which leads to

$$e^{2\delta/k_B T} = (m_p^*/m_n^*)^{1/2} . \tag{3.3}$$

For $\Delta \ll 4t$ this gives

$$\delta \simeq \alpha k_B T/2 , \tag{3.4}$$

α being defined by Eq. (2.36). For the materials of interest here, as noted earlier, $\alpha \ll 1$ and we shall generally set $\delta = 0$ in what follows.

From Eqs. (2.34)–(2.36) for TTF-TCNQ, with $4t = 0.5$ eV and $\Delta = 215$ K,[22] $m_n^* = 0.198 m_0$, $m_p^* = 0.225 m_0$. With this, for $\delta = 0$ we obtain from Eq. (3.1) and (3.2), using the fact that there are 8.8×10^{13} chains/cm^2, the carrier concentrations $n = p \simeq 10^9/\text{cm}^3$ at 10 K. According to Fig. 1 of Ref. 2 a sample still intrinsic at 10 K has $\sigma = 10^{-5}$ $\Omega^{-1}\,\text{cm}^{-1}$, leading to $\mu \simeq 2 \times 10^4$ $\text{cm}^2/\text{V sec}$ for an electron or hole in TTF-TCNQ.[24] Similar considerations lead to $\mu \simeq 10^4$ $\text{cm}^2/\text{V sec}$ for electrons and holes in TSeF-TCNQ at 20 K.[24] More direct evidence for high mobility in this type of material comes from Hall measurements on $(\text{TMTSF})_2\text{PF}_6$, a more favorable case for such measurements due to its lower resistivity and higher mobility. The measured Hall mobility[5] is 10^5 $\text{cm}^2/\text{V sec}$ at 4 K, which was still in the intrinsic range for the sample concerned.

It is clear then that high mobility below the transition temperature is characteristic of this family of quasi-one-dimensional crystals, at least in the intrinsic range. That should not be totally unexpected. The low μ at 300 K is largely due to the many phonon branches characteristic of crystals with large molecules and complex crystal structure, and almost all of these modes freeze out at low T's. The internal modes which, as we have seen, are strongly coupled have energies of 350 K and greater on the TTF chains, 215 K and greater on the TCNQ chains. Thus, although they scatter effectively at high temperatures,[13] they cannot be expected to scatter at the low temperatures we are concerned with here. In fact, since there is a Maxwell-Boltzmann distribution, the only phonons with which carriers can interact at low temperatures are the long-wavelength acoustic modes. Another important contributing factor to the large mobility is the small effective mass, particularly for $(\text{TMTSF})_2\text{PF}_6$ with its small ratio of $\Delta/4t$. Furthermore, impurity and defect concentrations are expected to be small in these materials since, as pointed out particularly for $(\text{TMTSF})_2\text{PF}_6$, the growth process is self-purifying.[25] Finally, the scattering effect of such defects and impurities as is incorporated is expected to be small for carriers moving parallel to the chains, as has been discussed elsewhere.[20] In the next section we calculate the mobility due to acoustic phonon scattering and show that it is in good agreement with the measured values and values deduced from σ.

B. Matrix element for acoustic-mode scattering

We consider at first scattering by phonons with propagation vectors parallel to the chain direction. The perturbing Hamiltonian for scattering by these phonons will be taken to have the same form for $T<T_{MS}$ as for $T>T_{MS}$, notably[13]

$$H'_{e\text{-ph}}=N^{-1/2}\sum_{q,k} g(k,q)c^{\dagger}_{k+q}c_k(b_q+b^{\dagger}_{-q}) \; . \quad (3.5)$$

Here $b^{\dagger}_q$ and b_q are the creation and destruction operators for phonons with wave vector q and g the electron-phonon coupling constant,

$$g(k,q)=2i\left[\frac{\partial t}{\partial u}\right]_0\left[\frac{\hbar}{2M\omega_q}\right]^{1/2} \times[\sin(k+q)a-\sin(ka)] \; , \quad (3.6)$$

$(\partial t/\partial u)_0$ being the deformation potential (rate of change of t with nearest-neighbor spacing), M the mass of a lattice ion, and ω_q the phonon angular frequency. Actually $(\partial t/\partial u)_0$ is no longer a constant in the Peierls-distorted lattice but the distortion is quite small and particularly for an incommensurate case its effect should be inconsequential for long-wavelength acoustic modes. We note also that calculations for the incommensurate case show that the long-wavelength phonons are little changed below T_{MS}, showing only a slight mixing with low-q phasons, a second-order effect.[26] The wave vector of the phonon involved in scattering a thermal electron with wave vector k is found from conservation of momentum and energy [Eq. (2.32)], to be

$$q=\pm 2(k-k_F)\pm 2\langle m^{*}\rangle u/\hbar \; , \quad (3.7)$$

where u is the velocity of the phonon branch involved, and the upper signs are for emission, the lower for absorption. Since $u \simeq 10^5$ cm/sec, the term in u is small compared to the other for thermal electrons at $T\geq 4$ K, and will be dropped.

Although we are taking the perturbing Hamiltonian as the same, a change in the matrix element for scattering could arise from the different wave functions below T_{MS}, i.e., from the mixing of wave functions for k and $k-Q$. As in the case of superconductivity this results in "coherence factors" which depend on the relative amount of the different wave functions and on the scattering process concerned.[27] Since the phonons do not have sufficient energy to cause a transition between lower and upper subbands, the initial and final states are eigenfunctions of the diagonalized H_{el}, i.e., of the α's rather than the c's. We therefore transform $H'_{e\text{-ph}}$ to the α representation by using Eqs. (2.13). The result can be simplified by making use of the fact that $|q| \ll |k_F|$ to show that $g(k-Q,q)\simeq g(k,q)$. We may then simply add the contributions to the matrix element of c_k and c_{k-Q}, with the result

$$c^{\dagger}_{k'}c_k+c^{\dagger}_{k'-Q}c_{k-Q}=\sum_{i=1}^{2}(u_{i,k'}u_{i,k}+v_{i,k'}v_{i,k})\alpha^{\dagger}_{i,k'}\alpha_{i,k} \; . \quad (3.8)$$

where $k'=k\pm q$. For the transition probability we will need the absolute squared of the coefficient of $\alpha_{k'}\alpha_k$ for both upper and lower bands. Using (2.19) and neglecting the acoustic-mode contribution to the gap, we may write for either band

$$|u_{k'}u_k+v_{k'}v_k|^2 =\frac{(E_{k'}+E_k-\epsilon_{k'-Q}-\epsilon_k)(E_{k'}+E_k-\epsilon_{k-Q}-\epsilon_{k'})}{(2E_{k'}-\epsilon_{k'}-\epsilon_{k'-Q})(2E_k-\epsilon_k-\epsilon_{k-Q})} \quad (3.9)$$

For thermal electrons $E_{k'}\simeq E_k\simeq\Delta$, and the other terms in (3.9) are all small compared to Δ. Thus we expect the right-hand side of (3.9) to be close to unity. A more detailed examination shows that it differs from unity by quantities of second and higher order in $\hbar\omega_q/\epsilon_k$ and $\hbar\omega_q/E_k$. Since $\hbar\omega_q\leq k_BT/3$ for thermal electrons at 4 K in TTF-TCNQ or $(\text{TMTSF})_2\text{PF}_6$, the difference from unity of the right-hand side of (3.9) is a fraction of a percent and the coherence factor will be taken as unity. This would not be as good an approximation for hot electrons.

C. Calculation of relaxation time and mobility

From the above discussion we conclude that the matrix element is independent of the final state k'. It is then possible to show, by the methods of Ref. 13, for example, that a relaxation time $\tau(k)$ exists, given by the rate of scattering out of the state k. We find

$$[\tau(k)]^{-1}=2\pi a\hbar^{-1}|g(k,q)|^2 \times[n_q\rho(E_k+\hbar\omega_q) +(n_q+1)\rho(E_k-\hbar\omega_q)] \; , \quad (3.10)$$

where n_q is the number of phonons with wave vector q and $\rho(E_k\pm\hbar\omega_q)$ the density of states (per unit length) after absorption or emission. For thermal electrons, even at temperatures as low as 4 K, the phonon energy, $2\hbar u(k-k_F)$ according to Eq. (3.7), is small enough so that (1) equipartition holds and (2) the scattering may be considered elastic. The terms for emission and absorption in Eq. (3.10) may then be combined, and with the use of Eqs. (3.6), (3.7), (2.38), and (2.35) (we neglect the difference between m^{*}_n and m^{*}_p here) τ for thermal carriers may be written

$$\tau(k)=\left[\hbar a M u^2 t^2 \tan^2(k_F a)/\Delta \left[\frac{\partial t}{\partial u}\right]_0^2 k_B T\right] \times |k-k_F|^3/\sin^2[(k-k_F)a]\ . \tag{3.11}$$

Since $(k-k_F)a \ll 1$ for thermal electrons, $\tau(k)$ increases linearly with $|k-k_F|$, i.e., with the square root of energy ϵ measured from the band edge. We note that this energy dependence differs from that of τ for 3D acoustic mode scattering, which is proportional to $\epsilon^{-1/2}$, by precisely the factor that gives the difference between the 3D and 1D densities of states.

Of course, the crystals are not literally 1D, particularly at the low temperatures we are considering where estimates of the bandwidths transverse to the chains (from various measurements) are in almost all cases greater than $k_B T$. Nevertheless, the resistivity ratios below the transition, which should be roughly proportional to the ratios of band-edge masses, range from 200 to 300 to greater than 10^4. Thus we expect the mass anisotropy to be very large. To estimate the effect on τ along the chain direction of departure from 1D behavior we have considered the scattering by phonons propagating at an angle to the chain direction.[20] The major change in the matrix element is the replacement of $(\partial t/\partial u)_0$ by $\hat{e}_q \cdot \vec{\nabla} t$, $\hat{e}_q$ being the unit vector in the direction of polarization of the wave.[28] It is simpler to consider the effect of this for $(\mathrm{TMTSF})_2\mathrm{PF}_6$, where the planes of the molecules are essentially perpendicular to the chain direction. For an oblique LA phonon this results in $(\partial t/\partial u)_0$ in the matrix element for phonons with $\vec{q}$ parallel to the chains being multiplied by the factor $q_\parallel/(q_\parallel^2+q_\perp^2)^{1/2}$ when equipartition is valid, a smaller factor when $\hbar\omega_q$ is too large for equipartition. The result is that the square of the matrix element for oblique phonons is smaller than that for phonons propagating parallel to the chain by at least a factor $q_\parallel^4/(q_\parallel^2+q_\perp^2)^2$. Thus it falls off quite rapidly as $q_\perp$ increases, and scattering by LA phonons with $\vec{q}$ along the chain direction or at small angles to it is greatly favored. For such phonons, because of the large transverse mass, $q_\parallel$ is still essentially equal to $2(k-k_F)$. Thus $q \ll k$ for these phonons and the final state must have k still quite close to the chain direction. We conclude that the major change in the absolute square of the matrix element to allow for oblique phonons is the multiplying factor $q_\parallel^4/(q_\parallel^2+q_\perp^2)^2$. For the phonons that scatter significantly this factor is well approximated by

$$F=\frac{16(k-k_F)^4}{[4(k-k_F)^2+q_\perp^2]^2}\ .$$

This results in the overall τ with oblique phonons included being given by Eq. (3.11) times $\langle 1/F \rangle$ for the phonons with not too large $q_\perp$. Thus the average transition rate for all LA phonons as a group decreases by perhaps a factor of 2 because the phonons with $q_\perp \neq 0$ scatter less effectively than those with $q=q_\parallel$, and τ for LA phonons increases by perhaps a factor of 2. This decrease in scattering is to some extent offset by the contribution of transverse (TA) waves. The maximum scattering effect would be from TA phonons with $q=q_\perp$ so that they have the maximum displacement parallel to the chains. For the large transverse masses expected,[6] larger energy phonons would be required to satisfy conservation of energy and momentum and these would not be excited at 4 K. TA phonons making a smaller angle with the chains would have smaller scattering effect but larger abundance. It is reasonable to expect that TA phonons make some contribution to scattering in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ at 4 K, although probably not as much as LA phonons.

The case where the plane of the molecules is at a sizable angle to the chain direction, as in TTF-TCNQ, is more complicated. The effect of the factor $\hat{e}_q \cdot \vec{\nabla} t$ in the matrix element is that the LA phonons with the maximum scattering effect are not those with $\vec{q}$ parallel to the chain direction, but rather those with $\vec{q}$ perpendicular to the plane of the molecules. (Note that with a herringbone pattern for the stacking this does not specify a single $\vec{q}$.) Thus as $\vec{q}$ moves off the chain in an appropriate direction $\hat{e}_q \cdot \vec{\nabla} t$ increases. At the same time, however, $|\vec{q}|$ required for conservation of energy and momentum increases and ω_q increases, tending to decrease the scattering effect. Although a detailed calculation would be complicated, it is clear that inclusion of scattering by oblique phonons would not make much change in the average probability of scattering out of an initial state with $\vec{k}$ along the chain by an LA phonon. Similar considerations apply to TA phonons. We conclude that for either the $(\mathrm{TMTSF})_2\mathrm{PF}_6$ or the TTF-TCNQ type of structure the actual τ for motion along the chain direction is comparable to the value given by (3.11), which was calculated for 1D motion and phonons propagating parallel to the chains.

When a relaxation time exists it is straightforward to show that in a low electric field E the solution of the Boltzmann equation is[13]

$$f=f_0-e\vec{E}\cdot\vec{v}\tau\left[\frac{\partial f_0}{\partial E_k}\right]=f_0+f_1\ , \tag{3.12}$$

$\vec{v}$ being the carrier velocity. The current density and the mobility are given by[11]

$$\vec{j} = 2ne\mu\vec{E} = \eta e \sum_k f_1 \vec{v} \; , \qquad (3.13)$$

where η is the number of chains per cm^2 and we neglect the small difference between electron and hole mobilities. For thermal electrons or holes with E_k given by (2.32) and the mass taken from (2.35)

$$v = [4t^2 a \sin^2(k_F a)/\hbar\Delta](k - k_F)a \; . \qquad (3.14)$$

With f_0 taken as the Maxwell-Boltzmann distribution and τ obtained from Eq. (3.11) by replacing $\sin[(k-k_F)a]$ by $(k-k_F)a$, we obtain finally for thermal electrons, in the T range where equipartition holds for the phonons,[24]

$$\mu_{\mathrm{ac}} = \frac{8e}{2^{1/2}\pi} \frac{t^3 M u^2 \sin^3(k_F a)}{\hbar\Delta^{3/2} \left[\dfrac{\partial t}{\partial u} \right]_0^2 \cos^2(k_F a)} (k_B T)^{-1/2} \; . \qquad (3.15)$$

This is μ due to scattering by phonons moving parallel to the chains. As discussed earlier, however, we expect μ to be much the same if we take into account scattering by oblique phonons.

D. Comparison with experiment

For TTF-TCNQ μ evaluated from Eq. (3.15) using the parameters of Ref. 13 is 1.2×10^4 cm^2/V sec,[24] in good agreement with the value deduced earlier from the calculated n and measured σ. The value 0.2 eV/Å used for $(\partial t/\partial u)_0$ corresponds to a value of the dimensionless coupling constant λ $[=\rho(E_F)g^2(k_F,2k_F)/\hbar\omega_{2k_F}]$ for acoustic modes λ_{ac} of 0.24. An experimental determination of λ_{ac} for TCNQ has been made by Etemad,[29] through comparison of the observed vibronic (phase phonon) modes with the theory of Rice.[30] This gives $\lambda_{\mathrm{ac}}=0.1$. Of course, this value may be irrelevant here since the measured σ may come from the TTF stack. In any case, it should be pointed out that it must be considered approximate since Rice's theory does not treat the acoustic modes accurately. Some of the difficulties of an accurate treatment of the acoustic modes when internal modes are also present were discussed in Sec. II.

For (TMTSF)$_2$PF$_6$, Eq. (3.15) leads to $\mu_{\mathrm{ac}} = 1.2\times10^6$ cm^2/V sec at 4 K when we use the values $M=408$ amu (intermediate between the masses of TMTSF and PF$_6$), $u=3\times10^5$ cm/sec,[31] $\Delta=24$ K,[5] and $(\partial t/\partial u)_0=0.3$ eV/Å from the fit of the theory for $2k_F$ phonon scattering to σ for $T > T_{MS}$.[32] If other scattering processes contribute above T_{MS}, as seems likely,[32] the latter value is too high and the calculated μ_{ac} must be larger than 1.2×10^6 cm^2/V sec. In any case we expect both the electron mobility μ_n and hole mobility μ_p to be closely equal to μ_{ac} since $m_n \simeq m_p$ and, as shown earlier, the matrix elements for acoustic mode scattering are essentially equal for electrons and holes.

The mobilities have also been calculated from experimental data, notably Hall mobility μ_H and magnetoresistance, and much lower values found.[5] We shall discuss the experimental results and then give some reasons why we believe they lead to lower μ's. Assuming the change in resistivity $\Delta\rho$ in a magnetic field H is given by[5]

$$(\Delta\rho/\rho) = \mu_p \mu_n H^2/c^2 \qquad (4.1)$$

and $\mu_H = \mu_p - \mu_n$, Chaikin *et al.* obtain $\mu_p = 1.2\times10^5$ and $\mu_n = 0.24\times10^5$ cm^2/V sec at 4.2 K. From the discussion above it is difficult to see how to account for a difference of a factor 5 in μ_p and μ_n. It should be noted, however, that Eq. (4.1) was not satisfied by the experimental data over a wide range of fields. According to Fig. 2 of Ref. 5, $\Delta\rho/\rho$ looks linear, rather than quadratic, in H from ~5 to 55 kG. Further, it is seen from Figs. 3 and 4 of that reference that the Hall coefficient does not vary exponentially with $1/T$ from 10 to ~5 K, whereas ρ in that range is clearly exponential in $1/T$. Accurate exponential behavior is expected in this T range since $\rho = [(n+p)e\mu]^{-1}$ and n and p are, according to Eqs. (3.1) and (3.2), proportional to $T^{1/2}[\exp(-\Delta)/k_B T]$ since δ can be neglected, while from Eq. (3.15) $\mu \propto T^{-1/2}$. The latter prediction is, incidentally, in disagreement with the observed behavior of μ_H, which increases by a factor close to 20 in the range 10 to 4.2 K. Chaikin *et al.* suggest that the large T dependence of μ seen in μ_H, and also in the T dependence of the magnetoresistance, is due to the occupancy in the higher T part of this range of states higher in the band so that the effective mass is larger.[5] If this were the case, however, $\ln\rho$ vs $1/T$ would not be exponential in this T range, in contradiction to what is observed.

A reasonable explanation for some of these discrepancies is inhomogeneity of the samples. One obvious source is the cracking that generally occurs as the temperature is lowered. Another is variation with position of the gap. It is well known that random resistivity variations can strongly affect galvanomagnetic measurements, particularly in high-mobility materials.[33,34] The basic effect is the distortion of the lines of current flow, which can be very large at high fields in such materials even for small inhomogeneities in carrier concentration. The origin suggested for the gap variation has been strain since it is well known that the gap changes ~10% per kbar.[35] Strains corresponding to kbars of pressure should be found in the neighborhood of edge dislocations in these materials.[36,37] Recent x-ray topographic studies[38] have demonstrated sizable numbers of dislocations, as well as considerable surface and internal strain, in TTF-TCNQ grown under the usual conditions. It is likely that similar defects exist in typical $(\mathrm{TMTSF})_2\mathrm{PF}_6$ crystals, particularly in view of the common experience of sample cracking. The presence of gap variation on a scale large compared to the mean free path can explain a number of otherwise puzzling aspects of the low-T behavior of these materials.[36,37]

Two reasons can be cited, apart from inhomogeneity, for μ_H to be smaller than $\mu_n - \mu_p$, leading to the values deduced from μ_H being too small. One of these is the anisotropy of $(\mathrm{TMTSF})_2\mathrm{PF}_6$.[6] While μ_n or μ_p depends only on $1/m_{\parallel}$, the mass parallel to the chains, μ_H depends on $1/m_{\parallel}m_{\perp}$ since the magnetic field causes rotation around the constant energy surfaces.[39] Thus μ_H could be much smaller than $\mu_n - \mu_p$. A second reason is connected with the flattening of Hall constant R, μ_H, and ρ with decreasing T observed by Chaikin *et al.*[5] below ~5 K. This, plus the behavior of thermopower[40] and microwave conductivity[41] at low temperatures, suggests that another conduction process is taking over below ~5 K—conduction in discrete levels arising from defects or impurities.[42] If that is the case, μ at 4 K is a weighted average of the μ's of two types of carriers, those in the conduction or valence band and those in defect levels. Since the latter should have mobility much smaller than the former, this provides another reason for low values of μ_n and μ_p to be deduced from Hall and magnetoresistance data analyzed as though all the carriers are in the conduction and valence bands.

We note that the explanation of the nonlinear conductivity observed by Chaikin *et al.*[4] as a result of electron heating[36,37,43] is quite consistent with the foregoing discussion. For this mechanism to account for the observed 4 K 5% change in μ at a field of 20 mV/cm requires $\mu = 7.5\times10^6$ cm^2/V sec.[43] The carriers that can be heated by the field are the high-μ ones, those in the conduction or valence band. The value of 7.5×10^6 cm^2/V sec is not far out of line with μ_n or μ_p calculated from Eq. (3.15). We conclude that the band mobilities in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ at 4 K are indeed greater than 10^6 cm^2/V sec, more than an order of magnitude greater than the values deduced from the experimental data.[5]

IV. SUMMARY

Starting from a site Hamiltonian for the electrons, with terms for elastic energy due to the various possible lattice modes in a molecular crystal (the analog of the SSH Hamiltonian for polyacetylene[9]), and transforming to the momentum representation we have derived an expression for the CDW gap parameter for the case of arbitrary band filling. It is seen that the contributions to the gap of internal modes are $\pi/2$ out of phase with those of acoustic modes and librons. Minimizing the free energy with respect to Δ, we have obtained the gap equation for the case of arbitrary band filling and internal modes only determining the gap. From the Hamiltonian we have also obtained wave functions, effective masses, and densities of states for arbitrary band filling, valid for both CDW and SDW cases. Using the wave functions, we show that, when acoustic-mode scattering can be considered elastic (i.e, carriers not hot), the matrix element for this scattering process is the same below the transition as above. From this matrix element we have derived the relaxation time for scattering and the mobility for 1D acoustic-mode scattering in the low electric field or linear region. This predicts mobilities in the chain direction that are very high but in good agreement with the measured mobilities at low temperatures for TTF-TCNQ and TSeF-TCNQ and in fair agreement with that for $(\mathrm{TMTSF})_2\mathrm{PF}_6$. The agreement with a 1D calculation when these materials are literally two dimensional or three dimensional at low temperatures (k_BT is less than the transverse bandwidth) is due to the large mass anisotropy.

In the case of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ the calculated μ_{ac} at 4 K is an order of magnitude greater than μ_p and μ_n derived from the measured Hall mobility and magnetoresistance at that temperature.[5] We attribute the discrepancy to (1) sample inhomogeneity; (2) $(\mu_H/\mu) < 1$ due to the anisotropy of m and τ; (3) the measurements including the effect of much lower μ carriers moving (probably hopping) in extrinsic (soliton) levels arising from defects or impurities. These carriers should dominate the conduction for T below 4 K in the samples measured. We conclude that μ at 4 K for conduction- and valence-band carriers in a good sample of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is actually greater than 10^6 cm^2/V sec.

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