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Band transport in quasi-one-dimensional conductors in the phonon-scattering regime and application to tetrathiofulvalene-tetracyanoquinodimethane

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Starting from a simple model for the lattice vibrations in a molecular crystal, I develop the transport theory for noninteracting electrons in a tight-binding band scattered by one- and two-phonon processes. The matrix elements for scattering by acoustic phonons, by librons, and by internal-mode phonons are obtained in the usual way from a simple Hamiltonian. For the one-phonon (1p) processes it is shown that a relaxation time exists and the Boltzmann equation is easily solved. With this solution formal expressions are obtained for conductivity σ and thermopower Q. These are evaluated for the acoustic and libron cases for degenerate material in order to display the specific dependences on bandwidth, Fermi energy, phonon frequency, temperature, etc. Approximate expressions are also obtained for σ and Q for two-phonon (2p) processes. The formalism is then applied to calculate σ and Q numerically for tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) for which the basic model should be reasonably valid in the temperature range $\sim 100 < T < 300$ K. It is shown that the requirement that the Fermi level be the same for TTF and TCNQ, while the lattice constant and bandwidth change with temperature leads to the charge transfer's decreasing $\sim 20\%$ from 60 to 300 K. The internal modes, for which the frequencies and coupling constants are fairly well known, are found to account for one-quarter of the resistivity at 300 K. The coupling constants for the other 1p processes required to match the observed resistivity versus T are of the order of those deduced theoretically and experimentally for the LA mode, and therefore seem reasonable. The bandwidths that give good fits for σ and Q, and are consistent with most other experiments, are 0.5 eV for TCNQ, half that for TTF. Similar fits are obtained by including some 2p processes, up to 1/3 of the total scattering. Calculations are carried out also for tetraselenufulvalene-tetracyanoquinodimethane (TSeF-TCNQ). The large pressure dependence of σ at 300 K for TSeF-TCNQ, $\sim 18\%$/kbar, is well explained by the pressure-variation of the bandwidth and acoustic-mode frequencies, plus some smaller effects. The additional 10%/kbar observed for TTF-TCNQ may be largely due to greater changes for TTF due to its small bandwidth. In contrast to all of the above, the proponents of the "two-libron" theory of transport for TTF-TCNQ claim that 1p scattering is negligible in the range $\sim 100 < T < 300$ K, 2p processes being predominant. These claims are examined and found quite unconvincing. Allowing for the uncertainty in the coupling to LA and TA phonons, I find that the contribution of 2p scattering must be less than 50% at room temperature and smaller, of course, below; it may be negligible at all temperatures.

I. INTRODUCTION

After large numbers of experiments and much ferment, a model of tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) above the Peierls transition that is widely, if not universally, accepted has emerged. Collective transport, early espoused by some as explaining many phenomena in the entire range from the Peierls transition temperature $T_p = 53$ K to room temperature,[1] has been abandoned as a model above ~100 K, or at the most 150 K. Under x rays the fluctuations are barely visible at 150 K, even less so above, and the coherence length at 150 K is quite small. Consistent with this there has been an accumulation of evidence that coupling between the chains is sufficiently strong to prevent T_p being depressed much below the mean-field value.[2] There remains a possibility that fluctuating charge-density waves contribute to transport below ~100 K or perhaps 150 K. Recent experimental results[3(a)] showing a dip in conductivity at temperatures below 150 K around the pressure where commensurability is achieved[3(b)] have been interpreted as evidence for such collective transport.

Another important question has been the role of U, the Coulomb repulsion for a second electron on the same site. Magnetic-susceptibility measurements, among others, have been interpreted as showing "that U is comparable to or larger than the bandwidth, at least on one stack."[4] Recent calculations by Bloch[5(a)] demonstrate that, for materials where charge transfer is not close to complete, screening by the conduction electrons may make U relatively unimportant. Examples of compounds where many types of evidence indicate that this screening is taking place are hexamethylene-tetraselenafulvalene-tetracyanoquinodimethane (HMTSF-TCNQ) and tetraselenafulvalene-tetracyanoquinodimethane (TSeF-TCNQ). TTF-TCNQ is not a clear-cut case, however, in that x rays show $4k_F$ fluctuations,[5(b)] interpreted by a number of authors as the effect of intermediate or large U. Since the spacing and charge transfer on the TCNQ chain are very close to those for the TCNQ chain in TSeF-TCNQ, it is reasonable to conclude that U is not important on that chain but may be significant on the TTF chain.[5(c)] Consistent with that, there is evidence, to be discussed, that the bandwidth is considerably smaller for TTF, making the effect of U more important. However, the contribution of the TTF chain to the conductivity is less than that of the TCNQ chain, of the order of $\frac{1}{4}$, as will be seen. I conclude that a reasonable model for transport in the range 100 or 150 to 300 K is based on single-particle scattering in a tight-binding band.

Since ρ for TTF-TCNQ as well as many analogous compounds was found experimentally to vary with temperature T as $AT^{2.3}+B$, B being negligible for many samples above 100 or 150 K, initial efforts to account for the resistivity concentrated on mechanisms that could produce the $T^{2.3}$ dependence. Three such mechanisms were proposed: (1) electron-electron scattering,[6] (2) two-libron scattering,[7] and (3) scattering by phonons of molecular (internal mode) vibrations.[8] As regards the first mechanism, it was soon realized that scattering of electrons by electrons on the same chain could not remove momentum from the electron distribution.[7,8] To give rise to resistivity, the scattering would have to be by electrons or holes on the other chain. No detailed theory of such a process has been presented. A major argument against this mechanism is the fact that many compounds in which it is well documented that conduction is by a single chain, either TTF or TCNQ, have resistivity comparable to that of TTF-TCNQ. The two-libron theory asserts that two-phonon scattering is predominant. This theory will be discussed further subsequently. The third theory could account well for the magnitude and temperature dependence of ρ, using fairly well known values of frequency and coupling constants for the molecular modes, provided the bandwidths of TCNQ and TTF were taken as $\frac{1}{4}$ and $\frac{1}{8}$ eV, respectively. These values were objected to as smaller than indicated by various experiments and theories. The conclusive argument brought against this theory, however, was that it could not account for the large pressure dependence of ρ, a decrease of ~25%/kbar at 300 K. If the data on pressure dependence are used to deduce volume dependence, and correction is made for the sizable thermal expansion of TTF-TCNQ, it is concluded that ρ at constant volume, ρ_V is much closer to linear in T than quadratic.[9,10] On this basis it was proposed that scattering by all phonons, not only those based on molecular vibrations, is significant.[11]

It is the major part of the program of the present paper to calculate the transport coefficients arising from all one-phonon (1p) and two-phonon (2p) scattering processes for noninteracting electrons in a quasi-one-dimensional tight-binding band. This will be carried out in Sec. II. In Sec. III the theory will be compared, as well as can be done, with experimental data for TTF-TCNQ. Although there is a large body of data, there are still too many parameters poorly known or unknown to do a conclusive calculation. It will be shown, however, that resistivity and thermopower can be fit in the range 100 to 300 K with values of the various parameters that are reasonable and consistent with the results of most other experiments, including pressure experiments. Section IV will be devoted to some remarks on the two-libron theory.

II. THEORY OF PHONON SCATTERING IN QUASI-ONE-DIMENSIONAL MATERIALS

Using a model for the chains similar to what is found for TTF-TCNQ and its analogs, we first describe the types of lattice vibrations. Since the vibrations for these compounds are complicated, we simplify them in some respects for the calculations of this section. The matrix elements for the different types of phonon scattering are then derived from the usual one-dimensional Hamiltonian for noninteracting electrons. A relaxation time is shown to exist for the 1p processes. The Boltzmann equation is solved for these and formal expressions for the conductivity σ and thermopower Q are written down. These must be evaluated numerically when phonons based on molecular modes are included. For the elastic scattering cases, however, expressions are obtained for σ and Q displaying clearly the dependences on bandwidth, phonon frequency, charge transfer, etc. In the case of 2p scattering, the Boltzmann equation is not solved but approximate expressions are obtained for σ and Q from the momentum relaxation time.

A. Model of the lattice vibrations

Since, as indicated earlier, the lattice vibration spectrum is quite complicated in the organic crystals considered, we calculate for a simplified model in order to gain more physical insight. We therefore perform the calculations for the case of one molecule per unit cell. The molecules are assumed to be planar and stacked at an angle to the chain direction, as shown in Fig. 1. The lattice vibrations are conveniently divided into external and internal modes. The latter are based on the molecular vibrations and there are $3m-6$ of them, m being the number of atoms in a molecule. The remaining six modes arise from the three translational and three rotational degrees of freedom. In a lattice of high enough symmetry[12] the translational and rotational modes do not mix with each other at the center of the Brillouin zone ($q=0$) and

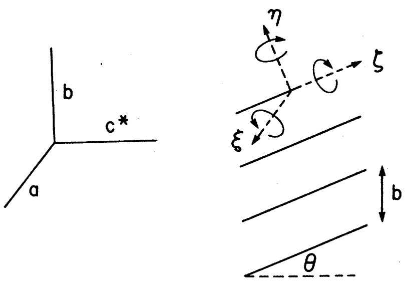

FIG. 1. Coordinate system and model chain of planar molecules showing tilt angle θ, lattice constant b, and rotation axes for the librations. ζ and ξ ($\parallel a$) correspond to the long and short axes of the molecule, respectively, and η to the axis perpendicular to the plane of the molecule.

perhaps at other high symmetry points, but in general do mix elsewhere. In the theoretical development of this section it will be assumed that there are six distinct branches, three based on translations and three on rotations, that do not mix anywhere in the zone. Each of the rotations, or librations, is assumed to take place about one of the three inertial axes, indicated on the top molecule in Fig. 1, although this is not in general true. These branches are optical, i.e., their frequencies do not go to zero in the limit that $q \to 0$. With the stacking axis the high-conductivity direction, the important acoustic modes for scattering the electrons are those that propagate along the stacking axis, taken as b in Fig. 1. These consist of longitudinal (LA) modes with displacements along the b axis and two transverse (TA) modes with displacements that we take to be in the directions indicated c^* and a in Fig. 1, since neutron scattering indicates that the TA vibrations are primarily in these directions in TTF-TCNQ.[13,14] The quanta of the acoustic branches will be called translons, in analogy to those of the rotational branches being called librons.

B. Matrix elements for phonon scattering

To deduce the coupling of the electrons or holes to the lattice vibrations, we start from the usual Hamiltonian for noninteracting electrons on a chain of N identical molecules,[15]

$$H=\sum_{j=1}^{N}\epsilon_j a_j^\dagger a_j+\sum_{n=1}^{G}\sum_{q}\left(b_{q,n}^\dagger b_{q,n}+\tfrac{1}{2}\right)\hbar\omega_{q,n}+\sum_{i,j=1}^{N}\left(t_{ij}a_i^\dagger a_j+\text{H.c.}\right),\qquad(2.1)$$

where $a_j^\dagger$ and a_j are the creation and annihilation operators, respectively, for an electron on the jth molecule, t_{ij} the overlap integral, and $b_{q,n}^\dagger$ and $b_{q,n}$ the creation and annihilation operators, respectively, for a phonon with wave vector q and frequency $\omega_{q,n}$. The subscript n indicates the branch, of which there are G in all. We assume, as usual, that all conduction electrons (or holes) are in the same (nondegenerate) molecular orbital. In the spirit of the tight-binding approximation, we shall consider only overlap between nearest neighbors.

There are two obvious sources of coupling between the electrons and lattice vibrations. First, the overlap or transfer integral is a function of the spacing and relative orientation of the adjacent molecules j and $j\pm 1$. This couples the electrons to the intermolecular lattice vibrations. The transfer integral may also be affected by the internal vibrations but this effect would seem to be small. Second, the energy ϵ_j of the electron on the jth site is affected by the internal vibrations at the site j, coupling the electrons to those vibrations.[15] In addition, ϵ_j includes a contribution of the crystal potential at the site and this is modulated by the intermolecular vibrations. The matrix element arising from this latter source was shown for anthracene to be small compared to that arising from modulation of the transfer integral.[16] It is likely to be larger in the crystals under consideration here due to the charge transfer. Although it is straightforward to obtain the expression for this contribution, we do not include it since it brings in one more unknown parameter, possibly of little importance.

To calculate the coupling constant arising from the modulation of the transfer integral by the intermolecular vibrations, we make use of the fact that the vibration amplitudes are small and expand t_{ij} in a Taylor series[15]:

$$t_{ij}=t_0+\left(\frac{\partial t}{\partial u}\right)_0(u_i-u_j)+\frac{1}{2}\left(\frac{\partial^2 t}{\partial u^2}\right)_0(u_i-u_j)^2+\cdots\,.\qquad(2.2)$$

Here u_i represents the displacement of the ith molecule from its thermal equilibrium position. $(\partial t/\partial u)_0$ stands for the rate of change of t_{ij} with the distance between nearest neighbors, the subscript 0 indicating evaluation at the equilibrium value of that distance. t_0 is the usual transfer integral, evaluated for the molecules in their equilibrium positions, i.e.,

$$t_0=-\int\phi^*(\vec{r}\pm\vec{b})H\phi(\vec{r})d^3r\,,\qquad(2.3)$$

where $\phi(\vec{r}\pm\vec{b})$ and $\phi(\vec{r})$ represent orbitals centered at adjacent lattice sites. The expression (2.2) can be specialized for the case of acoustic modes by taking[17]

$$\vec{u}_j=\sum_{\pm q,n}\hat{e}_{q,n}\left(\frac{\hbar}{2MN\omega_{q,n}}\right)^{1/2}e^{iqR_j}\left(b_{q,n}+b_{-q,n}^\dagger\right),\qquad(2.4)$$

where $\hat{e}_{q,n}$ is the polarization vector of the vibration with wave vector q in the (acoustic) branch n, M the mass of a molecule, and R_j the coordinate of the jth molecule. We insert (2.2) and (2.4) into (2.1) and make the usual Fourier expansions for $a_j^\dagger$ and a_j in terms of the operators $a_{\vec{k}}^\dagger$ and $a_{\vec{k}}^\dagger$ that create and annihilate particles in the Bloch state of wave vector $\vec{k}$. After some straightforward manipulation, we obtain from the term of (2.2) linear in $\vec{u}$ the perturbing Hamiltonian for the interaction of the electrons with acoustic phonons of the branch n:

$$H_1' = N^{-1/2} \sum_{q,k} g_{1,n} a_{k+q}^\dagger a_k (b_{q,n} + b_{-q,n}^\dagger) , \tag{2.5}$$

$g_{1,n}$ being the coupling constant for one-phonon (1p) processes. For acoustic scattering this constant may be written[15]

$$g_{1t,n} = 2i \left(\frac{\partial t}{\partial u_n}\right)_0 \left(\frac{\hbar}{2M\omega_{q,n}}\right)^{1/2} [\sin(k+q)b - \sin kb] . \tag{2.6}$$

This form for $g_{1t,n}$ and the resulting matrix element had been obtained earlier by Friedman.[16] If we had calculated the coupling to acoustic modes arising from ϵ_j there would be an additional term in Eq. (2.6) of similar form and proportional to $(\partial \epsilon_j / \partial u_n)_0$. Since we are not explicitly including this term, it is understood that $(\partial t / \partial u_n)_0$ includes a contribution of unknown size, arising from $(\partial \epsilon_j / \partial u_n)_0$.

With the coupling constant in the form (2.6), the matrix element derived from (2.5) is a function of the final state wave vector, $k+q$, complicating integration of the Boltzmann equation. Fortunately, since the materials of concern are degenerate in the temperature range we deal with, and acoustic-mode scattering is essentially elastic, scattering may be considered to take place from $\pm k$ to $\mp k$. Incorporating this into (2.6) we may write

$$g_{1t,n} = \pm i \left(\frac{\partial \epsilon_0}{\partial u_n}\right)_0 \left(\frac{\hbar}{2M\omega_{2k,n}}\right)^{1/2} \sin kb , \tag{2.7}$$

where we have introduced the bandwidth ϵ_0, which equals $4t$. Thus the matrix element is written as a function of the initial state only.

A similar development may be carried out for the linear perturbing term in the Hamiltonian due to the librational modes. This leads again to the expression (2.5), with the coupling constant

$$g_{1l,n} = 2i \left(\frac{\partial t}{\partial \theta_n}\right)_0 \left(\frac{\hbar}{2I\omega_{q,n}}\right)^{1/2} [\sin(k+q)b - \sin kb] , \tag{2.8}$$

θ being the angle of libration and I the moment of inertia of the molecule appropriate to the particular libration. For degenerate material this may also be approximated by the form

$$g_{1l,n} = \pm i \left(\frac{\partial \epsilon_0}{\partial \theta_n}\right)_0 \left(\frac{\hbar}{2I\omega_{2k,n}}\right)^{1/2} \sin kb . \tag{2.9}$$

We consider now the effect of the term of (2.2) quadratic in u. Using Eq. (2.4) and the Fourier expansions for $a_j^\dagger$ and a_j we obtain the perturbing potential for interaction with the branch n,

$$H_2' = N^{-1} \sum_{k,q,q'} g_{2,n} a_{k+q+q'}^\dagger a_k (b_{q,n} + b_{-q,n}^\dagger)(b_{q',n} + b_{-q',n}^\dagger) , \tag{2.10}$$

the electron interaction now being with two phonons having wave vectors q and q'. For the acoustic modes the coupling constant is found to be

$$g_{2t} = \frac{1}{4} \left(\frac{\partial^2 \epsilon_0}{\partial u^2}\right)_0 \frac{\hbar}{2M(\omega_{q,n}\omega_{q',n})^{1/2}} f_2(k,q,q') , \tag{2.11}$$

while for the librons it is[7]

$$g_{2l} = \frac{1}{4} \left(\frac{\partial^2 \epsilon_0}{\partial \theta^2}\right)_0 \frac{\hbar}{2I(\omega_{q,n}\omega_{q',n})^{1/2}} f_2(k,q,q') . \tag{2.12}$$

In these expressions,

$$f_2(k,q,q') \equiv \cos(k+q+q')b - \cos(k+q)b - \cos(k+q')b + \cos kb . \tag{2.13}$$

In principle, q and q' could come from different branches, n and n'. In that case $(\partial^2 \epsilon_0 / \partial u_n^2)$ would be replaced by $(\partial^2 \epsilon_0 / \partial u_n \partial u_{n'})$, etc., in (2.11), with the corresponding replacements in (2.12).

It is clear that the drivatives of ϵ_0 (or t) with respect to the various possible displacements angular or linear, play an important role in the theory. In what follows we shall call them deformation potentials, since they play a somewhat similar role to the deformation potentials used in semiconductors and metals.[17]

To obtain the coupling to internal vibrations we expand ϵ_j in terms of $Q_n(j)$, normal coordinate for the nth internal vibration on the jth molecule, e.g.,[18]

$$\epsilon_j = \epsilon_{j0} + \left(\frac{\partial \epsilon_j}{\partial Q_n(j)}\right)_0 Q_n(j) + \frac{1}{2} \left(\frac{\partial^2 \epsilon_j}{\partial Q_n(j) \partial Q_m(j)}\right)_0 Q_n(j) Q_m(j) + \cdots , \tag{2.14}$$

where ϵ_{j0} is the electron energy at the jth site (molecular orbital energy plus effect of the crystal potential) in the absence of internal vibration. It is convenient to use dimensionless Q_n's, obtained by multiplying the usual normal coordinate by $(\omega_n/\hbar)^{1/2}$.[19] We now make the Fourier expansion

$$Q_n(j)=N^{-1/2}\sum_q e^{iqR_j}Q_n(q)\,, \tag{2.15}$$

where $Q_n(q)$ is the dimensionless normal coordinate for the nth phonon branch [corresponding to the internal vibration $Q_n(j)$] at wave vector q. Using

$$Q_n(q)=2^{-1/2}(b_{q,n}+b^{\dagger}_{-q,n})\,, \tag{2.16}$$

we obtain from the term in the expansion (2.14) linear in Q_n a perturbing potential in the form (2.5). The coupling constant for this case is given by[20]

$$g_{1i,n}=2^{-1/2}\left(\frac{\partial\epsilon_j}{\partial Q_n(j)}\right)_0\,. \tag{2.17a}$$

It is convenient to write this in the form

$$g_{1i,n}=g_n\hbar\omega_n\,, \tag{2.17b}$$

where g_n is the dimensionless coupling constant defined and calculated by Lipari *et al.*[18] As discussed in that reference, the only normal modes coupled to the electrons by terms linear in the Q_n's are those with the symmetry of the molecule (a_g for TCNQ, for example). This limits the modes that can interact with the electrons to 10 for TCNQ and 7 for TTF. We do not consider the contribution of higher order terms; two-phonon processes are unlikely for the temperature range of interest for the high-energy phonons of the internal-mode branches.

The quantity required for the calculation of the scattering time due to any of the processes above is the absolute square of the matrix element of H' for that process between the initial and final states of the system. For any of the 1p processes, from Eq. (2.5), this is given by

$$|\langle k'|H'_{1,n}|k\rangle|^2=N^{-1}|g_{1,n}|^2 \times\delta(k'-k\mp q)\times\begin{cases} n_q & \text{absorption}\\ n_q+1 & \text{emission}\,,\end{cases} \tag{2.18}$$

where $g_{1,n}$ is given by the expressions (2.6), (2.8), or (2.17) and the upper sign in the δ function is for absorption, the lower for emission. The possibility of umklapp processes will be neglected here since, as will be discussed, they do not appear important for the materials of concern in this temperature range. For the 2p absorption process we obtain from Eq. (2.10),

$$|\langle k'|H'_{2,n}|k\rangle|^2=N^{-1}|g_{2,n}|^2 \times\delta(k'-k\mp q\mp q')\times\begin{Bmatrix} n_q\\ n_q+1\end{Bmatrix}\begin{Bmatrix} n_{q'}\\ n_{q'}+1\end{Bmatrix}, \tag{2.19}$$

where one factor is chosen from each pair of braces depending on whether the corresponding phonon is absorbed or emitted, and the signs in the argument of the δ function chosen accordingly to satisfy conservation of crystal momentum. The quantity $g_{2,n}$ is given by (2.11) or (2.12) and (2.13).

A significant deduction can be made from (2.18) and the expressions for $g_{1,n}$: An acoustic mode for which $(\partial t/\partial u_n)_0$ vanishes, or a libration for which $(\partial t/\partial\theta_n)_0$ vanishes, will not give rise to 1p scattering. It can be seen from Fig. 1 that, by symmetry, the TA(a) mode is an example of the former, while the η and ζ rotations are examples of the latter. These modes, as well as all the others, are expected to give rise to 2p scattering.

C. Relaxation times for scattering

For dc fields the Boltzmann equation is the statement that in the steady state the rate of change of the distribution f due to applied fields is balanced by $(\partial f/\partial t)_c$, the rate of change of f due to collisions. For a small applied electric field we assume, as usual, a solution of the Boltzmann equation in the form

$$f=f_0(\epsilon)+f_1(\epsilon,\vec{\mathrm{E}})\,,\quad f_1\ll f_0 \tag{2.20}$$

where $f_0(\epsilon)$ is the thermal equilibrium distribution,

$$f_0=\{\exp[(\epsilon-\epsilon_F)/k_BT]+1\}^{-1}\,. \tag{2.21}$$

The function f_1 is linear in the electric field and an odd function of the velocity of the carriers.

To calculate the rate of change of f due to collisions we introduce $P(k,k')$, the probability of scattering per unit time from an initial state k to an empty final state in unit length of momentum space around k'. We assume perturbation theory to be valid, leaving its justification for the materials of interest to be discussed later. By the golden rule, then,

$$P(k\rightarrow k')=(2\pi/\hbar)|\langle k'|H'|k\rangle|^2\rho(k')\,, \tag{2.22}$$

where $\rho(k')$ is the number of final states per unit length of $\vec{\mathrm{k}}$ space. With this, we may write

$$\left(\frac{\partial f(k)}{\partial t}\right)_c=\int\{f(k')P(k'\rightarrow k)[1-f(k)] -f(k)P(k\rightarrow k')[1-f(k')]\}\,dk'\,, \tag{2.23}$$

where k' varies from $-\pi/b$ to $+\pi/b$. To evaluate (2.23) we substitute for f the expression (2.20). The group of terms obtained by replacing f by f_0, i.e.,

$$\int\{f_0(k')P(k'\rightarrow k)[1-f_0(k)] -f_0(k)P(k\rightarrow k')[1-f_0(k')]\}\,dk' \tag{2.24}$$

clearly vanishes because it represents the rate of change of f_0 due to collisions. Of the remaining terms for the 1p processes we have discussed, those with $f_1(k')P(k\rightarrow k')$ or $f_1(k')P(k'\rightarrow k)$ in the integrand also vanish. This is so because $f_1(k')$ is odd in the velocity v', thus in k', and for all the 1p processes considered the matrix elements, and therefore $P(k\rightleftharpoons k')$, are independent of the final state k'. Thus the only terms left are those involving $f_1(k)$, and the collision term may be written as

$$\left(\frac{\partial f(k)}{\partial t}\right)_c=-\frac{f_1(k)}{\tau}=-f_1(k)\left(\frac{1}{\tau_{\text{em}}}+\frac{1}{\tau_{\text{abs}}}\right), \tag{2.25}$$

where the relaxation times τ_{em} and τ_{abs} are given by

$$\frac{1}{\tau_{\text{em, abs}}}=\int\{P_{\text{em,abs}}(k\rightarrow k')[1-f_0(k')] + P_{\text{abs,em}}(k'\rightarrow k)f_0(k')\}\,dk'. \tag{2.26}$$

The first term of $1/\tau_{\text{em}}$ ($1/\tau_{\text{abs}}$) actually represents the rate of scattering out of k by emission (absorption), while the second term arises from the change in the transitions into k from k' due to the change $f_1(k)$ in the occupation probability of the state k. τ_{em} and τ_{abs} may be written in different form by making use of the relation derived from the vanishing of (2.24), or more specifically the vanishing of the integrand in (2.24). This leads to

$$\frac{P_{\text{abs}}(k'\rightarrow k)}{P_{\text{em}}(k\rightarrow k')}=\frac{f_0(k)}{f_0(k')}\,\frac{1-f_0(k')}{1-f_0(k)}\,. \tag{2.27}$$

With (2.27), Eq. (2.26) may be rewritten as

$$\frac{1}{\tau_{\text{em,abs}}}=\int P_{\text{em,abs}}(k\rightarrow k')\left(\frac{1-f_0(k')}{1-f_0(k)}\right)dk'\,. \tag{2.28}$$

For elastic scattering $f_0(k')=f_0(k)$ and the factor in large parentheses is unity.

In evaluating the τ's it is convenient, since P_{em} and P_{abs} contain a δ function involving ϵ_k and $\epsilon_{k'}$, to replace $\rho(k')dk'$ by $\rho(\epsilon_{k'})d\epsilon_{k'}$. For the one-dimensional case $\rho(k)=1/2\pi$ for states of one spin direction. With ϵ given by the usual one-dimensional tight-binding expression

$$\epsilon=(\epsilon_0/2)(1-\cos kb), \tag{2.29}$$

we obtain

$$\rho_k(\epsilon)=\rho(k)\,\frac{dk}{d\epsilon}=\frac{1}{2\pi b}\,\frac{1}{[\epsilon(\epsilon_0-\epsilon)]^{1/2}} \tag{2.30}$$

for the density of states at k with one spin direction. We use the notation $\rho_k(\epsilon)$ here because this is smaller by a factor 4 than the $\rho(\epsilon)$ ordinarily used, which includes both the states at $+k$ and $-k$ and the two spins.

With Eqs. (2.22), (2.18), and (2.30) used in (2.28), we obtain for the single-phonon scattering processes

$$\frac{1}{\tau_{\text{em, abs}}}=\frac{|g_{1,n}|^2}{\hbar}\left\{\begin{matrix} n_{q,n}+1 \\ n_{q,n}\end{matrix}\right\}\int\delta(\epsilon_{k'}-\epsilon_k\pm\hbar\omega_{q,n})[\epsilon_{k'}(\epsilon_0-\epsilon_{k'})]^{-1/2}\left(\frac{1-f_0(\epsilon_{k'})}{1-f_0(\epsilon_k)}\right)d\epsilon_{k'}\,. \tag{2.31}$$

For the internal modes, scattering with emission is possible to either $-k'$ or $+k'$, by means of phonons $k'+k$ or $-(k'-k)$, respectively, provided $\epsilon_{k'}=\epsilon_k-\hbar\omega_{q,n}$. For scattering by an internal mode n we therefore obtain[8]

$$\frac{1}{\tau_{\text{em}}}=\frac{2}{\hbar}(g_n\hbar\omega_n)^2(n_{q,n}+1)\times\frac{H(\epsilon-\hbar\omega_n)}{\{(\epsilon-\hbar\omega_n)[\epsilon_0-(\epsilon-\hbar\omega_n)]\}^{1/2}}\times\left(\frac{1-f_0(\epsilon-\hbar\omega_n)}{1-f_0(\epsilon)}\right). \tag{2.32}$$

where $g_{1,n}$ has been taken from Eq. (2.17b). The function $H(\epsilon-\hbar\omega_n)=1$ provided $\epsilon>\hbar\omega_n$, 0 otherwise. It is included here (and a similar function later in τ_{abs}) to ensure that the final state lies within the band. By a similar procedure we find[8]

$$\frac{1}{\tau_{\text{abs}}}=\frac{2}{\hbar}(g_n\hbar\omega_n)^2 n_{q,n}\,\frac{H[\epsilon_0-(\epsilon+\hbar\omega_n)]}{\{(\epsilon+\hbar\omega_n)[\epsilon_0-(\epsilon+\hbar\omega_n)]\}^{1/2}}\times\left(\frac{1-f_0(\epsilon+\hbar\omega_n)}{1-f_0(\epsilon)}\right). \tag{2.33}$$

The variation with ϵ/ϵ_0 of τ_{em} and τ_{abs} is shown in Figs. 2(a) and 2(b) for a set of parameters suitable for internal modes in TCNQ. It is seen that, in accordance with Eqs. (2.32) and (2.33), $\tau_{\text{em}}\rightarrow 0$ at $\epsilon=\hbar\omega_n$, while $\tau_{\text{abs}}\rightarrow 0$ at $\epsilon=\epsilon_0-\hbar\omega_n$. This occurs because of the singularities in the density of final states at $\epsilon=0$ and ϵ_0, respectively. It is not expected to be literally true, however, because the small lifetime for an electron in levels with $\epsilon\simeq\hbar\omega_n$ or $\epsilon\simeq\epsilon_0-\hbar\omega_n$ will cause broadening of these levels. Use of (2.32) and (2.33) would nevertheless not be expected to cause a significant error in calculating the conductivity, for example, unless perhaps the Fermi energy happened to coincide with one of the levels concerned. The dips get increasingly narrow as ϵ increases from 0 for τ_{em}, or decreases from ϵ_0 for τ_{abs}, because of the increasing number of phonons with which the electron can interact. The interplay between that number of phonons and the density-of-final-states factor is what determines the overall skewed bell shape of these τ's as a function of ϵ. We note that the τ's of (2.32) and

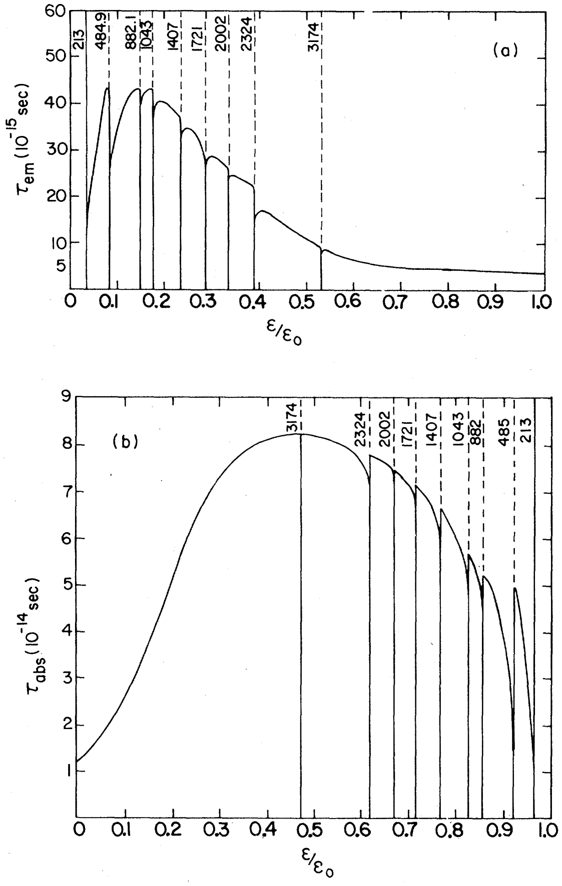

FIG. 2. τ_{em} (a) and τ_{abs} (b) of Eqs. (2.32) and (2.33), respectively, plotted for $T=300$ K, $\epsilon_0=6000$ K, $\epsilon_F=1200$ K, and internal-mode frequencies and coupling constants of Table I for TCNQ.

(2.33) are valid also for nondegenerate material, being somewhat simpler for that case since the factor in large parentheses may be taken as unity, filling of the states being unimportant in limiting transitions. These τ's have been used in calculations for NMP-TCNQ (Ref. 21) and complex TCNQ salts.[22]

In the case of acoustic-mode scattering, which we have noted is essentially elastic, for an electron at $+k_F$ (k_F being the Fermi wave vector) only backward scattering affects the conductivity. From Eqs. (2.31) and (2.7), using again the fact that the scattering is elastic, we obtain for the $1t$ case

$$\frac{1}{\tau_{\mathrm{em},\,1t;\;\mathrm{abs}\,,\,1t}}=\left(\frac{\partial\epsilon_0}{\partial u_n}\right)_0^2\frac{\sin kb}{M\epsilon_0\,\omega_{2k,n}}\times\begin{cases}n_q+1\,,\\ n_q\,.\end{cases}\tag{2.34}$$

Here we have used Eq. (2.29) to eliminate $[\epsilon(\epsilon_0-\epsilon)]^{1/2}$. Equation (2.34) may be put in another form[23] by making use of the dispersion relation for a linear vibrating chain in the harmonic approximation,[17]

$$\omega_{2k}=\omega_0\sin kb\,,\tag{2.35}$$

where ω_0, related to the force constant and M, is the maximum frequency of the branch. With this, combining absorption and emission terms we get

$$\frac{1}{\tau_{1t}}=\left(\frac{\partial\epsilon_0}{\partial u_n}\right)_0^2\frac{1}{M\epsilon_0\omega_{0,n}}(2n_q+1)\,.\tag{2.36}$$

When equipartition is valid,

$$2n_q+1\simeq 2k_BT/\hbar\omega_{2k,n}\,.\tag{2.37}$$

In that case τ_{1T} may be written as

$$\frac{1}{\tau_{1t}}=\left(\frac{\partial\epsilon_0}{\partial u_n}\right)_0^2\frac{k_BT}{\hbar M\omega_{0,n}^2}\,\frac{1}{[\epsilon(\epsilon_0-\epsilon)]^{1/2}}\,,\tag{2.38}$$

a convenient form because it displays explicitly the ϵ dependence of τ. Unlike the case of internal mode scattering, (2.36) and (2.38) may not be valid for nondegenerate material because the approximation of elastic scattering may be poor.

For scattering by a single libron the situation is quite similar to that for scattering by a single translon. When the approximations of elastic scattering and equipartition are valid we may write the relaxation time for this case in the form

$$\frac{1}{\tau_{1l}}=\frac{2}{\hbar}\left(\frac{\partial\epsilon_0}{\partial\theta_n}\right)^2\frac{\sin kb}{I\epsilon_0\omega_n^2}k_BT\,,\tag{2.39}$$

where we have dropped the subscript $2k$ on ω since the libron branches are expected to be fairly flat, i.e., dispersionless, at least for our simple model. For that reason, Eq. (2.35) does not apply and τ_{1l} cannot be written in a form analogous to (2.38) for τ_{1t}.

For the 2p processes the dependence on k' of the collision term cannot be eliminated, and a relaxation time in the sense of Eq. (2.25) does not exist. To estimate the conductivity for this case it is convenient to calculate a momentum relaxation time, to be denoted by τ_{2p}. This time differs from the mean free time between collisions by the factor $\langle 1-\cos\chi\rangle^{-1}$, χ being the angle between $\vec{k}$ and $\vec{k}'$. Since only backward collisions are significant in this case, $\langle 1-\cos\chi\rangle^{-1}=\frac{1}{2}$. We may then take

$$\frac{1}{\tau_{2p}}=2\sum_q\sum_{q'}P(k\rightarrow k')\,,\tag{2.40}$$

where $P(k\rightarrow k')$ is given by (2.22), with (2.19) and (2.11) or (2.12) specifying the matrix element for this case. If we again neglect the phonon energy compared to that of the electron, scattering can only take an electron from $\pm k$ to $\mp k$. To make the argument of the δ function in (2.19) vanish, then, requires that

$$q'=-q-2k\,.\tag{2.41}$$

This condition eliminates the summation over q'

in (2.40). With q' given by (2.41) the quantity $f_2(k, q, q')$ defined in (2.13) becomes

$$f_2(k, q, q') = 2[\cos kb - \cos(k+q)b] . \tag{2.42}$$

When the summation over q is changed into an integration we obtain for the case that both phonons are absorbed,

$$\frac{1}{\tau_{2p}} = 2\left(\frac{2\pi}{\hbar}\right)\frac{Nb}{2\pi}G^2\rho_k(\epsilon)\left(\frac{k_BT}{\hbar}\right)^2\int_{-\pi/b}^{-2k+\pi/b}\frac{f_2^2}{\omega_q^2\omega_{q'}^2}dq, \tag{2.43}$$

where $\rho_k(\epsilon)$ is the density of states of one spin at k or $-k$ [given by (2.30)], f_2 is given by (2.42), and

$$G = \begin{cases} \dfrac{\hbar}{8NM}\left(\dfrac{\partial^2\epsilon_0}{\partial u^2}\right)_0 & \text{translons}, \\ \dfrac{\hbar}{8NI}\left(\dfrac{\partial^2\epsilon_0}{\partial \theta^2}\right)_0 & \text{librons}. \end{cases} \tag{2.44}$$

The quantities n_q and $n_{q'}$ in the matrix element have been replaced by $kT/\hbar\omega_q$ and $kT/\hbar\omega_{q'}$, respectively. Also, the integration limits have been set in (2.43) so that the phonons and the electron stay within the first Brillouin zone. For the libron case, ω_q and $\omega_{q'}$ are constants, equal to each other in fact if both librons are from the same branch. Integration of (2.43) is then straightforward and yields τ_{2l} for the case that q and q' are absorbed. It is readily seen that the other three processes—absorption of q and emission of $-q'$, emission of $-q$ and absorption of q', and emission of q and q'—lead to the same result as (2.43). Combining all four processes, we obtain for the momentum relaxation time due to scattering by two librons from the nth branch[24]

$$\frac{1}{\tau_{2l}} = \left(\frac{\partial^2\epsilon_0}{\partial\theta_n^2}\right)_0^2\left(\frac{k_BT}{I\omega_n^2}\right)^2\frac{F_l(kb)}{\hbar[\epsilon(\epsilon_0-\epsilon)]^{1/2}}, \tag{2.45}$$

where

$$F_l(kb) = [(\pi - kb)(1 + 2\cos^2 kb) - \tfrac{5}{2}\sin 2kb]/4\pi . \tag{2.46}$$

For the translon case the analogous function to $F_l(k_Fb)$ will be different due to the dependence of ω_q on q.

D. The transport coefficients

It is straightforward to solve the one-dimensional Boltzmann equation under the assumption that a relaxation time τ exists, which we have shown to be the case for the 1p processes. To terms linear in the electric field intensity $\vec{E}$, making use of Eq. (2.20), we have

$$\left(\frac{\partial f}{\partial t}\right)_{\vec{E}} = -e\vec{E}\cdot\nabla_{\vec{p}}f \simeq -e\vec{E}\cdot\vec{v}(\partial f_0/\partial\epsilon), \tag{2.47}$$

where e is the magnitude of the charge on the electron. For the one-dimensional case the velocity, from Eq. (2.29), is given by

$$v = (b/\hbar)[\epsilon(\epsilon_0-\epsilon)]^{1/2} = (\epsilon_0 b/2\hbar)\sin kb . \tag{2.48}$$

With the use of Eq. (2.25) for the collision terms we obtain the solution for low electric fields:

$$f_1 = -e\vec{E}\cdot\vec{v}\tau(\partial f_0/\partial\epsilon). \tag{2.49}$$

The current density and energy flux are then given by

$$j = \mathfrak{N}e\sum_{\vec{k}} f_1\vec{v} \tag{2.50}$$

and

$$\vec{w} = \mathfrak{N}\sum_{\vec{k}}(\epsilon - \epsilon_F)f_1\vec{v}, \tag{2.51}$$

where $\mathfrak{N}$ is the number of chains/cm^2 and the summation over $\vec{k}$ is to be taken over all states (both spins) per unit length of chain. It is convenient to convert the summation into an integration over ϵ.

$$\sum_{\vec{k}} F(\vec{k}) = 2\int_{-\pi/b}^{+\pi/b}F(k)\rho(k)dk = \int_0^{\epsilon_0}F(\epsilon)\rho(\epsilon)d\epsilon, \tag{2.52}$$

where $\rho(\epsilon)$ represents the density of states at $+k$ and $-k$ and with both spin directions, being $4\rho_k(\epsilon)$ given by Eq. (2.30). Using Eqs. (2.49) and (2.52) we then obtain from (2.50)

$$\sigma \equiv (j/E) = -\int_0^{\epsilon_0}\sigma(\epsilon)(\partial f_0/\partial\epsilon)d\epsilon, \tag{2.53}$$

where

$$\sigma(\epsilon) = \mathfrak{N}e^2v^2\tau\rho(\epsilon). \tag{2.54}$$

To calculate the mobility μ from (2.53) it is necessary to divide σ by e times the carrier concentration $\mathfrak{N}n$, where n is the number of carriers per unit chain length. Using Eqs. (2.52) and (2.30) we obtain

$$n = \sum_{\vec{k}} f_0 = (2/\pi b)\int_0^{\epsilon_0}f_0(\epsilon)[\epsilon(\epsilon_0-\epsilon)]^{-1/2}d\epsilon. \tag{2.55}$$

Note that, despite the use of Fermi-Dirac statistics, carrier concentration is in general not constant in a two-chain conductor but varies with temperature because charge transfer changes as ϵ_F and the bandwidths change with temperature. This will be discussed further in Sec. III A.

The thermopower Q may be evaluated from the Kelvin relation

$$Q = w/jT, \tag{2.56a}$$

w/j being the Peltier heat. With Eqs. (2.49)–(2.52), (2.56a) for the thermopower of one type of chain becomes

$$Q=\frac{1}{eT}\,\frac{\int_0^{\epsilon_0}(\epsilon-\epsilon_F)\,v^2\tau\rho(\epsilon)(\partial f_0/\partial\epsilon)d\epsilon}{\int_0^{\epsilon_0}v^2\tau\rho(\epsilon)(\partial f_0/\partial\epsilon)d\epsilon}\,. \qquad (2.56\text{b})$$

For a material with two types of chain, having individual thermopowers Q_n and Q_p and conductivities σ_n and σ_p, the combined thermopower is the weighted average,

$$Q=(Q_n\sigma_n+Q_p\sigma_p)/(\sigma_n+\sigma_p)\,. \qquad (2.57)$$

When the scattering process is elastic, as is reasonable to assume for translon and libron scattering in degenerate material, integration of the expressions for σ and Q may be simplified by concentrating on properties at the Fermi energy. This will be carried out in the next section. However, when internal-mode scattering is operative, either alone or in combination with elastic processes, it is necessary to integrate (2.53) and (2.56) numerically. To do this, it is convenient to replace $(\partial f_0/\partial\epsilon)$ by $-f_0(1-f_0)/k_BT$, obtained from Eq. (2.21), and introduce the dimensionless variable $y=\epsilon/\epsilon_0$. The integrals are then conveniently evaluated by Gaussian-type numerical integration.

E. Transport coefficients for the cases of elastic scattering

Considerable insight may be gained by studying translon or libron scattering alone for the degenerate case. In the preceding section it was found that the integrals that must be evaluated to obtain σ and Q are of the form

$$K_n=-\int_0^{\epsilon_0}\epsilon^n\sigma(\epsilon)(\partial f_0/\partial\epsilon)d\epsilon\,, \qquad (2.58)$$

$\sigma(\epsilon)$ being the quantity defined in Eq. (2.54). To evaluate K_n we take advantage of the fact that $(\partial f_0/\partial\epsilon)$ is nonvanishing only in the neighborhood of $\epsilon=\epsilon_F$ to make a Taylor-series expansion of the coefficient of $(\partial f_0/\partial\epsilon)$ around ϵ_F. This leads to the result, to second-order terms in kT/ϵ_F,[25]

$$K_n=\epsilon_F^n\sigma(\epsilon_F)+\frac{\pi^2}{6}(k_BT)^2\frac{d^2}{d\epsilon^2}[\epsilon^n\sigma(\epsilon)]_{\epsilon_F}\,. \qquad (2.59)$$

To first order in T we have then, from (2.53) and (2.54),

$$\sigma=[\mathfrak{N}e^2v^2\tau\rho(\epsilon)]_{\epsilon_F}\,. \qquad (2.60)$$

To obtain σ for 1p acoustic scattering we use Eq. (2.34) for τ and assume equipartition, Eq. (2.37). Inserting Eq. (2.48) for v and $\rho(\epsilon)=4\rho_k(\epsilon)$, we may write for σ, due to scattering by the nth acoustic branch,

$$\sigma_{1t,n}=\frac{\mathfrak{N}e^2bM\omega^2_{2k_F,n}\epsilon_0^2}{h(\partial\epsilon_0/\partial u_n)^2k_BT}\,. \qquad (2.61)$$

Similarly, we obtain for 1p libron scattering

$$\sigma_{1l,n}=\frac{\mathfrak{N}e^2bI\omega^2_{2k_F,n}\epsilon_0^2}{h(\partial\epsilon_0/\partial\theta_n)^2k_BT}\,. \qquad (2.62)$$

We see that, under equipartition, σ for the 1p processes is proportional to T^{-1} and to the square of the frequency of the phonon with wave vector $2k_F$. Also σ is proportional to the square of the bandwidth.[26]

For the 2p case the solution (2.49) of Boltzmann equation is not valid since a relaxation time does not exist. One should nevertheless obtain a reasonable approximation to σ for two-libron scattering by inserting the momentum relaxation time, Eq. (2.45) for that case, in Eq. (2.60). This leads to

$$\sigma_{2l}=\frac{\mathfrak{N}e^2bI^2\omega_n^4\epsilon_0^2\sin^2k_Fb}{4hF_l(k_Fb)(\partial^2\epsilon_0/\partial\theta_n^2)^2(k_BT)^2}\,, \qquad (2.63)$$

where $F_l(k_Fb)$ is defined in (2.46). As expected, because two phonons are involved, this σ is proportional to ω^4 and T^{-2}, as well as to ϵ_0^2.

It is informative to write down what the conductivity would be for internal phonon scattering in the limit $\hbar\omega_n\to 0$. Inserting into Eq. (2.60) τ for the internal modes obtained by letting Eqs. (2.32) and (2.33) go to that limit, we obtain

$$\sigma_{\text{int}}\underset{\hbar\omega\to 0}{\sim}\frac{\mathfrak{N}e^2b\epsilon_0^2\sin^2k_Fb}{2h(g\hbar\omega)^2(2n_q+1)}\,. \qquad (2.64)$$

Since k_Fb depends little on ϵ_0, σ_{int} in this limit is clearly proportional to ϵ_0^2. This remains essentially true when $\hbar\omega$ is not assumed small compared to ϵ_F.

Consider now the thermopower for the case of elastic scattering. When Q, given by Eq. (2.56), is expressed in terms of K_n, we obtain

$$Q=(eT)^{-1}(K_1/K_0-\epsilon_F)\,. \qquad (2.65)$$

Using (2.59) for K_n we obtain a useful general expression for Q, valid to lowest order in k_BT/ϵ_F,

$$Q=\frac{\pi^2}{3}\frac{k_B^2T}{e}\left(\frac{d\ln\sigma(\epsilon)}{d\epsilon}\right)_{\epsilon_F}\,. \qquad (2.66)$$

With Eq. (2.54) inserted for $\sigma(\epsilon)$, Q becomes

$$Q=\frac{\pi^2}{3}\frac{k_B^2T}{e}\left(\frac{1}{v^2\rho}\frac{d}{d\epsilon}(v^2\rho)+\frac{1}{\tau}\frac{d\tau}{d\epsilon}\right)_{\epsilon_F}\,. \qquad (2.67)$$

When v and ρ are expressed in terms of ϵ, we obtain for the first term

$$\left(\frac{1}{v^2\rho}\frac{d}{d\epsilon}(v^2\rho)\right)_{\epsilon_F}=\frac{1}{2}\frac{\epsilon_0-2\epsilon_F}{\epsilon_F(\epsilon_0-\epsilon_F)}\,. \qquad (2.68)$$

For 1p acoustic-mode scattering, with τ given by Eq. (2.38), where the energy dependence is clearly displayed, we find

$$\left[\frac{1}{\tau_{1t}}\left(\frac{d\tau_{1t}}{d\epsilon}\right)\right]_{\epsilon_F}=\left(\frac{1}{v^2\rho}\frac{d}{d\epsilon}(v^2\rho)\right)_{\epsilon_F}\,. \qquad (2.69)$$

Thus the term in $d\tau/d\epsilon$ makes precisely the same contribution to Q for this case as the first term, the so-called "band" term, giving

$$Q_{1t}=\frac{\pi^2}{3}\frac{k_B}{e}\frac{k_BT}{\epsilon_0}\frac{1-2\epsilon_F/\epsilon_0}{(\epsilon_F/\epsilon_0)(1-\epsilon_F/\epsilon_0)}\,. \tag{2.70}$$

Since ϵ_F/ϵ_0 is determined by the charge transfer, which does not vary a great deal with temperature, Q for this case depends essentially on T and ϵ_0^{-1}. It is easily seen that this expression for Q still holds when there is scattering by more than one type of acoustic phonon. Also, it is valid for the case of internal phonon scattering in the limit $\hbar\omega\to 0$. It will be seen, however, when we discuss the results of numerical integration for Q, that when $\hbar\omega$ is not assumed vanishingly small, the internal modes may make quite a different contribution to Q.

The case of one-libron scattering is an interesting one. Here τ is given by Eq. (2.39), where it is seen that its energy dependence is given by $(\sin k_Fb)^{-1}$, which is proportional to $[\epsilon(\epsilon_0-\epsilon)]^{-1/2}$. The resulting $[(1/\tau)d\tau/d\epsilon]_{\epsilon_F}$ is the negative of that for the translon case, just canceling the band term and giving $Q_{1l}=0$. In other words, if there were only one-libron scattering present Q would vanish because $\sigma(\epsilon)$ is independent of ϵ for this case. Comparing the τ's for the $1t$ and $1l$ cases, Eqs. (2.34) and (2.39), respectively, we see that what makes the $1t$ case different from this one is the dispersion of the acoustic phonons; ω_{2k_F} is a function of ϵ for the acoustic phonons but for the librons it is not because we have assumed them dispersionless. Actually, the libron branches can be expected to have some dispersion so Q_{1l} may be finite though small.

We can also get an estimate of Q for the two-libron case by inserting Eq. (2.45) in the expression (2.67) for Q. This leads to

$$Q_{2l}=Q_{1t}-\frac{\pi^2}{3}\frac{k_B}{e}k_BT\left(\frac{1}{F_l(kb)}\frac{d}{d\epsilon}F_l(kb)\right)_{\epsilon_F}, \tag{2.71}$$

where Q_{1t} is given by Eq. (2.70) and

$$\left(\frac{1}{F_l(kb)}\frac{d}{d\epsilon}(F_l(kb))\right)_{\epsilon_F}=-\frac{1+2\cos^2k_Fb+2(\pi-k_Fb)\sin 2k_Fb+5\cos 2k_Fb}{2\pi\epsilon_0\sin k_Fb\,F_l(k_Fb)}, \tag{2.72}$$

$F_l(kb)$ being given by (2.46a). Again, Q increases linearly with T, as anticipated from Eq. (2.66), but the dependences on ϵ_F and ϵ_0 are clearly different from those for the 1p cases.

III. APPLICATION TO TTF-TCNQ

Many properties of TTF-TCNQ must be known or calculated in order to determine the transport from the formalism of Sec. II. We consider first the determination of the Fermi energy. The requirement that the Fermi level be the same on the two types of stacks leads to the prediction of a not inconsiderable change in charge transfer with temperature, calculated in Sec. III A. In Sec. III B we consider briefly how the lattice vibrations for TTF-TCNQ differ from those of the model set up in Sec. II A. The implications of this for σ due to phonon scattering in TTF-TCNQ are considered in the next section. Here the choice of the various parameters for numerical calculations is discussed, and results given. This is followed by a discussion of the results of the application of the theory to TTF-TCNQ. Finally there is a brief section on the explanation of the pressure dependence of σ within the framework of this theory.

A. Determination of the charge transfer and ϵ_F

From neutron scattering experiments,[13] $2k_F$ has been identified as $0.295b^*$ at $T\sim 60$ K, corresponding to a charge transfer $\rho=0.59$. An increase in temperature above 60 K must, as noted earlier, cause the Fermi level and therefore ρ to change both due to the change in temperature and the resulting change in volume. The latter effect has been directly demonstrated in pressure experiments.[27,28] The temperature variation of these quantities can be calculated along the same lines as used to calculate their variation with pressure.[3]

For a two-chain quasi-one-dimensional conductor the charge transfer, equal to the product of electron (or hole) concentration and the lattice constant b, may be written, by transforming (2.55),

$$\rho=nb=pb=\frac{2}{\pi}\int_{y=0}^{1}f_0(y)[y(1-y)]^{-1/2}dy\,, \tag{3.1}$$

where $y\equiv\epsilon/\epsilon_0$. In the form (2.21) for f_0, ϵ_F $(\equiv y_F\epsilon_0)$ represents the distance between the Fermi level and the band edge, the latter taken as the bottom of the band for electron conduction and the top for hole conduction. In the limit $T\to 0$ the integral in (3.1) can be evaluated explicitly to give

$$\rho=1-(2/\pi)\sin^{-1}(1-2y_F)\,. \tag{3.2}$$

Thus, if there were no Peierls transition and ρ were 0.59 at $T=0$, we would conclude from (3.2) that $y_F=0.2$ for both bands at $T=0$, independent of their bandwidths. Knowing that $\rho=0.59$ at 60 K for each of the bands,[13] and assuming values for the two bandwidths at this temperature, one can determine the y_F's for the two bands, $y_F^Q(60)$ and $y_F^F(60)$, respectively, by evaluating (3.1) numerically for each band. (This is conveniently done by evaluating the integral for different y_F's until the result $\rho = 0.59$ obtained.) At 60 K both y_F's are found to be quite close to 0.2, with very little dependence on the bandwidths. The condition that the Fermi level must be the same for the two bands is then used to establish the relative position of the band centers. Given the rates of change of the bandwidths with lattice expansion, which begins to be visible at 60 K, bandwidths can be calculated for each T greater than 60 from

$$\epsilon_0(T) = \epsilon_0(60) - (\partial\epsilon_0/\partial b)[b(T) - b(60)] . \qquad (3.3)$$

The correct values of $y_F^F(T)$ and $y_F^Q(T)$ must satisfy the condition that any shift of the Fermi level on one chain (measured from the band center) must be accompanied by the same shift on the other chain. In practice one calculates nb and pb from Eq. (3.1), given the calculated bandwidths, using pairs of $y_F^F(T)$ and $y_F^Q(T)$ that keep the Fermi energies of the two bands aligned. The correct pair of $y_F^F(T)$ and $y_F^Q(T)$ is the pair that leads to $nb = pb$, which then equals $\rho(T)$.

The calculations just described have been carried out for TTF-TCNQ for various values of the bandwidths and their rates of change with expansion. The values of $b(T)$ for Eq. (3.3) were taken from x-ray measurements.[29] In Fig. 3 are shown the results for various values of $\partial\epsilon_0/\partial b$ and room temperature bandwidths of 0.5 and 0.25 eV for TCNQ and TTF, respectively. Change in ϵ_0 of TTF from 0.25 to 0.4 eV, however, affected the results by only a few percent at the highest temperatures and less below. Values of $\partial\epsilon_0/\partial b$ ($= 4\partial t/\partial b$) calculated for TCNQ are in the range 0.68 (Ref. 30) to 0.6 eV/Å,[31] thus in between the two larger values used for the figure. It is useful to compare $\partial\epsilon_0/\partial b$ also with the values deduced from pressure measurements. With the room-temperature compressibility of 0.47%/kbar (Ref. 32) and $b = 3.819$ Å, $\partial\epsilon_0/\partial b = -0.84$ eV/Å corresponds to $\partial\epsilon_0/\partial P = 0.015$ eV/kbar or $(1/\epsilon_0)(\partial\epsilon_0/\partial P) = 3\%$/kbar for $\epsilon_0 = 0.5$ eV. The expected value of the rate of bandwidth change with pressure at 300 K based on the theoretical calculations of $\partial t/\partial b$ mentioned above, is between 2 and 3%/kbar.[9,33] In excellent agreement with this, the observed variation of ρ with P at very low temperatures,[27] where the compressibility is known to be a factor 2 smaller than at 300 K,[27] has been accounted for with $(1/\epsilon_0)(\partial\epsilon_0/\partial P)$ in the range 1% to 1.5%.[3] Somewhat in disagreement is the value deduced by Welber *et al.* from optical data.[34] Determining the plasma energy $\hbar\omega_P$ to be 1.2 eV by use of a Drude model, they calculate from the shift of the reflectivity with pressure that the rate of change of bandwidth is less than 1%/kbar. However, the use of a Drude model for determining ω_P is questionable; it has been found, for example, that, while deuteron irradiation reduces the dc conductivity at 300 K by nearly a factor 2, there is no accompanying change in the position or shape of the plasma edge.[35] The energy at which the dielectric constant goes through zero has been determined by electron-energy-loss experiments to be 0.75 eV.[36] For energies in this neighborhood, up to 1 eV at least, the shift with pressure is greater than at 1.2 eV.[34] Thus we feel that the estimate of less than 1%/kbar (Ref. 34) is not reliable and the correct $\partial\epsilon_0/\partial b$ at room temperature is ~0.7 eV/Å, in agreement with the calculated values. It is expected then that the correct variation of ρ with T lies between the two lower curves of Fig. 3. If $\partial\epsilon_0/\partial b$ is somewhat smaller for TTF than TCNQ, as is suggested by some of the theoretical calculations, it should lie closer to the middle curve.

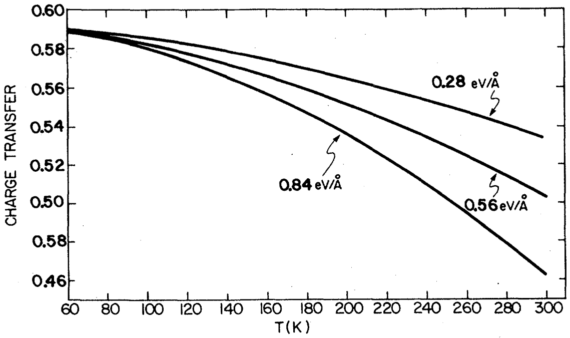

FIG. 3. Calculated variation of charge transfer with temperature for three different values of $\partial\epsilon_0/\partial b$.

B. Lattice vibrations of TTF-TCNQ

With four molecules per unit cell in TTF-TCNQ there are 24 external mode branches rather than the six considered in the simplified model. At $q = 0$ these break down into three acoustic branches and 21 optical branches.[37] Both at $q = 0$ and away from it group theory allows all the optical branches to be a mixture of translations and librations of the individual molecules. Stated differently, the equations of motion cannot be separated into translations and librations for a molecular crystal with such low symmetry and high unit cell complexity.[12,37] The proportions of the mixture are expected to be a function of the location in the Brillouin zone. An example of mixing of branches is provided by TA(a^*) and TA(c^*). According to neutron scattering data[14] these two branches appear to cross at room temperature around $2k_F$. Since they belong to the same representation, the actual situation must be that there are two mixed branches formed which repel each other. As additional evidence for this, perhaps, one of these two branches shows a somewhat unusual dispersion. The LA branch, on the other hand, shows the expected dispersion [see Eq. (2.35)] and it appears reasonable to assume that it is not much affected by mixing. Little information is available on the external optical branches from neutron scattering, although one, with considerable dispersion, has recently been seen.[38] However, low temperature far-infrared absorption based on a bolometric technique has provided some additional information.[39] In particular, it is found that the ξ librons, corresponding to rotation about the long axis of the molecule, are strongly mixed with translations and have frequencies ranging from 122 to 179 K, much higher than earlier estimates of the libron frequencies.

Although mixing can in principle occur between internal modes and external modes of comparable frequency, the frequencies of most of the internal modes for the TTF and TCNQ molecules are so high that this effect is in all likelihood negligible. In any case, no evidence for mixing of the totally symmetric a_g modes was found in Ref. 39, although the lowest lying a_u mode of TTF was found strongly mixed. We therefore use for the a_g modes the measured molecular frequencies, given in Table I.

C. Calculated σ and Q for TTF-TCNQ

The mixing of the TA(c^*) and TA(a^*) branches, and the facts that the libron branches are very unlikely to have the symmetry assumed in Sec. II and are in general mixtures of translations and rotations, combine to blur the distinctions between branches so far as the possibility of 1p or 2p processes is concerned. Thus 1p scattering should be possible from most, if not all, branches. This probably does not result in a large increase in 1p scattering over what might have been expected with the simplified model, since the mixing of branches produces also a mixing of the derivatives $\partial\epsilon_0/\partial u_n$, $\partial\epsilon_0/\partial\theta_n$, etc., i.e., the deformation potentials. It does make it more difficult, however, to calculate or otherwise determine these quantities, particularly so in the absence of detailed knowledge about much of the lattice-mode spectrum.

TABLE I. Frequencies and coupling constants for internal phonons.

TCNQ		TTF	
$\hbar\omega$ [a] (K)	g [b]	$\hbar\omega$ [a] (K)	g [a]
213	1.54	353	0.16
485	0.70	684	1.33
882	0.20	1059	0.49
1043	0.24	1574	0.16
1407	0.20	2184	0.62
1721	0.22	2238	0.23
2002	0.20	4436	0.03
2324	0.49		
3174	0.13		
4392	~0		

[a] N. O. Lipari, M. J. Rice, C. B. Duke, R. Bozio, A. Girlando, and C. Pecile Int. J. Quantum Chem. Symp. 11, 583 (1977).

[b] M. J. Rice, L. Pietronero, and P. Brüesch, Solid State Commun. 21, 757 (1977).

For the LA branch, if we neglect possible mixing, since the dispersion obeys (2.35), and contribution of the internal modes, the required deformation potential is $(\partial t/\partial u_b)_0$. Band-structure calculations, as noted in Sec. III A, have produced values for $(\partial t/\partial u_b)_0$ of -0.17 eV/Å (Ref. 30) and -0.15 eV/Å (Ref. 31) for TCNQ. Also, as discussed in III A, the observed low-temperature variation of charge transfer with pressure is in good agreement with these values. We therefore took the deformation potential constant for the LA branch to be 0.2 eV/Å. Since not much is known about deformation potentials for the TA(c^*) mode and all the other external modes that contribute to 1p scattering, these were all lumped together, with a deformation potential denoted $(\partial t/\partial u_{c*})_0$ that was treated as a parameter in the calculations. For the internal modes the frequencies and coupling constants were those listed in Table I.

The bandwidth for TCNQ was taken as 0.5 eV or 6000 K, a value which is generally agreed to be in accord with experiment. Although the TTF bandwidth is thought to be smaller, there is no agreement on its value. It was therefore taken to be a parameter in the calculations, with values ranging from 3000 to 4500 K.

As indicated in the Introduction the volume dependence of σ is quite large in TTF-TCNQ. Although the volume dependence of some of the quantities that enter into σ is known, it is unknown for some of the others. The calculations were done therefore for constant volume. σ was evaluated numerically from Eqs. (2.53) and (2.54) and Q from Eq. (2.56). Inserted for τ was the reciprocal of the sum of the reciprocals of the individual τ's included. For the $1t$ processes τ was taken from Eq. (2.36). The quantity ω_0 was taken as 8.6 MeV for LA phonons, 5.5 MeV for TA(c^*) phonons.[14] Equipartition was not assumed for any of the modes. The energy $\hbar\omega_{2k_F}$ for LA phonons was taken as 85 K, for TA(c^*) phonons 57 K.[13,14] The remaining numerical values required, as well as those already specified, are listed in Table II. When 2p

TABLE II. Values used for calculations on TTF-TCNQ.

$(\partial t/\partial u)_{\mathrm{LA}}$	−0.20 eV/Å	M	204 amu
$\hbar\omega_{2k_F}$(LA)	85 K	b	3.819×10^{-8} cm
$\hbar\omega_{2k_F}$(TA)	57 K	$\mathfrak{N}$	$8.79\times10^{13}/\mathrm{cm}^2$
$\hbar\omega_0$(LA)	8.6 meV	ϵ_0(TTF)	3000–4500 K
$\hbar\omega_0$(TA)	5.5 meV	ϵ_0(TCNQ)	6000 K
$(\partial t/\partial u_{c*})$	0.24 eV/Å (case I)	$(\partial t/\partial u_{c*})$	−0.20 eV/Å (case II)

processes were included, since neither the deformation potential nor $I\omega^2$ are known, these were lumped together with $F_l(k_F b)$ and treated as a parameter.

A set of results (case I) including only 1p processes is shown in Fig. 4. The deformation potential constants were assumed to be the same for TTF as for TCNQ, and ϵ_0(TTF) was taken as 3000 K. To achieve a value of σ at 300 K in the range 800 (Ref. 40) to 900 $\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ with the values of the other parameters chosen required $(\partial t/\partial u_{c*}) = -0.24$ eV/Å. Since this is of the same order of magnitude as $(\partial t/\partial u_b)$, it appears to be a reasonable value. If the TA(c^*) motion were as described in Fig. 1 and Sec. II A, it would have a sizable longitudinal component of motion due to the tilt of the molecules. This in itself would make its deformation potential of the order of that for the LA vibration. In addition, this motion causes a change in registry of adjacent molecules which should have a comparable effect on the transfer integral. Thus it is clearly expected that the pure TA(c^*) motion have a deformation potential comparable to that of LA. With the mixing of different motions, the scattering effect may be spread out over different branches, as discussed, but the net effect should still be comparable. In addition, some 1l scattering effect should add in here also. Thus the finding that $(\partial t/\partial u_{c*})$ is comparable to $(\partial t/\partial u_b)$ gives support to the idea that 1p processes account for most of the resistivity in this temperature range.

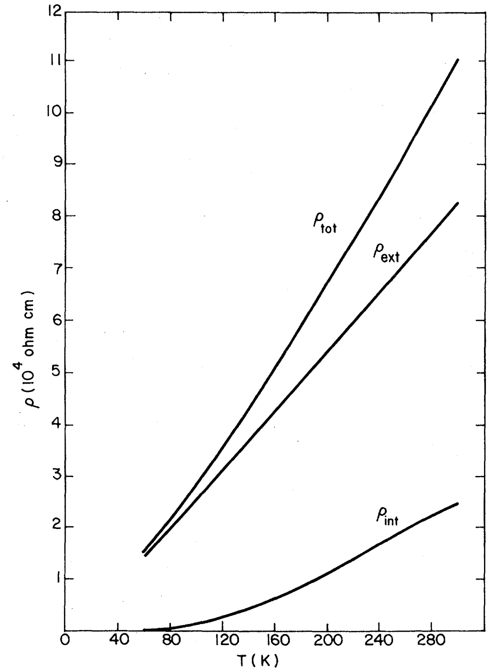

FIG. 4. Calculated resistivity at constant volume ρ_v including only 1p processes (case I) with the parameters of Tables I and II, and breakdown into external- and internal-mode scattering.

As expected, ρ due to the external modes varies linearly with T except for the lowest temperatures where departure from equipartition, for the LA phonons primarily, is not totally negligible. The variation of n_q with temperature accounts, of course, for the strong temperature dependence of ρ_{int}. The total resistivity ρ_v varies quasilinearly with T, the variation being close to linear at high temperatures and getting steeper at low temperatures, qualitatively in agreement with the deductions of Friend *et al.*[10] and Cooper.[9] If ρ_v is characterized as proportional to T^{λ}, the average λ for the case of Fig. 4 is 1.23, while that of Friend *et al.* is 1.29. However, they have underestimated the value of λ since they assumed that ρ is affected only by b-axis length changes, whereas it is almost as much affected by changes in the transverse dimensions.[41] A larger value of λ could be obtained by incorporating higher energy phonons, such as the mixed ξ branch librons[39] mentioned in Sec. III B, or by introducing 2p scattering. The results of a calculation doing the latter will be described shortly, after a discussion of the separate contributions of the TTF and TCNQ chains.

In Fig. 5 is shown the breakdown of σ_v of Fig. 4 into the contributions of TTF and TCNQ. It is seen that, although the ratio varies somewhat with temperature, $(\sigma_Q/\sigma_F)\simeq 4$ over the entire range. It increases at the higher temperatures because of the strong coupling of TTF to the internal mode at 683 K. The factor 4 ratio is due to the factor 2 ratio assumed in the bandwidths, since $\sigma \propto \epsilon_0^2$. That σ_F is considerably less than σ_Q is deduced from two types of data: (1) The Hall constant R over a wide temperature range is close to what one would expect if only the TCNQ chain were conducting[42]; (2) the thermopower at room temperature has a relatively large negative value and decreases linearly with T.[43] Of course, a ratio $(\sigma_Q/\sigma_F)\simeq 4$ could result instead from the deformation potentials for TTF being twice as large as for TCNQ. It has been found, in fact, that both σ and Q can be fit equally well with $\epsilon_0(\mathrm{TTF}) = 4500$, for example, instead of 3000, with correspondingly

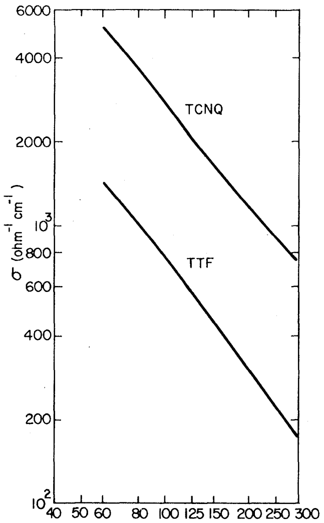

FIG. 5. Separate contributions to σ at constant volume of the TTF and TCNQ chains for the calculation with 1p processes only (case I).

larger values of the deformation potentials. However, such theoretical estimates as there are have the deformation potential constants smaller for TTF than TCNQ rather than larger, lending support to the smaller values of ϵ_0(TTF). Additional support comes from other sources, such as the magnitude of the susceptibility, χ. If χ is not considerably enhanced by the effect of large U, which is the likely situation according to the discussion in the Introduction, the smaller ϵ_0 helps to account for its magnitude.[44] The only disagreement with an ϵ_0 of 3000 K for TTF comes from the decomposition of EPR data,[45] which suggests that ϵ_0 of TTF is quite close to ϵ_0 of TCNQ. There are, however, serious questions as to the accuracy of the decomposition; these are discussed elsewhere.[46]

It is of interest to determine the scattering times and mean free paths to which the σ's of Fig. 5 correspond. With the room temperature transfer taken as 0.50, on the basis of the discussion in Sec. IIIA, the calculated mobilities for TCNQ and TTF at 300 K are 4 cm^2/V sec and 1 cm^2/V sec, respectively. A bandwidth of 0.5 eV for TCNQ then leads, with the use of Eq. (2.60), to $\tau(\epsilon_F)=5\times10^{-15}$ sec and, with $v_F=1.2\times10^7$ cm/sec, a mean free path l at 300 K of 1.6 lattice constants. It is interesting to note that the effective mass at ϵ_F is twice the free-electron mass. For TTF at 300 K with $\epsilon_0=0.25$ eV, τ is half as large, v_F half as large, and l a quarter as large, or ~ one-half a lattice constant. Certainly the use of simple first-order perturbation theory to calculate σ is not well justified for TTF at 300 K. Also, there are the complications of level shifts and the resultant band distortions produced by the self energy[23] which are expected to be significant for TTF at 300 K because of the small bandwidth. However, with decreasing temperature τ and l grow as $T^{2.3}$, the bandwidth increases, decreasing the effect of U, and the self-energy effects decrease, so the justification for using the golden rule exists at lower temperatures. In that sense, use of the foregoing theory at room temperature constitutes an extrapolation, but one that can hardly cause much error in the calculated σ since σ_F is considerably smaller than σ_Q.

It is worthwhile to estimate the maximum amount that 2p scattering processes could contribute at room temperature. This will also serve to summarize a good deal of the preceding discussion of results. The estimate will be confined to the TCNQ chain since that accounts for most of the conductivity. Also, instead of working with the total σ, we shall, in the interest of greater insight, calculate μ for each scattering process separately (from σ for that process divided by $\rho\mathcal{N}e/b$) and combine the reciprocals of the separate μ's to obtain a total μ. For the internal modes, numerical calculation gives $\mu_{\text{int}}=15$ cm^2/V sec. Since the observed $\mu=4$ cm^2/V sec for TCNQ, the internal modes contribute $\sim\frac{1}{4}$ of the resistivity. For the LA and TA modes μ may be calculated from Eq. (2.61). With $(\partial t/\partial u)_{\text{LA}}=-0.2$ eV/Å and the other parameters as given in Table II we obtain $\mu_{\text{LA}}=20$ cm^2/V sec. The smallest value of $(\partial t/\partial u)_{\text{LA}}$ that can fit the pressure data, according to the discussion of Sec. IIIA, is -0.15 eV/Å [corresponding to $(1/\epsilon_0)(\partial\epsilon_0/\partial b)\simeq 2\%$/kbar]. For this value $\mu_{\text{LA}}=35$ cm^2/V sec. A minimum value of the deformation potential for the TA(c^*) vibration may be obtained by assuming that only that component of the motion contributes that decreases the distance between adjacent molecules. This gives $(\partial t/\partial u)_{\text{TA}(c^*)}=(\partial t/\partial u)_{\text{LA}}(\tan 34°)$, 34° being the tilt angle. The effect on σ_{1t} of the smaller deformation potential is just cancelled by the effect of the lower frequency of the TA vibrations, with the result that $\mu_{\text{TA}(c^*)}$ calculated with this low value of deformation potential equals μ_{LA}. If these μ's are taken as 20 cm^2/V sec, corresponding to the higher deformation potential for LA modes, combination with μ_{int} leads to $\mu=6$ cm^2/V sec for all three. Comparison with the observed μ of 4 cm^2/V sec leads to the conclusion that $\frac{1}{3}$ of the scattering is still unaccounted for. For the low value of the LA deformation potential the combined μ would be 8 cm^2/V sec, according to which $\frac{1}{2}$ of the scattering is still unaccounted for. We have, however, certainly underestimated the TA(c^*) scattering and completely neglected $1l$ scattering, including what comes from the mixing of the libron branches with translations, as found for the ζ librons. Thus the part that is unaccounted for and might be due to 2p processes is certainly less than $\frac{1}{2}$. According to our present knowledge, there is no property that requires that there be any 2p scattering at 300 K; it could be negligible.

To show, nevertheless, what the effects are on σ and Q of incorporating some 2p external-mode scattering we have included some typical calculations (case II), shown in Fig. 6. The amount of 2p scattering was chosen (arbitrarily) to contribute $\sim\frac{1}{3}$ of the total resistivity. To account for the remainder of the resistivity by 1p scattering was found to require the parameter $(\partial t/\partial u_{c*}) = -0.20$ eV/Å, coincidentally the same as the deformation potential for LA scattering. This equality still leaves the TA(c^*) scattering predominant, however, since the lower TA phonon frequency means there are more of these phonons to scatter. As in the case of Fig. 4, ρ_v is fairly close to linear at high temperatures but gets steeper with decreasing T. On the average $\rho_v \propto T^{1.43}$ of this case. The individual σ's, shown in Fig. 7, are little changed except for varying somewhat more steeply with T.

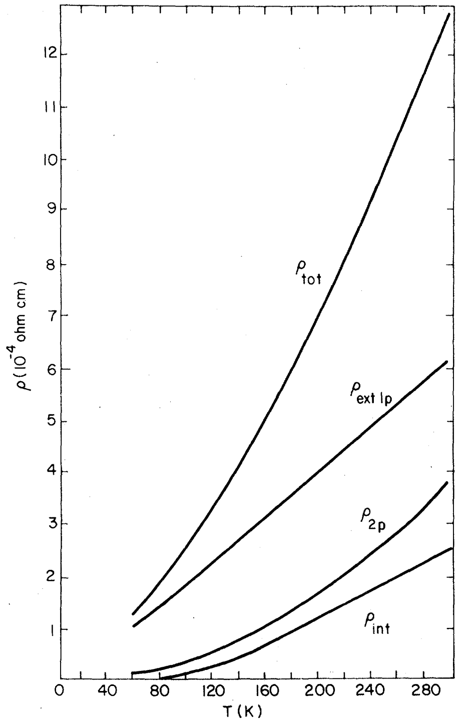

FIG. 6. Calculated ρ_v versus temperature with 1p and 2p scattering (case II), the latter chosen arbitrarily to contribute $\sim\frac{1}{3}$ of ρ_v, for the parameters of Tables I and II. The lower curves give the breakdown into the different scattering processes.

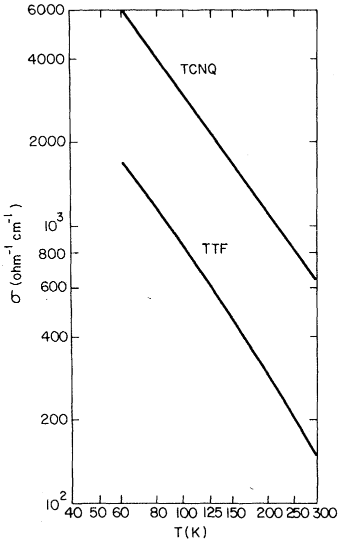

FIG. 7. Separate contributions to σ at constant volume of the TTF and TCNQ chains for the calculation with 1p and 2p processes (case II).

The results for the thermopower calculated from Eqs. (2.56) and (2.57) with the parameters of case I are shown in Fig. 8. Almost identical results are obtained for case II, at least in the approximation that $F_l(k_F b)$ defined in Eq. (2.46) is taken constant. None of the scattering has been assigned to 1l processes which, as noted earlier, make a different and probably smaller contribution to Q from the 1t processes since their dispersion is different. The curve shown is for ϵ_0(TTF) = 3000 but, as indicated earlier, an almost identical curve can be obtained for ϵ_0(TTF) = 4500 if the deformation potentials are adjusted upward suitably.

It is of interest to consider the contribution to Q of the two chains. Since the 1t scattering contribution to Q is predominant according to our model, Q for the individual chains should be given fairly well by Eq. (2.70). This should certainly be the case at 100 K, for example, where the small

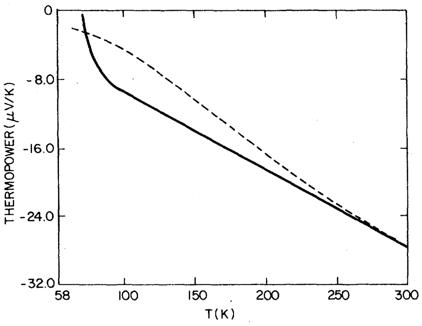

FIG. 8. Measured thermopower (solid line, taken from Ref. 43) and calculated thermopower (parameters of case I) versus temperature.

degree of excitation of the internal modes makes their scattering relatively unimportant. At 100 K Q calculated from (2.70) for TCNQ, with $\epsilon_0 = 0.5$ eV, $(\epsilon_F/\epsilon_0) = 0.2$, is -17.5 μV/K, while Q calculated including the internal modes is -15 μV/K. Similarly for TTF, with $\epsilon_0 = 0.25$ eV, Q calculated from (2.70) is $+35$ μV/K while the value including internal modes is $+29$ μV/K. At 300 K this close similarity continues to hold for TCNQ, the two values being -53 and -48 μV/K, respectively. It does not hold as well for TTF, however, where the corresponding values are $+106$ and $+61$ μV/K, respectively. The difference stems from the fact that the internal modes that interact most strongly with TCNQ have low enough energy that they are close to satisfying equipartition at 300 K, while this is not true for TTF, as indicated earlier.

It is reasonable that Q should be considerably less dependent on pressure or volume than σ. The individual Q's depend on volume only through ϵ_0 and ϵ_F/ϵ_0, neither of which is strongly V dependent. The σ's, which are more V dependent, according to the pressure experiments, occur in numerator and denominator so that a major portion of the V dependence should cancel out. It is therefore not entirely unreasonable to compare the calculated Q vs T with Q vs T measured at ambient pressure. As can be seen in Fig. 8, the agreement is not bad. It could have been improved, undoubtedly, by further adjustments in parameters but that would not prove anything more.

D. Calculated σ and Q for TSeF-TCNQ

Similar calculations were carried out for TSeF-TCNQ, which has the same lattice structure as TTF-TCNQ and somewhat larger conductivity.[47] So far as transport is concerned, the big difference between TTF- and TSeF-TCNQ is that, in the temperature range we are concerned with, Q for the latter is small and positive.[48] It rises gradually from 3 to 4 μV/K as the temperature decreases from 300 to 120 K and then a little more rapidly to a peak of 7 to 8 μV/K before dropping precipitously at ~40 K, close to the Peierls transition.[49] Since the lattice constant along the stacking direction is slightly larger than that for TTF-TCNQ, it is expected that ϵ_0 for the TCNQ chain in TSeF-TCNQ is slightly smaller; it was taken rather arbitrarily as 5640 K. From a number of kinds of data,[49,46] ϵ_0 for TSeF is expected to be substantially larger than ϵ_0 for TTF. If the ratio of TSeF to TCNQ bandwidths is chosen as it was by Etemad *et al.*,[49] ϵ_0 of TSeF comes out ~6000 K. Calculations were done for this value as well as 7000 K. The frequencies ω_{2k_F} were taken the same for TSeF-TCNQ as for TTF-TCNQ since the effect of the larger mass of Se is offset by the charge transfer being larger in TSeF-TCNQ, 0.63 vs 0.59. It has been estimated that, due to the larger mass, the frequencies for the internal modes should be ~10% smaller for TSeF than TTF, but the effect of these modes is small enough overall so that the correction was not considered worth making.

Unfortunately there is no good estimate for the intrinsic conductivity of TSeF-TCNQ. Since values of ~800 ohm^{-1} cm^{-1} have been measured, that is a lower limit. Extensive efforts to obtain purer, more perfect crystals have not been made for this material as for TTF-TCNQ. If the deformation potential constants for both chains were to have the values listed in Table II, an increase in ϵ_0 of the donor chain from 3000 to 6000 K would increase its contribution to σ by a factor 4. Since, as seen earlier, TTF provided only $\frac{1}{5}$ of the conductivity of TTF-TCNQ, this increase in the donor chain contribution would make σ of TSeF-TCNQ 1.5 times σ of TTF-TCNQ (allowing for a 10% decrease due to the decrease in TCNQ bandwidth). The intrinsic σ of TSeF-TCNQ would then be ~1200 ohm^{-1} cm^{-1}. It will not be that high, however, if, as argued by Schultz,[50] the deformation potential for acoustic modes is larger for TSeF than TTF.

With an uncertainty of perhaps a factor 1.5 in the intrinsic σ, the detailed numerical values obtained to fit a given σ are not particularly significant. As for the case of TTF-TCNQ there is no problem in fitting σ for any value in the range that the intrinsic value must lie in, with reasonable parameters, and the resulting resistivity is quasilinear in T, as was found experimentally also for TSeF-TCNQ.[51] One useful conclusion does emerge from this exercise, however. Whatever the value of σ, for bandwidths of 6000 and 5640 K it is possible to obtain Q small and positive, varying little with temperature above the Peierls transition temperature, provided the deformation potential constants are chosen smaller for TSeF than for TCNQ. If they are actually larger, then the bandwidth of TSeF must be substantially larger than that of TCNQ, i.e., the ratio must be greater than 6000 : 5640. A larger bandwidth for TSeF is consistent with the low value of magnetic susceptibility at room temperature, ~$\frac{1}{2}$ that of TTF-TCNQ.[52]

E. Pressure dependence

We consider in this section how to account for the strong pressure dependence of σ in these materials, 25–28%kbar for TTF-TCNQ,[53] ~18%/kbar for TSeF-TCNQ,[54] at 300 K. One quantity that clearly gives rise to pressure dependence is the bandwidth, which may be taken to vary 2.5%/kbar according to the discussion of Sec. III A. With σ having been shown proportional to ϵ_0^2 for all the processes we consider, this leads to an increase in σ of 5%/kbar. External phonon frequencies vary considerably with pressure in organic crystals, typically 4% to 6%/kbar in anthracene, naphthalene,[55] and pyrene,[56] with the larger percentage applying to the lower frequencies. It has been argued that TTF-TCNQ should not be compared to these materials because of the charge transfer and its metallic nature. However, the elastic and anharmonic properties exhibited by TTF-TCNQ are entirely usual for a molecular crystal. Its compressibility and expansivity, and their anisotropies, are quite comparable to those of anthracene, naphthalene, and pyrene.[57] Further, according to neutron scattering data,[14] for $q \simeq 2k_F$, ω of the TA(a^*) phonon increases by ~20% as T decreases from 295 to 84 K. With the known compressibility, this temperature decrease is equivalent to ~5 kbars of pressure. Thus ω for TA(a^*) increases ~4%/kbar and it is reasonable to expect such behavior at room temperature for other external modes with comparable frequencies. For 1p scattering, where $\sigma \propto \omega^2$, this gives an increase of ~8%/kbar, while for 2p scattering, with $\sigma \propto \omega^4$, there would be an increase of ~16%/kbar. Additional small contributions from the charge transfer, b, and internal-mode frequencies add up to a few %/kbar. Thus one can account quite well for the full 18%/kbar observed for TSeF-TCNQ with perhaps a small amount of 2p scattering. The origin of the additional 7% to 10% observed for TTF-TCNQ is not clear. Possibly there is a greater percentage of 2p processes in TTF-TCNQ, although this is quite unlikely to account for all of the difference. Some of the difference could well arise from the smaller bandwidth of TTF. Evidence that pressure decreases the ratio $\sigma_{\mathrm{TCNQ}}/\sigma_{\mathrm{TTF}}$ comes from the rapid decrease of the Hall constant under pressure[42] as well as the decrease of $|Q|$ under pressure.[58] Note that for the same value of $\partial\epsilon_0/\partial u$ the percentage changes in ϵ_0(TTF) and σ_{TTF} are larger because ϵ_0(TTF) $< \epsilon_0$(TCNQ). One may speculate that the increase in ϵ_0 of TTF under pressure has an enhanced effect on its contribution to σ due to increasing coherence of transport on this chain, or due to decrease in the effect of U, which, as mentioned earlier, may not be negligible in such a narrow band.

IV. TWO-LIBRON THEORY

As discussed earlier, of the theories that have been advanced to account for transport in TTF-TCNQ at temperatures well above the Peierls transition, the only one still a serious contender beside the theory presented in this paper is the two-libron theory. That theory is similar to the present one in being based on band transport of weakly interacting electrons that are scattered by phonons. The major difference is that the only scattering process considered effective is two-phonon scattering, whereas in the theory of this paper one-phonon scattering is taken to be predominant.

The two-libron theory first appeared before it was appreciated that the $T^{2.3}$ dependence of ρ is in large part due to volume expansion rather than "intrinsic" T dependence arising from the scattering mechanism. Assuming that the librational motion takes place about inertial axes, as was illustrated in Fig. 1, and recognizing that the matrix elements for 1p processes would vanish for the η and ζ rotations, the proponents of this theory postulated that the scattering was due to one or other of these branches. When it was subsequently pointed out that the resistivity at constant volume is quasilinear,[9,10] the two-libron theory adherents took the position that, since $\rho_{2l} \propto T^2/\omega^4$, a substantial increase in ω at constant volume occurs to cancel out the excess T dependence of ρ_{2l}. This was backed up with a calculation of ω based on the assumption that it is determined by a force constant derived from a Lennard-Jones potential with a single intermolecular distance parameter.[59] From this calculation they concluded[60] that for T rising from 60 to 300 K, ω would increase 20% at constant volume, while it decreases 25% at ambient pressure. The net change in ω then as T goes from 60 to 300 K would be a decrease of 5%.[60] This is in disagreement with the finding, mentioned in Sec. III, that ω for the TA(a^*) mode decreases ~20%. Further, it is in disagreement with the behavior of anthracene, naphthalene, and pyrene, for which the change in ω at constant volume is much less than that at constant pressure.[57] To counter the latter argument, Weger *et al.* (WGK),[61] agreeing that TTF-TCNQ should be compared with these organics, claimed that the comparison should be made at 10–12 kbar of pressure, where the compressibility of TTF-TCNQ matches that of anthracene and naphthalene. This argument is totally unconvincing. The measured ratio of expansivity to compressibility for TTF-TCNQ equals that for pyrene *at ambient pressure*.[57] Thus it would be even more appropriate to compare TTF-TCNQ with pyrene at ambient, which, as noted above, shows a much smaller change in ω with T at constant volume than is required to account for the quasilinear ρ_v.

As has been demonstrated in the body of this paper, scattering by 1p processes can account for σ for ~$100 < T < 300$ K with quite reasonable values of the deformation potentials and other parameters. It is therefore necessary for the two-libron theory adherents to explain how 1p processes can be ineffective in scattering. In earlier work,[62] they postulated that this is the case because the interaction between carriers and $2k_F$ phonons is so strong that momentum lost by carriers to these phonons is returned to the carriers before it can be dissipated in phonon-phonon scattering. More recently,[60] for $T>150$ K they hypothesize that the relative ineffectiveness of 1p processes is due to their weaker coupling to the carriers. They estimate that at 300 K the scattering frequency for a 1p process is 3×10^{14}/sec while that for a 2p process is 3×10^{15}/sec.[60] The scattering times, which are the reciprocals of these frequencies, are then 3×10^{-15} and 3×10^{-16} sec, respectively. Insertion of the latter time into the Uncertainty Principle gives an uncertainty in energy of 2 eV, several times the bandwidth; this estimate for the 2p scattering rate is clearly much too large. The estimated 1p scattering time, on the other hand, is in good agreement with the value obtained in Sec. III C. It thus helps support the thesis that 1p scattering is predominant, rather than the reverse.

Finally, the ζ librons, as noted earlier, have been found to have much higher frequencies, in the range 85–125 cm^{-1}, than the 40–70 cm^{-1} expected.[60, 62] This would greatly decrease their scattering effect in 2p processes, where $\sigma \propto \omega^4$.

V. SUMMARY AND CONCLUSIONS

Based on a simplified model in which one type of molecular motion—a translation or a rotation—is associated with each external branch, scattering rates for one- and two-phonon processes have been determined for electrons in a quasi-one-dimensional tight-binding band. A relaxation time $\tau(k)$ is shown to exist for scattering by one translon, one libron, or one internal-mode phonon. For elastic scattering $\tau(k)$ involves simply the rate of scattering out of k, but for inelastic scattering, in the degenerate case, there is also a factor arising from the Pauli Principle. For internal modes the matrix element is independent of carrier energy, leading to τ inversely proportional to the density of final states. This latter factor causes τ for both emission and absorption to be a strongly varying function, going to zero at the energies for which a 1p process will take an electron to a band-edge state. For the $1t$ and $1l$ cases the electronic part $|g|^2$ of the square of the matrix element is proportional to v_F^2/ω_{2k_F}, the latter factor coming from the amplitude of oscillation of the molecules. Phonon abundance (i.e., n_q or n_q+1) under equipartition contributes another factor of $1/\omega_{2k_F}$ to the matrix element. For the $1t$ case with the usual dispersion, $\omega_{2k_F} \propto v_F$, the matrix element is again energy independent and the sole energy dependence of τ_{1t} comes from the inverse of the density of final states. Since the translon scattering has been assumed elastic, this means $\tau_{1t} \propto v_F$ and goes to zero only for $\epsilon=0$ or $\epsilon=\epsilon_0$. For the $1l$ case, on the other hand, dispersion is probably small and ω_{2k} does not cancel out the ϵ dependence of v_F. If the dispersion is neglected, $\tau_{1l} \propto v_F^{-1}$ or, in other words, there is a constant mean free path for $1l$ scattering. For the elastic scattering 1p cases the expressions for σ and Q, obtained from the solution of the Boltzmann equation, can be integrated explicitly. It is found that σ is proportional to ϵ_0^2, as it is also for the internal-mode case, and to $\omega_{2k_F}^2$. It is inversely proportional to the square of the appropriate deformation potential and also to T. For the $2l$ case $\sigma \propto \omega^4\epsilon_0^2/T^2$ and depends also on $k_F b$ in a complicated way. As in the three-dimensional case, Q is found proportional to a sum of energy derivatives of $\log(v^2\rho)$ (band term) and $\log\tau$. The two terms are equal and add in the $1t$ case, but subtract in the dispersionless $1l$ case, leaving $Q=0$ for that case. In the former case Q depends only on T/ϵ_0 and ϵ_F/ϵ_0.

In TTF-TCNQ, as distinguished from the simplified model, it is not possible (except perhaps for high symmetry points of the Brillouin zone) to associate any particular external branch of the lattice vibration spectrum with either translations or rotations, much less with translations or rotations associated with a particular axis. As a consequence it is not possible to say definitely that any particular branch gives rise to only 1p or 2p processes. In fact the TA(a^*) and TA(c^*) branches appear to be mixed, which means that both would give rise to both processes. On the assumption that mixing effects are not important for the LA branch, which does show the expected dispersion, its deformation potential was taken as that obtained from band-structure calculations and some experiments. It is then possible, given the intrinsic resistivity, to determine the deformation potential for 1p scattering from all other branches lumped together. The latter deformation potential is found to be of the order of that taken for LA, 0.2 eV/Å. That and the observed quasilinear temperature dependence of ρ_v give strong support to the thesis that 1p scattering can account for most of the resistivity of TTF-TCNQ in the range 100 or 150 to 300 K. Using the minimum values of deformation potentials for LA and TA modes consistent with pressure experiments I conclude that these modes plus the internal modes account for at least $\frac{1}{2}$ the scattering at 300 K. To fit thermopower as well as conductivity requires $\sigma_{\mathrm{TCNQ}} \simeq 4\sigma_{\mathrm{TTF}}$. With deformation potentials taken the same for the two chains this requires a 2 : 1 ratio of bandwidths. To get a smaller ratio of bandwidths would require larger deformation potentials for TTF than TCNQ, whereas such evidence as there is points to the reverse. With such a small σ for TTF, the use of simple perturbation theory is not well justified at room temperature, but the justification improves with decreasing temperature.

Conductivity and thermopower of TSeF-TCNQ can be fitted with similar deformation potentials. It is noteworthy that, to obtain the observed small and positive Q, if coupling to acoustic modes is larger for TSeF than for TTF, as has been suggested by Schultz, the bandwidth of TSeF must be more than twice that of TTF. This could help explain the small susceptibility observed for TSeF-TCNQ. The pressure dependence of the conductivity of TSeF-TCNQ is well accounted for by changes in bandwidth and in the frequencies of the external modes, plus some smaller effects. The larger pressure dependence observed for TTF-TCNQ, it is suggested, is attributable to changes associated with the very narrow TTF band.

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