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Thermoelectric power of 1:2 tetracyanoquinodimethanide (TCNQ) salts

Esther M. Conwell
Xerox Webster Research Center, Webster, New York 14580

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A distinctive feature of a number of 1:2 tetracyanoquinodimethanide (TCNQ) salts, such as triethylammonium-(TCNQ)$_2$ [TEA-(TCNQ)$_2$], quinolinium-(TCNQ)$_2$, and acridinium-(TCNQ)$_2$ is a constant thermopower $Q \simeq -60$ μV/K over a wide temperature range, $\gtrsim 100$ K, along the highly conducting or TCNQ chain direction. These salts are characterized by ρ, the fraction of filled sites on the TCNQ chain $\simeq 1/2$. Past calculations of Beni *et al.* have shown that the extended Hubbard model with very strong on-site Coulomb repulsion and zero bandwidth can account for the magnitude and temperature variation of Q for quinolinium-(TCNQ)$_2$ and acridinium-(TCNQ)$_2$. I discuss the approximation of zero bandwidth and conclude that it is not justifiable. I then show that a near-constant value close to -60 μV/K for temperatures $\gtrsim 100$ K can be obtained using a model (although not the extended Hubbard model) with two bands having nearly identical widths and scattering times and retaining the feature of very strong on-site repulsion. Near identity of the two bands is reasonable for $\rho \simeq 1/2$. This model can also account for the magnitude and temperature variation of the conductivity of these salts over the same large temperature range.

It was first pointed out by Buravov *et al.*[1] that, although the temperature variation of the thermopower is usually quite different from one TCNQ salt to another, the 2:1 salts quinolinium (TCNQ)$_2$, acridinium-(TCNQ)$_2$, and 3,3-diethylthiazolinocarbocyaninium-(TCNQ)$_2$ [DTC-(TCNQ)$_2$] are similar in showing an approximately constant $Q \simeq -60$ μV/K from $T \lesssim 300$ K down to $T \gtrsim 100$ K in the first two cases, to ~200 K in the third case. Below this temperature the magnitude of Q falls off, quite rapidly in the two former cases, although remaining negative. In Fig. 1 we show Q vs T of quinolinium-(TCNQ)$_2$, representative of this group. Similar behavior has been found for N-methylquinolinium-(TCNQ)$_2$.[2] For triethylammonium-(TCNQ)$_2$ [TEA-(TCNQ)$_2$],[3] and N, N, N′, N′-tetramethyl-*p*-phenylenediamine-(TCNQ)$_2$ [TMPD-(TCNQ)$_2$],[4] Q is also observed to be essentially constant at -60 μV/K from ~300 down to ~150 K, but then, in contrast to the behavior of the compounds mentioned earlier, it grows more negative below 150 K. The data for TEA-(TCNQ)$_2$ are shown in Fig. 1. It is usually assumed that each cation has a full positive charge in these materials which leads to $\rho = \frac{1}{2}$. If all the TCNQ's were equivalent, on a simple band model these compounds would be metallic with quarter-filled bands. In the case of TEA-(TCNQ)$_2$, x-ray studies[5] show, however, that the TCNQ chain is a linear chain of dimers with two different, alternating, interdimer spacings. The repeat unit is then four TCNQ units, with two electrons per tetrad, which leads to a band structure with a gap at the quarter-filled band position, making the material an insulator at $T = 0$ K.[6] X-ray studies are available for some of the other compounds mentioned above, e.g., quinolinium-(TCNQ)$_2$,[7] and acridinium-(TCNQ)$_2$.[8] They show all TCNQ's to be equivalent in these compounds, at least to the precision of these x-ray measurements.

The Hubbard model has been used extensively in studies[8a-14] of the thermopower for TCNQ salts. It was assumed that all TCNQ sites are equivalent so that, in the absence of correlations, the electrons occupy one fourth of the states in the band. Kwak and Beni[13] were able to fit quinolinium-, acridinium-, and DTC-(TCNQ)$_2$ data with Q calculated from an extended Hubbard model with infinite on-site repulsion U for a second electron, zero band-

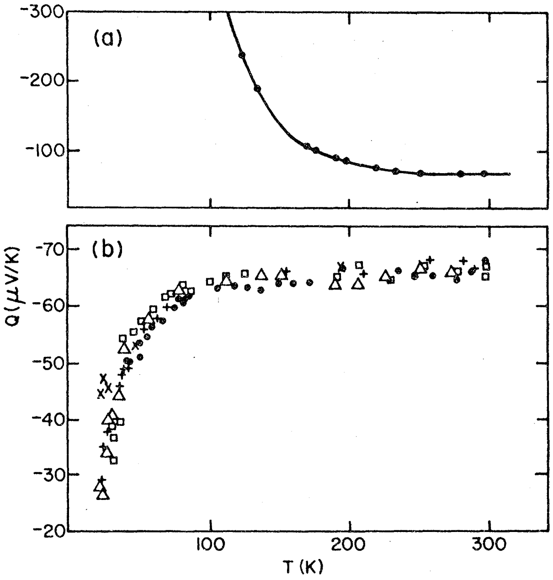

FIG. 1. Thermopower vs temperature for (a) TEA-(TCNQ)$_2$ (from Ref. 3) and (b) quinolinium- (TCNQ)$_2$ (from Ref. 11).

width, and incomplete charge transfer. The assumption of zero bandwidth cannot, however, be justified, as will be detailed. Furthermore, it is not clear how this model could account for other properties, notably conductivity variation with temperature, of these materials. In this paper I show that the behavior of the thermopower can be accounted for by a model which retains the feature of infinite on-site repulsion and has electrons and holes in bands of nonzero width. This model also leads to good quantitative fits to conductivity versus temperature for these materials.

Let us begin with a brief description of the calculations of Kwak and Beni.[13] The Hamiltonian that was used for the calculations is

$$H=U\sum_{l}\eta_{l\uparrow}\eta_{l\downarrow}+V\sum_{l}\eta_{l}\eta_{l+1}-t\sum_{l,\sigma}(c^{\dagger}_{l,\sigma}c_{l+1,\sigma}+\text{H.c.})\,, \tag{1}$$

where U and V are the on-site and nearest-neighbor Coulomb interactions, respectively; t is the nearest-neighbor tight-binding transfer integral; $c^{\dagger}_{l,\sigma}$ $(c_{l,\sigma})$ creates (destroys) an electron of spin σ at the lth site; $\eta_{l\sigma}=c^{\dagger}_{l\sigma}c_{l\sigma}$ is the corresponding number operator; $\eta_l=\eta_{l\uparrow}+\eta_{l\downarrow}$.[13] The assumption $U=\infty$ (strong-coupling limit) was made throughout to simplify the calculations. It is instructive to consider first, as was done in Ref. 13, the case $V=0$ and $t\neq 0$, i.e., nonzero bandwidth. In this case the band is split in two by the large U and the carriers are all in the lower Hubbard band.[14] With $V=0$ the Hamiltonian (1) can be transformed into that for the tight-binding model and the thermopower expressed in terms of that for an ordinary (i.e., uncorrelated) tight-binding band, Q_0.[11] Q_0 was evaluated on the arbitrary assumption that the carriers form a degenerate gas with a scattering time τ independent of energy. For $\rho=\frac{1}{2}$ this leads to the prediction of a constant thermopower $-60\ \mu V/K$ for all temperatures, which is in disagreement with experiment at low temperatures. No value of ρ led to Q vs T for this model in agreement with the experimental data at low temperatures. From this Kwak and Beni concluded that $V\neq 0$, i.e., off-site correlations must be taken into account. This they were able to do for $U=\infty$ and $t=0$, or zero bandwidth. They found that a fit to the experimental data for quinolinium-, acridinium-, and DTC-(TCNQ)$_2$ over the entire temperature range could be obtained for $\rho\lesssim\frac{1}{2}$ and $V\sim 100$ K, within 10%. It should be noted that these calculations do not apply to TEA- or TMPD-(TCNQ)$_2$. According to Fig. 5 of Ref. 13, to account for $|Q|$ increasing, as it does in these latter two compounds, rather than decreasing at low temperatures, would require $\rho>\frac{1}{2}$. Since the extra electrons cannot come from the cations, they must come from donor impurities or defects. The presence of donor levels would affect the location of the Fermi energy, and through that the thermopower, particularly at low temperatures. Since they were not taken into account, the calculations of Ref. 13 do not apply to TEA- or TMPD-(TCNQ)$_2$. [Of course, they would not apply to TEA-(TCNQ)$_2$ in any case since it has a gap at the $\frac{1}{4}$ band level due to lattice periodicity.] As a corollary, if the $\rho<\frac{1}{2}$ required to obtain the correct low-temperature behavior of Q for quinolinium-(TCNQ)$_2$, etc., were due to acceptor impurities or defects, the calculations would not be valid for those cases either.

In considering the significance of the above results, it is useful to remember the definition of Q:

$$Q=w/Tj\,, \tag{2}$$

where w and j are the energy ϵ (measured relative to ϵ_F, the Fermi energy) and charge, respectively, transported across unit area in unit time. If ϵ_F is outside the band, as is generally true in the Kwak and Beni calculations, it is convenient to split $\epsilon-\epsilon_F$ into two parts, i.e.,

$$\epsilon-\epsilon_F=(\epsilon_b-\epsilon_F)+(\epsilon-\epsilon_b)\,, \tag{3}$$

where ϵ_b denotes the band edge. Corresponding to these two parts there are two terms in the thermopower. For the first term on the right-hand side the integrals involved in w and j differ only by a constant factor, so that the thermopower may be written

$$Q=\mp\frac{k_B}{|e|}\left(\frac{|\epsilon_b-\epsilon_F|}{k_BT}+\frac{|\Delta\epsilon_T|}{k_BT}\right), \tag{4}$$

where k_B is the Boltzmann constant and e is the electronic charge; the upper sign is for electrons, the lower is for holes. The term $|\Delta\epsilon_T|$ represents a weighted average of the energy transported per carrier (across unit area in unit time) relative to the band edge. It was evaluated by Kwak and Beni for the materials we are interested in using the Kubo formalism.[13]

Neither of the terms in (4) is well estimated under the approximation of zero bandwidth used in Ref. 13. Consider the first term; the approximation $t=0$ should be all right when ϵ_F is many k_BT from the band edge and the bandwidth ϵ_0 is small compared to k_BT.[10,12] The first condition is not satisfied at any temperature for the calculations of Ref. 13. From Eq. (30) of this reference we find, for $\rho=\frac{1}{2}$, $\epsilon_F-\epsilon_b=V-k_BT\ln 2$. With $V\simeq 100$ K, at most temperatures in the range of the fit $\epsilon_F-\epsilon_b<k_BT$, and nowhere is it large compared to k_BT. The bandwidth is, of course, not well known for these materials but there is no reason to think

it small compared to k_BT. Kwak and Beni[13] apparently consider $t = 240$ K a reasonable estimate, which makes the width of the lower band 480 K, certainly larger than k_BT over the entire temperature range concerned. Thus the approximation $t = 0$, in finding the location of ϵ_F, is certainly not justified.

Since the second term on the right-hand side of (4) represents a weighted average of the energy of a carrier relative to the band edge, the conclusion appears inescapable that this term is underestimated by calculating in the zero bandwidth limit. For example, for $\rho \ll 1$ this average energy should be $\sim\frac{1}{2}k_BT$ for the bandwidth $\epsilon_0 \gtrsim k_BT$. That would make this term as large as or larger than $(\epsilon_F - \epsilon_b)/k_BT$ for $T < 100$ K in the case we have been discussing. If $\rho \simeq 1$ the average $\epsilon - \epsilon_b$ would be higher, bandwidth permitting. The effect of correlations, introduced by taking U, $V \neq 0$, is clearly to push carriers up to higher energy levels than they would otherwise occupy. Another inaccuracy that stems from the use of $t = 0$ is the loss of the dependence of $\Delta\epsilon_T$ on the details of the scattering. This occurs because in a band of zero width all states have the same probability of occupancy. The effect of the dependence on the scattering is not minor. To get an idea of its order of magnitude, consider the situation that a scattering relaxation time τ exists such that $\tau \propto |\epsilon - \epsilon_b|^\nu$, where ν is independent of temperature. For the three-dimensional case with Maxwell-Boltzmann statistics, Herring[15] has noted that $|\Delta\epsilon_T|/k_BT = \frac{5}{2} + \nu$. As ν ranges from $-\frac{1}{2}$ for lattice scattering to $+\frac{3}{2}$ for impurity scattering, $|\Delta\epsilon_T|/k_BT$ varies from two to four. It is noteworthy that, over the entire range of ν, $|\Delta\epsilon_T| > \frac{3}{2}k_BT$ as a result of a weighting factor v^2, v being the carrier speed, in the integrand. For the degenerate 1-dimensional (1-D) case we obtain from Eqs. (5) and (6) of Ref. 11, for $\tau \propto |\epsilon - \epsilon_b|^\nu$,

$$Q = -\frac{\pi^2 k_B{}^2 T}{3|e|}\left(\frac{1}{2(\epsilon_F - \epsilon_b)} + \frac{\nu}{\epsilon_F - \epsilon_b}\right). \tag{5}$$

A similar expression for Q is obtained from Eqs. (5) and (7) of Ref. 11, with $\epsilon_F - \epsilon_b$ replaced by t, for the degenerate 1-D tight-binding case with $\rho = \frac{1}{2}$. It is apparent that a similar range in ν, $-\frac{1}{2} < \nu < \frac{3}{2}$, causes great changes in Q for these 1-D cases. Note that the term $\Delta\epsilon_T$ vanishes for $\nu = 0$ only in the case of complete degeneracy, where the averaging is not carried out over the distribution. For $T \neq 0$, particularly for a narrow band, averaging over the distribution is necessary[16] and $\Delta\epsilon_T$ will not vanish even for $\nu = 0$. The optical-mode scattering, with which we have accounted for the mobility in tetrathiafulvalenium-tetracyanoquinodimethanide (TTF)-(TCNQ),[16] N-methylphenazinium-tetracyanoquinodimethanide (NMP)-(TCNQ),[17] quinolinium- and acridinium-$(\mathrm{TCNQ})_2$,[18] is strongly energy dependent because, for one thing, the ability of an electron to emit an optical phonon is strongly energy dependent. The dependence of τ on ϵ cannot, however, be written as a simple power law.[16]

We conclude from the above discussion that calculations of Q based on $t = 0$ are not to be relied on. Nevertheless, Refs. 8a–13 demonstrate clearly that a large on-site Coulomb repulsion has a significant effect on the thermopower. As is made most evident perhaps, by Chaikin and Beni,[12] a major source of the dependence of Q on correlation is the effect of correlation on the location of the Fermi energy. It is also pointed out by these authors[13] that U should be large for the 2:1 salts, larger than for the simple salts where there is a higher proportion of polarizable cations.

I show now that a constant $Q \simeq -60$ μV/K over a wide range is naturally obtained with a model in which there are strong on-site correlations, $U \gg k_BT$, although $V \ll k_BT$, and conduction electrons and holes in two similar bands of nonzero width. Conduction by both electrons and holes was suggested by Farges and Brau[6] for TEA-$(\mathrm{TCNQ})_2$ since the Hall constant[19] and Q in one of the directions transverse to the TCNQ chain were found to be positive.[3] It of course arises quite naturally in TEA-$(\mathrm{TCNQ})_2$ since, as noted earlier, x-ray analysis leads to a gap at the highest level that would be filled at $T = 0$. This gap is somewhat greater than k_BT over the temperature range of concern here. We have assumed in discussing the mobility[18] that a similar gap exists in the other $\rho = \frac{1}{2}$ materials under discussion. Its possible origin will be discussed later. Since we have assumed $V \ll k_BT$, it is not the gap that arises in the extended Hubbard model. (If $V \gg k_BT$, as shown by Chaikin and Beni,[12] a high-temperature $Q = -60$ $\mu V/K$ for $\rho = \frac{1}{2}$ will not result.) As was noted earlier, the case $U = \infty$, $V = 0$, and t arbitrary has been considered by Kwak and Beni.[13] They find, for $\rho < 1$, that the probability of occupation $f(\epsilon)$ of a state with energy ϵ is given by

$$f = (1 + \tfrac{1}{2}e^{(\epsilon - \epsilon_F)/k_BT})^{-1}. \tag{6}$$

This result was also obtained by Lewis[20] for the case $t = 0$. The distribution (6) differs from the Fermi-Dirac one in the factor $\frac{1}{2}$, which arises from the fact that, although there are two spin directions, the states may only be singly occupied. (This follows from the restriction to single occupation of sites. Two electrons in the same state would have the identical probability distribution over the sites.) The location of the Fermi energy is obtained from the condition that the number of electrons per unit length along the chain η_l equals

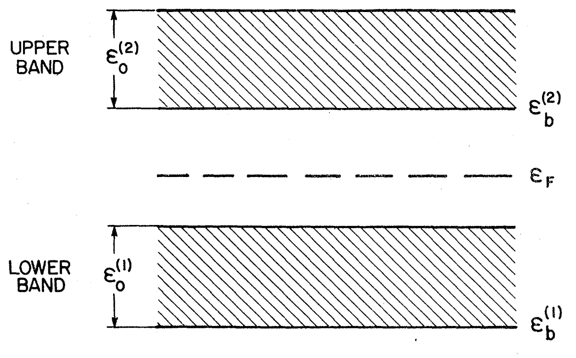

FIG. 2. Energy-level diagram of two-band model.

the number of holes per unit length p_l. Referring to Fig. 2, we may write

$$\eta_l = \int_{\epsilon_b^{(2)}}^{\epsilon_b^{(2)}+\epsilon_0^{(2)}} f(\epsilon)\frac{\rho_2(\epsilon)}{L}\,d\epsilon \tag{7a}$$

$$p_l = \int_{\epsilon_b^{(1)}}^{\epsilon_b^{(1)}+\epsilon_0^{(1)}} [1-f(\epsilon)]\frac{\rho_1(\epsilon)}{L}\,d\epsilon\,, \tag{7b}$$

where the density of states in the ith band is given by

$$\rho_i(\epsilon)/L = (2\pi a)^{-1}[(\epsilon-\epsilon_b^{(i)})(\epsilon_0^{(i)}+\epsilon_b^{(i)}-\epsilon)]^{-1/2}\,, \tag{8}$$

a being the lattice spacing. The factor 2 in $\rho_i(\epsilon)$ reflects the fact that only $\frac{1}{4}$ of the states are in either of the two bands of concern here. For the determination of ϵ_F it is unimportant what this factor is, however, since it is the same for each of the two bands. We consider the limiting case in which the gap ϵ_G is large enough so that η_l and p_l are small, and

$$\begin{aligned} &e^{(\epsilon_F-\epsilon)/k_BT} \gg 1 \quad \text{for the lower band}\,,\\ &e^{(\epsilon-\epsilon_F)/k_BT} \gg 1 \quad \text{for the upper band}\,. \end{aligned} \tag{9}$$

This is equivalent to the Maxwell-Boltzmann limit for Fermi-Dirac statistics. In this case we find from Eqs. (6)–(8) that

$$\eta_l = (\pi a)^{-1}F(\epsilon_0^{(2)})\exp[(\epsilon_F-\epsilon_b^{(2)})/k_BT]\,, \tag{10a}$$

$$p_l = (4\pi a)^{-1}F(\epsilon_0^{(1)})\exp[(\epsilon_0^{(1)}+\epsilon_b^{(1)}-\epsilon_F)/k_BT]\,, \tag{10b}$$

where

$$F(\epsilon_0) \equiv \int_0^{\epsilon_0} e^{-\epsilon/k_BT}[\epsilon(\epsilon_0-\epsilon)]^{-1/2}\,d\epsilon\,. \tag{11}$$

Equating (10a) and (10b) we find

$$\epsilon_F = \frac{\epsilon_b^{(1)}+\epsilon_0^{(1)}+\epsilon_b^{(2)}}{2} - k_BT\ln 2 + \frac{k_BT}{2}\ln\frac{F(\epsilon_0^{(1)})}{F(\epsilon_0^{(2)})}\,. \tag{12}$$

In the symmetric case $\epsilon_0^{(1)}=\epsilon_0^{(2)}$, ϵ_F lies below midgap by $k_BT\ln 2$. This term arises, of course, from the $\frac{1}{2}$ in Eq. (6).

To calculate the thermopower when there are both electrons and holes present, with concentrations n and p, mobilities μ_n and μ_p, thermopowers Q_n and Q_p, respectively, we use

$$Q = (Q_n n\mu_n + Q_p p\mu_p)/(n\mu_n + p\mu_p)\,. \tag{13}$$

In the symmetric case that the two bands have the same width and scattering processes, (13) goes to

$$Q = \tfrac{1}{2}(Q_n + Q_p)\,. \tag{14}$$

Using (4) we then obtain

$$Q = \frac{k_B}{2|e|}\left(-2\ln 2 + \frac{|\Delta\epsilon_T|_p}{k_BT} - \frac{|\Delta\epsilon_T|_n}{k_BT}\right)\,. \tag{15}$$

If the widths and scattering processes for the two bands are the same, as was assumed to obtain (14), then $|\Delta\epsilon_T|_p = |\Delta\epsilon_T|_n$ and $Q=-k_B/|e|\ln 2 = -60$ μV/K. I have shown, therefore, that a constant thermopower -60 μV/K is obtained when conduction is by equal numbers of electrons and holes occupying narrow bands with on-site repulsion $U \gg k_BT$ and symmetric in the sense that the bandwidths and mobilities are the same. *This result does not rely on any assumptions about transport in highly correlated bands; it is also independent of the detailed form of* $\rho(\epsilon)$. With $\rho \simeq \frac{1}{2}$, it is not unlikely, as will be discussed later, that the electron and hole bands will have the desired symmetry. Small departures from total symmetry in the numbers of electrons and holes, bandwidths, or scattering processes can account for the small differences from -60 μV/K observed in the high-temperature range in these compounds. The steep drop in $|Q|$ observed at low temperatures for quinolinium-(TCNQ)$_2$, etc., (see Fig. 1) can be attributed to the presence of residual holes arising either from incomplete transfer or from acceptor levels provided by impurities or defects. Similarly, I postulate the presence of residual electrons due to donor levels to account for the sharp increase in $|Q|$ found at low temperatures in TEA-(TCNQ)$_2$. In either case, as T decreases below 300 K, both n and p decrease. The -60 μV/K value can be maintained, however, until the carrier concentration becomes comparable to the concentration of residual electrons or holes, as the case may be. When the temperature is lowered beyond this point, the location of ϵ_F changes and the behavior of Q is determined, according to Eq. (4), by the residual electrons or holes. The fact that the resistivity gets very high and the measurements too difficult to make before Q becomes positive in the quinolinium- and acridinium-(TCNQ)$_2$ cases[11] I attribute to the residual holes occupying band-edge states that are localized by disorder,[18] specifically the random orientation of the cations.

We have been successful in accounting in detail for the conductivity variation with temperature in several of the salts that are the subject of this paper with the same two-band model except that correlations were neglected.[18] I shall show now that the introduction of strong on-site correlations should not alter the good fit to the experimental data. In Ref. 18 we calculated the carrier concentrations from Eq. (7) using Fermi-Dirac statistics. With the conditions (9) satisfied and ϵ_F at midgap, where it would be for symmetric bands with no correlation, this leads to

$$\eta_t = e^{-\epsilon_G/2k_BT} \int_0^{\epsilon_0} e^{-\epsilon/k_BT} \frac{\rho_2(\epsilon)}{L}\, d\epsilon \,. \tag{16}$$

It is easily seen that the identical result is obtained from (7a) in the limit (9) when f and ϵ_F are taken from (6) and (12), respectively. Thus if the same $\rho(\epsilon)$ is used for the correlated and uncorrelated cases, the same $\eta_t(T)$ and $p_t(T)$ result.[21] The mobility was obtained in this model, for quinolinium- and acridinium-$(TCNQ)_2$ specifically,[18] from the scattering by optical phonons derived from the molecular vibrations. As noted earlier, this mechanism accounts well for the mobilities in TTF-TCNQ[16] and NMP-TCNQ.[17] Although numerical calculations have not been done for TEA-$(TCNQ)_2$ it appears that its mobility, as well as that of many other 1-D compounds, should be well fit by the same model.[22] The fact that the peak in its conductivity has not yet been reached at 300 K is consistent with a larger gap than that found for the other salts mentioned. In Refs. 16–18 the mobility was calculated by solving the Boltzmann equation for carriers scattered by optical phonons in a simple tight-binding band with no account taken of correlations. Nevertheless, it is reasonable to expect it to be valid in the limit $U \to \infty$. From calculations in this limit Beni, Holstein, and Pincus[23] have concluded that, although the magnetic behavior is that of a set of localized spins, the kinetic effects correspond to the appropriate density of spinless, noninteracting fermions. Their calculations did not include the effect of phonons. Rice has recently considered the $U = \infty$ limit with phonons present and, following the arguments of Bernasconi *et al.*,[24,25] shown that the behavior as spinless noninteracting fermions occurs for arbitrary instantaneous intramolecular geometry.[26] Thus the presence of strong Coulomb interactions does not affect the kinetics of the carriers. It could still affect the mobility through its effect on the statistics, i.e., on the location of the Fermi energy. However, in the "Maxwell-Boltzmann" limit Eq. (9) the dependence of μ on ϵ_F drops out. As noted in Ref. 18, the approximation (9) is quite good for quinolinium- and acridinium-$(TCNQ)_2$, except perhaps close to 300 K for the latter.

We return now to the question of the origin of the gap in the compounds other than TEA-$(TCNQ)_2$. It is perhaps not possible to rule out, on the basis of x-ray diffraction data,[7,8] a gap at the quarter-filled band position arising from Peierls distortion in quinolinium-$(TCNQ)_2$ and acridinium-$(TCNQ)_2$. It is noteworthy that x-ray diffraction of TTF-TCNQ below the Peierls transition temperature (and taken after evidence for the transition had been obtained by diffuse x-ray scattering) showed no observable static lattice deformation associated with the changes in symmetry or cell doubling.[27] The size of the distortion would be expected to be smaller than that in TEA-$(TCNQ)_2$ in any case, since the gaps are smaller.[18] Also, the cation disorder referred to earlier makes accurate determination of the structure more difficult. Another possible origin for a gap at the quarter-filled band position in these salts is Coulomb coupling between charge-density waves on neighboring TCNQ chains.[18] This model, proposed by Woynarovich, *et al.*,[28] although similar in some respects to the Peierls distortion model, differs in that it allows a sizable gap to exist with relatively smaller distortion. Thus it would presumably be more difficult to detect by x rays than the Peierls distortion. With $\rho \simeq \frac{1}{2}$ either of the two mechanisms discussed in this paragraph, or their combination, would be expected to lead to the required symmetry between the electron and hole bands.

In summary, I have shown that the distinctive saturation at $-60\ \mu$V/K of the thermopower of a number of 1:2 TCNQ salts is well accounted for by conduction in two highly correlated symmetric bands formed by the opening of a gap at the quarter-filled band level. The same model, plus scattering by the optical phonons arising from molecular vibrations, explains also conductivity versus temperature over the range in which the thermopower saturation is observed, at least for the salts of this group whose conductivity has been studied quantitatively. The required energy gap is known from x-ray evidence to be present in TEA-$(TCNQ)_2$. X-ray evidence for a gap has not yet been found for the other compounds of this group.

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