(1975).
[10]S. Ciraci and I. P. Batra, Phys. Rev. B 15, 3254 (1977).
[11]E. E. Lafon and C. C. Lin, Phys. Rev. 152, 579 (1966); R. C. Chaney, T. K. Tung, C. C. Lin, and E. E. Lafon, J. Chem. Phys. 52, 361 (1970).
[12]J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).
[13]A. Liebsch, Phys. Rev. Lett. 38, 248 (1977).
[14]R. S. Mulliken, J. Chem, Phys. 33, 1833 (1955); I. P. Batra, S. Ciraci, and W. E. Rudge, Phys. Rev. B 15, 5858 (1977).
[15]K. Jacobi, M. Scheffler, K. Kambe, and F. Forstmann, Solid State Commun. 22, 17 (1977).

Mobility in Tetrathiafulvalene–Tetracyanoquinodimethane (TTF-TCNQ)

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I account for the magnitude and temperature dependence of the mobility of TTF-TCNQ in the range 150–300 K by scattering of the carriers by optical phonons derived from the symmetric molecular vibrations. The only adjustable parameters are the widths of the conduction bands on TCNQ and TTF chains, chosen as 3000 and 1500 K, respectively. I also obtain estimates of the coupling to acoustic phonons and the unbroken chain lengths by fitting conductivity data down to 70 K.

TTF-TCNQ first attracted attention because its conductivity is very high for an organic material. Recent reports, based on measurements at the University of Pennsylvania of many carefully prepared and mounted samples, give the room-temperature conductivity σ_{RT} as $660 \pm 130\ \Omega^{-1}\ \mathrm{cm}^{-1}$.[1] With decreasing temperature σ increases, reaching a peak σ_p at about 58 K, reported for some samples to be as high as $(100-150)\sigma_{RT}$.[1] From neutron-scattering studies it has been deduced that there is a charge transfer of $\rho = 0.59$ electrons from TTF to TCNQ.[2] With the carrier density n calculated from this, I deduce from $\sigma = ne\mu$ (where μ is mobility) that the sum of electron and hole mobilities, in $\mathrm{cm}^2/\mathrm{V\ sec}$, is 3 ± 1 at room temperature, and 300–450 at the peak. These values of μ and its temperature dependence are similar to those I have deduced recently for electrons along the TCNQ chain in *N*-methyl-phenazinium tetracyanoquinodimethane (NMP-TCNQ).[3] I have been able to account well for the magnitude and behavior above 60 K of μ in that case by the interaction of electrons in a tight-binding band with the molecular vibrations. Here I have succeeded in extending these calculations to TTF-TCNQ.

Different explanations have been offered for the magnitude and temperature dependence of σ above 58 K. One theory is that many-body collective effects are involved. Specifically, contributions to σ are supposed to arise from charge-density wave fluctuations which slide via time-dependent phases.[1] From a one-dimensional (1D) calculation, Lee, Rice, and Anderson found that fluctuations are important, reducing the Peierls-transition temperature T_P to about one-fourth the mean-field value, $T_P^{(0)}$.[4,5] This makes $T_P^{(0)} \simeq 250$ K for TTF-TCNQ. For $T_P < T < T_P^{(0)}$, they showed that the density of states $D(\epsilon)$ at the Fermi energy ϵ_F is reduced by 50% or more below $T_F^{(0)}/2$. More recently, however, Horovitz, Gutfreund, and Weger, by including the effect on T_F of interchain coupling, showed that, for TTF-TCNQ, fluctuations are *not* important and $T_P \simeq T_P^{(0)}$ as determined by a 1D calculation.[6] As a consequence, $D(\epsilon)$ and the conduction are not expected to show deviations from single-particle behavior until T is close to T_F, i.e., 54 K.

The evidence cited for a collective-mode contribution to σ is the strong dip observed in $\sigma(\omega)$ at low frequencies.[7] This has been interpreted as representing a gap or pseudogap of 1100 cm^{-1} (0.14 eV) in the density of states.[7] Since $\sigma(\omega)$ drops by more than an order of magnitude at 300 K, as well as at lower temperatures, it has been suggested that at the higher T's, rather than representing $D(\epsilon)$, "... the pseudogap in $\sigma(\omega)$ is in essence a mobility gap caused by the strong dynamic fluctuations ... below the mean-field temperature."[7] This is in conflict with the findings of Ref. 6 and even Ref. 5. It should be noted also that the dip in $\sigma(\omega)$ changes little from 300 to 5 K, where there is a real gap. From studies of photoconductivity, Eldridge[8] finds strong evidence that the peak at 1100 cm^{-1} is part of an absorption band that begins at $\sim 315\ \mathrm{cm}^{-1}$, the latter corre-

sponding to the Peierls gap.

Another mechanism proposed to account for the variation of σ with T above 58 K is electron-electron (e-e) scattering between electrons on TCNQ and holes on TTF.[9,10] The basis for this was the finding of Etemad *et al.* that their data, and some from other laboratories, could be fitted by a power law $\sigma^{-1}=\rho_0+\rho_2 T^2$ in the range 60–250 K.[9] The ratios σ_P/σ_{RT} for the samples in their study were $\lesssim 20/1$. In another study, including higher-quality samples as judged by values of σ_P/σ_{RT} as high as 35/1, Groff *et al.*[11] found a somewhat similar law for σ^{-1} in the range 60–300 K. However, the exponent of T was significantly higher than 2, ranging from 2.23 to 2.40 for different samples. All samples were well represented by $\lambda=2.33$. Thus e-e scattering cannot account for the observed T dependence. In fact, for a 1D case it leads to $\sigma^{-1}\propto T$, and there is some evidence that the criterion for one-dimensionality given in Ref. 10 *is* satisfied for TTF-TCNQ in the range of T concerned.[12] Apart from this, estimates of its possible importance[10] were inflated because the e-e collisions considered[13] were momentum-conserving ones. To affect σ the collisions must transfer momentum to either (1) the lattice, through unklapp processes, or (2) high-mass or low-μ carriers which contribute little to σ, as in the transition metals. As regard to (1), unklapp processes are expected to be much less frequent than momentum-conserving ones. This is particularly so for the present case where the maximum momentum change in an e-e collision is ~4 times the wave vector at ϵ_F, which for TTF-TCNQ is distinctly less than a reciprocal-lattice vector. Under mechanism (2) one might argue that the holes on TTF chains act like high-mass carriers to drain momentum from the electrons on TCNQ. However, as will be shown subsequently, the hole mobility is comparable to that of the electrons.

To extend the model used for NMP-TCNQ to the TTF-TCNQ case, one must generalize the calculations to account for Fermi-Dirac statistics.[3] The mobilities are high enough to use the Golden Rule. The energies $\hbar\omega_i$ and the coupling constants g_i for the optical phonons that interact significantly with the carriers have been calculated for the highest occupied orbitals of TCNQ, $TCNQ^-$, and TTF,[14] and also deduced experimentally for TCNQ.[15] Since the matrix element for scattering depends on the initial and final electron states only through the energy difference, $\hbar\omega_i$, between them, a relaxation time τ exists even for the distribution function f_0 degenerate, i.e.,

$$\frac{1}{\tau}=\frac{2}{h}\sum_i (g_i\hbar\omega_i)^2\left[(n_i+1)\frac{1-f_0(\epsilon-\hbar\omega_i)}{1-f_0(\epsilon)}\frac{H(\epsilon-\hbar\omega_i)}{(\epsilon-\hbar\omega_i)^{1/2}[\epsilon_0-(\epsilon-\hbar\omega_i)]^{1/2}}+n_i\frac{1-f_0(\epsilon+\hbar\omega_i)}{1-f_0(\epsilon)}\frac{H[\epsilon_0-(\epsilon+\hbar\omega_i)]}{(\epsilon+\hbar\omega_i)^{1/2}[\epsilon_0-(\epsilon+\hbar\omega_i)]^{1/2}}\right]^{-1}, \quad (1)$$

where n_i is the number of phonons in the mode with $\hbar\omega_i$; ϵ is the energy of the carrier measured from the band edge; ϵ_0 the bandwidth; and $H(A-B)=1$ for $A>B$, 0 for $A\leq B$. With this, the Boltzmann equation is readily solved, leading to integrals for μ and the thermoelectric power Q that must be evaluated numerically since the Fermi energy is not much larger than $k_B T$.

The values of $\hbar\omega_i$ and g_i used for the results of Fig. 1 are given in Table I. This leaves only the bandwidths to be chosen. Analysis of magnetic susceptibility and other types of data points to a bandwidth of 0.25–0.5 eV for TCNQ, while that for TTF appears to be about half as large.[16] Assuming that the upper limit of σ_{RT} cited earlier, 790 Ω^{-1} cm^{-1}, represents a sample without defects, I obtain agreement of theory with experiment for $\epsilon_0/k_B=3000$ K (0.25 eV) for TCNQ, 1500 K for TTF. For these bandwidths, as seen in Fig. 1(a), the calculated σ_{RT} for TCNQ is 3.5, for TTF 1 cm^2/V sec, giving a sum, $\sum\mu$, of 4.5 in good agreement with the upper limit cited earlier. These bandwidths, particularly that for TCNQ, must be considered lower limits since the intrinsic σ_{RT} could well be higher. Increase of ϵ_0/k_B of TCNQ from 3000 to 4000 would require the intrinsic σ_{RT} to be about 50% larger. The bandwidth could also be underestimated if the g values used are too low. Nevertheless, the theory with the bandwidths cited leads to a calculated Q_{RT} of -27 $\mu V/K$, in good agreement with experiment.[17] Also, in the range 150–300 K it is seen from Fig. 1(a) that $\sum\mu$, and therefore σ, varies essentially as $T^{-2.33}$, in agreement with experiment.[11]

Below 150 K, the calculated μ_{TTF} is much larger than μ_{TCNQ} because of the weak coupling of the TTF chain to the lower-energy molecular pho-

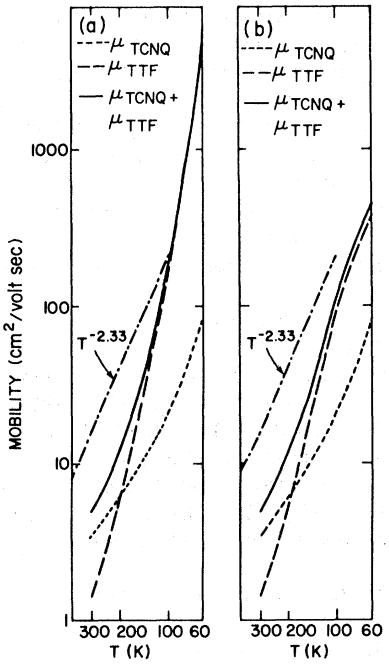

FIG. 1. (a) Calculated μ vs T due to optical-phonon scattering. (b) Calculate μ vs T due to optical-phonon scattering plus acoustic phonons of 52 K for TCNQ, 85 K for TTF, both with coupling constant $g = 0.35$.

nons. Certainly the calculation above overestimates the μ's at low T's because it neglects the coupling to acoustic phonons and possibly to other low-energy lattice modes. Guided in my choices by the neutron scattering data,[2] I have carried out numerical calculations in which an 85-K phonon interacts with the TTF chain, a 52-K phonon with the TCNQ chain. Actually the latter has little effect on the results since the electrons on TCNQ already have a strong interaction with relatively low-energy phonons. If we accept the experimental finding that $\sigma_P/\sigma_{RT} \simeq 100$, we must choose the coupling constant g no larger than 0.35 for the 85-K phonon. The results for $g = 0.35$ for both phonons are shown in Fig. 1(b). Comparison with Fig. 1(a) confirms that acoustic-phonon scattering has little effect above 150 K.

TABLE I. Values of $\hbar\omega_i$ and g_i used for the results shown in Fig. 1.

TTF [a]		TCNQ [b]	
$\hbar\omega$ (cm^{-1})	g	$\hbar\omega$ (cm^{-1})	g
245	0.16	148	1.54
475	1.33	337	0.80
736	0.49	613	0.20
1094	0.16	725	0.24
		978	0.20
		1196	0.22
		1396	0.20
		1615	0.49

[a]Ref. 14. [b]Ref. 15.

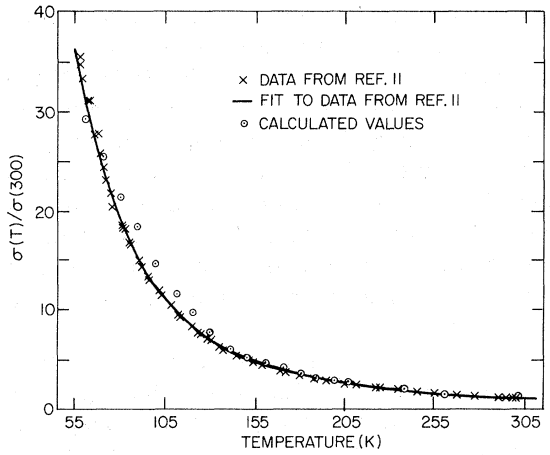

FIG. 2. Calculated $\sigma(T)/\sigma(300)$ for $\nu = 50$ vs data for sample with $\sigma_P/\sigma(300) = 35$. The temperature scale has been shifted 5° from that shown in Ref. 11 to correct for a constant deviation in the temperature readings for that sample (R. P. Groff, private communication).

From the large variations observed in σ_P/σ_{RT}[1,9,11] it is clear that some sort of defect scattering is present in actual samples. An obvious possibility is breaks in the chains. To incorporate this I assumed an additonal relaxation time $\tau_{def} = \nu a/v$, where νa represents the average chain length, a being the intermolecular spacing and v the velocity. This differs from the calculation of Rice and Bernasconi[18] in that the chain is not assumed to be a perfectly reflecting barrier. The relaxation time was then taken as the reciprocal of the sum of reciprocals of τ_{def} and (1), including the acoustic phonons. Numerical calculations led to the normalized σ vs T shown in Fig. 2 for $\nu = 50$, which is in good agreement with the sample having $(\sigma_P/\sigma_{RT}) = 35$.[11]

I have also calculated the single-particle $\sigma(\omega)$ by inserting the factor $(1+\omega^2\tau^2)^{-1}$ in the Boltzmann solution for σ before averaging. I find that $\sigma(\omega)$ for 300 K drops rapidly with increasing ω, being reduced by more than a factor of 2 at 500 cm^{-1}. This is consistent with τ_{TCNQ} calculated from (1) for $\epsilon \simeq \epsilon_F$ being $\sim 10^{-14}$ sec. Thus the model can explain a rapid drop in $\sigma(\omega)$.[7] It does not, of course, give the subsequent rise. A possible explanation for the rise, offered by Hinkel-

mann, is that for 1D systems the τ in $\sigma(\omega)$ for the frequency range concerned rises with ω.[19]

In summary, as I did earlier for NMP-TCNQ[3] and other TCNQ salts,[20] I have been able to account for the magnitude and temperature dependence of the mobility of TTF-TCNQ over a wide range of temperature, 150–300 K, by molecular optical-phonon scattering. We can extend the range of agreement of experiment and theory to close to T_P by incorporating acoustic-phonon and defect scattering.

The model can also explain large variations of σ with pressure, P.[21] Because of the dependence of τ on ϵ_0 and the relatively narrow bands, μ is quite sensitive to ϵ_0. Numerical calculations show σ varies more steeply than ϵ_0^2 for samples without defects. Since defect scattering is in general dependent on $\langle v \rangle$, still more rapid variation could occur for samples with $(\sigma_P/\sigma_{RT}) \simeq 15$, as were used for the measurements.[21] With the estimates of $d\epsilon_0/dP$ in Ref. 21, it appears quite likely that the observed variation of σ with P can be accounted for by our model. The relatively small bandwidths also make it possible to account for the large magnitude of the magnetic susceptibility χ around room temperature without invoking very large Coulomb correlations.[22] Some enhancement of χ on the TTF chain due to Coulomb repulsion may exist because of the very small bandwidth. This is consistent with the observations of "$4k_F$" scattering[23] for the TTF chain but not for TCNQ.

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[1]M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 13, 5111 (1976).

[2]R. Comès, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 1518 (1975); G. Shirane, S. M. Shapiro, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. B 14, 2325 (1976).

[3]A. J. Epstein, E. M. Conwell, D. J. Sandman, and J. S. Miller, to be published.

[4]P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).

[5]M. J. Rice and S. Strässler, Solid State Commun. 13, 1389 (1973).

[6]B. Horovitz, H. Gutfreund, and M. Weger, Phys. Rev. B 12, 3174 (1975).

[7]D. B. Tanner, C. S. Jacobsen, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 32, 1301 (1974), and 33, 1559 (1974), and Phys. Rev. B 13, 3381 (1976).

[8]J. E. Eldridge, Solid State Commun. 21, 737 (1977).

[9]S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, Phys. Rev. Lett. 34, 741 (1975).

[10]P. E. Seiden and D. Cabib, Phys. Rev. B 13, 1846 (1976).

[11]R. P. Groff, A. Suna, and R. E. Merrifield, Phys. Rev. Lett. 33, 418 (1974).

[12]G. Soda, D. Jerome, M. Weger, J. M. Fabre, and L. Giral, Solid State Commun. 18, 1417 (1976).

[13]E. Abrahams, Phys. Rev. 95, 839 (1954).

[14]N. O. Lipari, M. J. Rice, C. B. Duke, R. Bozio, A. Girlando, and C. Pecile, to be published. See also M. J. Rice and N. O. Lipari, Phys. Rev. Lett. 38, 437 (1977).

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

[16]E. F. Rybaczewski, L. S. Smith, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 34, 741 (1975).

[17]P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).

[18]M. J. Rice and J. Bernasconi, J. Phys. F 3, 55 (1973), and references cited therein.

[19]H. Hinkelmann, Solid State Commun. 18, 957 (1976).

[20]A. J. Epstein and E. M. Conwell, to be published.

[21]J. R. Cooper, D. Jerome, M. Weger, and S. Etemad, J. Phys. (Paris), Lett. 26, L-219 (1975).

[22]J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, Phys. Rev. B 15, 4738 (1977).

[23]J. P. Pouget, S. Khanna, F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 37, 437 (1976).