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Systematic study of the transitions in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and its selenium analogs

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We have carried out a comparative study of the dc conductivity in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and its isostructural selenium analogs TSeF-TCNQ (tetraselenafulvalene) and *cis/trans*-DSeDTF-TCNQ (diselenadithiafulvalene) below their metal-insulator transitions. Our study reveals the presence of a second transition in TTF-TCNQ at ~ 38 K and the absence of a similar transition in TSeF-TCNQ. We have characterized the 38-K transition and shown that it involves primarily the TTF chains. From the sharpness of the two transitions in TTF-TCNQ and the single transition at ~ 29 K in TSeF-TCNQ it is argued that they are related to a two- or three-dimensional ordering. The potentially disordered system DSeDTF-TCNQ does not possess any sharp transition. It is pointed out that the transition temperature defined as the sharp peak in the logarithmic derivative of the conductivity and not the conductivity itself relates more closely to the underlying thermodynamic transition. It is observed that the ratio of the zero-temperature gap to the transition temperature is the same in these systems and in many, if not all, other quasi-one-dimensional systems which undergo a metal-insulator transition. This ratio has a value of 8–10 and is considerably larger than 3.5 which is predicted by the mean-field theory. A model which is consistent with the observation of the transitions in these systems is suggested in which the coupling betwen TCNQ chains drives a two- or three-dimensional ordering of the fluctuation distortion giving rise to a metal-insulator transition.

I. INTRODUCTION

Understanding of the metallic behavior of TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) and the nature of its metal-insulator (M-I) transition continues to be a subject of great interest.[1,2] In a systematic effort to develop such understanding we have been engaged in a comparative study of TTF-TCNQ together with its selenium analogs TSeF-TCNQ (tetraselenafulvalene) and *cis/trans*-DSeDTF-TCNQ (diselenodithiafulvalene).[3] These three systems form an isostructural family of organic metals which offer a unique opportunity to study the effect of change in the various physical parameters such as mass, inter- and intrachain coupling, degree of charge transfer, etc., on their physical properties without changing their crystal structure. In an earlier study we reported the dc conductivity of these systems above their $M-I$ transition temperature.[4] The conductivity has a very similar behavior peaking at ~ 59, ~ 64, and ~ 38 K for TTF-TCNQ, DSeDTF-TCNQ, and TSeF-TCNQ, respectively. It was concluded that a common scattering mechanism, possibly a strong interchain electron-electron scattering, is responsible for the almost quadratic temperature dependence of the resistivity.

In this work we report a comparative study of σ, the dc conductivity along the chain axis, in the insulating phase of these isostructural organic metals. The experimental results are presented in Sec. II and their analysis is detailed in Sec. III. Our study reveals the presence of a second transition at 38 K in TTF-TCNQ at atmospheric pressure and absence of a similar transition in TSeF-TCNQ. We have characterized this transition and shown that it involves primarily the TTF chains. In Sec. IV the conductivity data are used to study the temperature variation of the gap parameters which shows an uncommon behavior in TTF-TCNQ. In Sec. V the experimental results are formulated into a phenomenological model based on a two- or three-dimensional ordering of fluctuating distortions explaining the behavior of the observed transitions in TTF-TCNQ and TSeF-TCNQ. The concluding remarks are presented in Sec. VI.

II. EXPERIMENTAL RESULTS

The dc conductivity measurements were carried out using a conventional four-probe technique. The data were accumulated by computer, a procedure that was found to be essential in collecting a large ensemble of data and its easy manipulation.

In Fig. 1(a) we show the data by plotting the logarithm of the resistance measured versus the inverse temperature for a representative sample of TTF-TCNQ grown in our laboratory. The semilog plot of the resistance instead of the resistivity and the limited temperature range have been chosen for clarity. The essential features of the data are as follows. The resistivity has a minimum at ~ 59 K and a very sharp rise at about 53 K. The width of the rise is about 1 K and pinpoints the position of the M-I transition temperature in agreement with the transition temperature determined by specific heat.[5] Between 53 and 38 K the resistivity has a smooth behavior followed by another sharp rise at ~ 38 K as pointed out earlier.[6] The width of

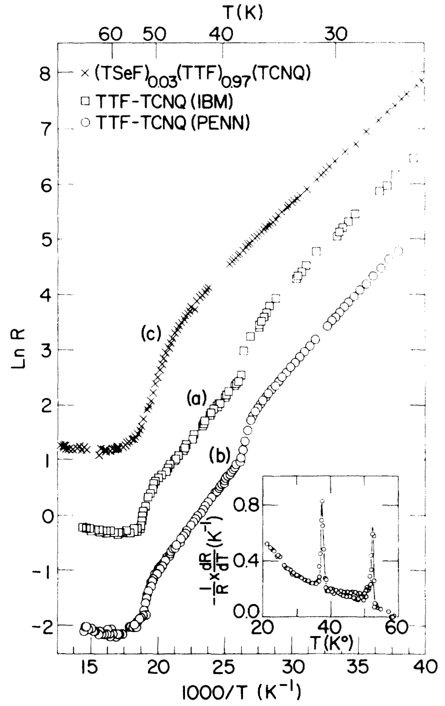

FIG. 1. Logarithm of resistance vs inverse temperature for (a) □, a typical TTF-TCNQ crystal grown at IBM; (b) ○, a typical TTF-TCNQ crystal grown at the University of Pennsylvania: (c) ×, a $(\mathrm{TSeF})_{0.03}(\mathrm{TTF})_{0.97}$ (TCNQ) crystal. Inset shows the logarithmic derivative of the resistance, for TTF-TCNQ shown in (b) vs temperature.

this rise is also about 1 K. It appears that the slope of the plot is discontinuous at 53 and 38 K. Figure 1(b) shows similar data taken by us on a typical sample of TTF-TCNQ grown at the University of Pennsylvania and kindly supplied for comparison. Similar results have also been obtained as early as the present work by the workers at the University of British Columbia.[7] A comparison of Figs. 1(a) and 1(b) indicates the degree to which the two transitions can be reproduced and characterized.[7] The extra conductivity above 53 K in the Pennsylvania samples is associated with the smaller value of the temperature-independent parameter ρ_0 in the expression

$$\rho(T) = \rho_0 + f(T) \qquad (1)$$

for the resistivity of these systems.[4,8]

The inset in Fig. 1 shows a plot of the logarthmic derivative of resistance $(1/R)(dR/dT)$ versus temperature for TTF-TCNQ derived by differentiating the data in Fig. 1(b). This is to emphasize the sharpness of the two transitions as well as to provide an easy way to define the transition temperatures, as the position of the peaks in this plot. The width of the transitions derived from the height of the peaks is an upper limit to the intrinsic width. A better estimate of the intrinsic width can be determined by a careful contactless microwave conductivity measurement where the samples can be free from strains due to silver-pasted contacts.[7a]

To characterize the two transitions further, we have exploited the isostructural property of TTF-TCNQ and TSeF-TCNQ and studied the whole range of alloy systems $(\mathrm{TSeF})_x\,(\mathrm{TTF})_{1-x}\,(\mathrm{TCNQ})$. The results will be detailed in a later publication.[9] A compound of interest for the present work is $(\mathrm{TSeF})_{0.03}\,(\mathrm{TTF})_{0.97}\,(\mathrm{TCNQ})$, where a small concentration of TSeF has selectively been placed on the TTF chains. The temperature behavior of the resistance in this sytem is shown in Fig. 1(c). The striking result is the apparent absence of the second transition at 38 K. A single peak in the logarithmic derivative of the conductivity indicates that there is a single, slightly smeared, transition at ~ 50 K.

In Fig. 2(a) the resistivity data for TTF-TCNQ are shown over an extended temperature range down to ~ 13 K. At lower temperatures the resistivity is slightly more sample dependent and has a weaker temperature dependence, resembling an impurity dominated contribution.[1] We therefore have omitted the part of the data below 13 K to emphasize the intrinsic behavior.

In the temperature range 38–13 K the conductivity decreases by four orders of magnitude. If we define an activation energy E by the relation

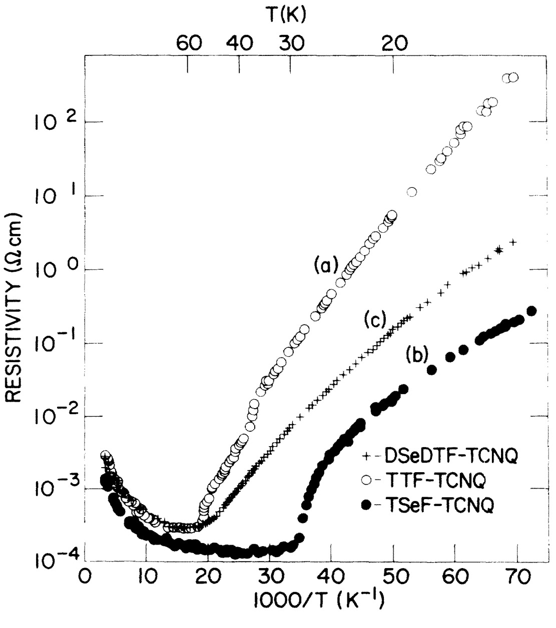

FIG. 2. Absolute resistivity vs inverse temperature for (a) ○, TTF-TCNQ; (b) ●, TSeF-TCNQ; (c), × DSeDTF-TCNQ.

$$\rho(T)=\rho_c e^{E(T)/T}, \tag{2}$$

where ρ_c is a constant prefactor, then it is found that, by a proper choice of ρ_c, $E(T)$ can be essentially constant for $T<38$ K and has the value

$$E(T)=230\pm 20\ \text{K}.$$

The uncertainty in $E(T)$ arises first from the fact that $E(T)$ is not strictly constant and second from the fact that it varies slightly from sample to sample. The slight curvature in the slope of the plot in Fig. 2(a) below 38 K can be eliminated if we define ρ_c to have a slight temperature dependence.

As we pointed out earlier,[6] the activation energy of the resistivity is about three times larger than that determined by the low-temperature magnetic-susceptibility measurement.[10] In the semiconducting state, therefore, TTF-TCNQ cannot be treated as a conventional semiconductor where the magnetic gap is the same as the single-particle excitation gap.

Figure 2(b) shows the temperature dependence of the resistivity in TSeF-TCNQ. The clear difference between the two systems, despite all their similarities,[4] is the absence of a second transition in TSeF-TCNQ. The single transition is characterized by the sharp rise in the resistivity at about 29 K with a typical width of about 2 K. We note that the slope of the plot appears to be discontinuous at the transition temperature similar to the case of TTF-TCNQ.

The peak in the conductivity of TSeF-TCNQ occurs in the range 38–42 K. We have found the temperature of this peak to be considerably more sample dependent than the peak in the logarithmic derivative of conductivity which occurs at ~ 29 K, about ten degrees lower in temperature. A smaller difference of ~ 6 K exists between the two peaks in TTF-TCNQ, where the specific heat[5] indicates that the thermodynamic transition coincides with the peak in the logarithmic derivative of the conductivity. In order to determine the transition temperature from conductivity measurements we should, therefore, consider the position of the peak in the logarithmic derivative of conductivity. We have elaborated on the physical significance of this assertion in Sec. IV.

Figure 2(c) shows the temperature dependence of the resistivity of DSeDTF-TCNQ. The absence of any sharp break in this plot distinguishes the temperature dependence of the conductivity of DSeDTF-TCNQ from that of TTF-TCNQ and TSeF-TCNQ. As a result it is harder to define the transition temperature. However, a broad maximum in the logarithmic derivative of the conductivity hints at a smeared transition centered at ~ 45 K. The smearing of the transition is probably due to the disorder caused by the random arrangement of the *cis/trans* DSeDT molecules in the cation chains.[4]

III. ANALYSIS AND DISCUSSION OF RESULTS

From the sharpness and reproducibility of the second anomaly in TTF-TCNQ we have proposed that there is a second transition in TTF-TCNQ at 38 K in atmospheric pressure.[6] We shall discuss below why the anomaly at 38 K is not an artifact of the measurements. Looking back, we can now see a variety of other experimental evidence indicating the presence of a second transition in TTF-TCNQ. An anomaly at 38 K was reported in the early measurements on the pressure dependence of the conductivity.[11,12] The thermoelectric power has a plateau in the same temperature range.[13] The single-crystal thermoreflectance has an abrupt shift in the relative intensity of the two components, polarized parallel and perpendicular to the chain axis, seen just above the plasma edge.[14] The nuclear spin-lattice relaxation rate T_1 of the TTF protons suddenly decreases faster as one cools down through ~ 38 K.[15] Finally, the thermal conductivity has a sudden drop at ~ 38 K,[16] and the magnitude of the drop corresponds to the observed anomaly in dc conductivity through the Wiedemann-Franz relation.

The first suggestion for a second transition in TTF-TCNQ was made by Jérome *et al.*[12] who observed the anomaly under pressure. Owing to experimental problems with the measurements, their suggestion was overshadowed by a common misinterpretation of the work of Cohen *et al.*[17] on the dc conductivity in TTF-TCNQ. In this latter work, it was shown that misaligned contacts plus a second peak in the anisotropy σ/σ_a, where σ_a refers to the conductivity along crystallographic a axis,[18] would result in anomalous structure in the apparent σ at ~ 38 K. A common misconception subsequently developed that *any anomaly* at ~ 38 K in σ is a signature of misaligned contacts[17] and has no other significance. To clear this misconception one needs only to realize that if σ and σ_a had smooth temperature dependences, i.e., their logarithm varied approximately linearly with inverse temperature, then the resultant anistropy σ/σ_a should vary with inverse temperature in a similar way, and σ should not have a second peak at ~ 38 K. The basic fact is that the anomaly in σ is the cause of the second peak in σ/σ_a, not vice versa, and misalignment of contacts only tends to amplify the appearance of the anomaly as it has in some cases.[12,17]

The sharpness of the two anomalies, as emphasized in the inset in Fig. 1, is also important because it indicates that the underlying transitions at ~ 53 and ~ 38 K are related to two- or three-dimensional ordering. This result has strong implications about the nature of the M-I transition at ~ 53 K.

To characterize further the two transitions in TTF-TCNQ we have also measured the conductivity along σ_a and σ_{c*}. Our preliminary measurements, not detailed here, indicate that the two sharp anomalies in σ at 53 and 38 K are exactly duplicated in σ_{c*}, while σ_a is different. As a result the anisotropy σ/σ_{c*} does not have any sizable structure around the two transition temperatures, while σ/σ_a has two peaks around 53 and 38 K.[17] This behavior may be related to the crystal structure of TTF-TCNQ[18] in the following way. Lines joining the two nearest neighbors along the chain axis and along the c axis join like molecules, while a line along the a axis joins a TTF to a TCNQ. Since the effects of the two transitions are identically reflected in σ and σ_{c*} it is tempting to consider TTF-TCNQ as sheets of TCNQ interleaved by sheets of TTF so far as the two transitions are concerned.

More insight into the origin of the two transitions can be gained by studying the selectively doped system $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$. In Fig. 3 we report the temperature dependence of the resistance of TTF-TCNQ, shown earlier in Fig 1(b), together with that of $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$, shown in Fig. 1(c). For comparison the two curves in Fig. 3 are now normalized to the same arbitrary room temperature values. We have also subtracted the constant term, related to ρ_0 in Eq. (1), to emphasize the temperature-dependent contributions to the resistance. Comparison of the two curves in Fig. 3 indicates that above 53 K and below 38 K the conductivity of the two compounds is almost the same. The striking result is that in the temperature range between 53 and 38 K there is *extra conductivity* in TTF-TCNQ.

Owing to isomorphism of the pure constituents, any effect of doping with TSeF will be due primarily to the electronic differences between TTF and TSeF and not their steric differences. Therefore, the conduction along TTF chains will be considerably more sensitive to doping by TSeF than the conduction along TCNQ chains. The absence of a transition at 38 K in $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$ as indicated in Figs. 1(c) and Fig. 3, then clearly shows that the sudden drop in the conductivity of TTF-TCNQ is due to a change in conduction along TTF, not along TCNQ, chains. The fact that this drop is so large, about a factor of three, means that between 53 and 38 K the net conductivity is dominated by the contribution due to the TTF chains. We note that the TTF conductivity in this temperature range is still activated. In other words, there are two different gaps in the single-particle excitation spectrum of the two chains, with the gap on the TTF chains being the smaller one in the temperature range between the two transitions.

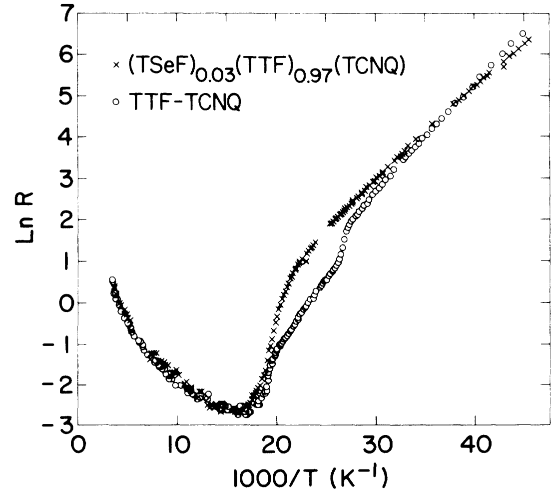

FIG. 3. Logarithm of the resistance value, normalized to the same arbitrary room temperature, vs the inverse temperature (o) for TTF-TCNQ, and ( ) for $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$. The temperature-independent contribution to the rssistance has been subtracted.

The idea that the transition at 38 K involves primarily the TTF chains is supported by the nuclear lattice relaxation rate of the protons on TTF molecules. This can best be seen in Fig. 3 of Rybaczewski *et al.*[15] which shows a sudden drop at ~ 38 K in the quantity $(T_1T)^{-1/2}$ related to the local magnetic properties of the TTF chain. No significant change at ~ 38 K in the same quantity for the TCNQ chains is observed.

The fate of the 38 K transition in the compound $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$ now becomes an interesting question. There are three possibilities that we should like to consider. (a) The second transition is still present at ~ 38 K or at a higher temperature but its effect on the conductivity along the chains is obscured because of the perturbations introduced by the TSeF molecules for conduction in this direction. To check this possibility one needs an experiment that is not sensitive to the conduction along the chains in these anisotropic systems, but which still shows the 38-K anomaly in pure TTF-TCNQ. Among the possible candidates[14-16] is the conductivity measurement along the c^* axis. The absence of the second anomaly in our preliminary measurements of σ_{c*} in $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$, not detailed here, indicates that the second transition is not present at ~ 38 K or at a higher temperature. The fact that the conductivity below ~ 38 K in TTF-TCNQ and $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$ is the same, as seen in Fig. 3, shows that the transition does not occur below 38 K in $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$. (b) The second transition now occurs simultaneously with the first transition. We do not favor this possibility in light of the work in progress on systems with less TSeF doping[9] which is consistant with the third possibility. (c) The second transition is smeared over a large temperature range so that its effect on the conductivity is not observable. The fact that the first transition is still sharp, with a width of about 3–4 K as seen in Fig. 1(c), would then support our assumption that the TSeF doping primarily affects the TTF chains.

IV. ACTIVATION ENERGY

The temperature variation of the gap parameter can be derived from the analysis of the conductivity data by rewriting Eq. (2)

$$E(T) = T[\ln\rho(T) - \ln\rho_c], \qquad (3)$$

where the activation energy $E(T)$ is directly related to the gap parameter. Commonly one chooses ρ_c such that $E(T)$ goes to zero at the M-I transition and then it should approach zero temperature with zero slope. To avoid the complications of two transitions, we should like to consider the experimental data on TSeF-TCNQ first.

In Fig. 4(a) we report the activation energy for TSeF-TCNQ derived from the data presented earlier in Fig. 2(b). The activation energy rises rapidly below ~ 29 K, at the same temperature defined by the peak in the logarithmic derivative of the conductivity, and approaches a constant value at lower temperatures. The semiconducting gap $2\Delta(T)$, defined as twice the activation energy, has a zero-temperature value of $2\Delta(0) \sim 230 \pm 50$ K for TSeF-TCNQ. In the temperature range $29 < T < 39$ K the gap appears to have a small nonzero value which may be related to sample inhomogeneities or resistive fluctuations in the metallic state or both.

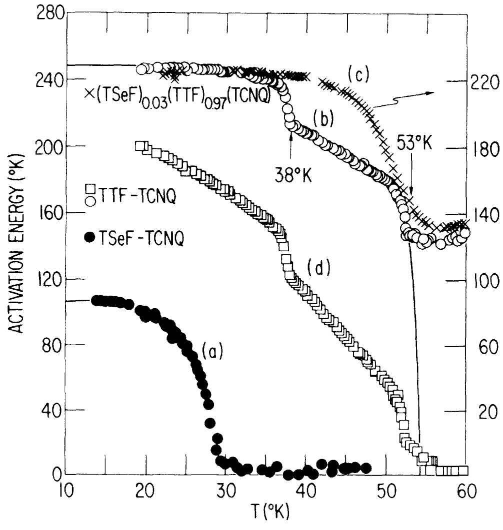

FIG. 4. Activation energy vs temperature for (a) o, TseF-TCNQ; (b) ●, TTF-TCNQ; (c) ×, $(\mathrm{TSeF})_{0.03}(\mathrm{TTF})_{0.97}(\mathrm{TCNQ})$; and (d) □, TTF-TCNQ with a different choice of ρ_c (see text). The activation energy for $(\mathrm{TSeF})_{0.03}(\mathrm{TTF})_{0.97}(\mathrm{TCNQ})$ shown has been shifted up by ~20 K for the clarity of the comparison.

The qualitative behavior of the semiconducting gap in TSeF-TCNQ as shown in Fig. 4(a) is similar to that predicted by the mean-field treatment of the Peierls transtion.[19] This behavior is characterized by a gap that is constant at low temperatures and goes to zero at the transition temperature with infinite slope. The experimental result shown in Fig. 4(a), however, is quantitatively different from the mean-field result. The ratio of the zero-temperature gap to the transition temperature in the mean-field approximation has a well-defined value of $2\Delta(0)/T_c = 3.5$, while the same ratio for the gap parameter in TSeF-TCNQ has a value of ~ 8.0. Such a discrepancy is not unique to TSeF-TCNQ. Similar differences are also present in other quasi-one-dimensional systems. For example, $2\Delta(0)/T_c$ has values of about 8, 9, and 10 for TTF-$\mathrm{Br}_{0.76}$,[20] N-methylphenazinium (NMP)-TCNQ,[21] and $[\mathrm{K_2Pt(CN)_4}]\mathrm{Br}_{0.3} \cdot 2(\mathrm{H_2O})$ better known as KCP, respectively. These values are tabulated in Table I. We emphasize that with the exception of being quasi-one-dimensional, they are very different systems. The reasonable agreement in the experimentally determined value of $2\Delta(0)/T_c$, which is about 2.5 times larger than the values predicted by the mean-field approximation, suggests the need for a common theory to explain the thermodynamics of the M-I transition in all quasi-one-dimensional systems. This observation is in agreement with the suggestion of Lee, Rice, and Anderson[23] that in pseudo-one-dimensional systems the three-dimensional transition temperature is significantly lower than the mean-field transition temperature of the isolated one-dimensional chains.

The temperature variation of the gap parameter in TTF-TCNQ is quite different because the right choice of ρ_c, required to determine the gap parameter from Eq. (3), is not clear. Figure 4(b) shows the variation of the activation energy for TTF-TCNQ using the data presented earlier in Fig. 2(a). Here ρ_c has been chosen such that the gap parameter approaches zero temperature with zero slope. Such a choice for ρ_c results in a nonvanishing gap parameter at all temperatures including the metallic regime. The nonvanishing gap does not seem to be related to the presence of two transitions in TTF-TCNQ as opposed to the single transiton in TSeF-TCNQ and the other mentioned systems.[20–22] To show this we have evaluated the gap parameter for $(\mathrm{TSeF})_{0.03}(\mathrm{TTF})_{0.97}(\mathrm{TCNQ})$, using the same criterion for the choice of ρ_c, and the data shown earlier in Fig. 1(c). The temperature variation of the resultant activation energy is shown in Fig. 4(c), which is shifted up by ~ 20 K to facilitate the comparison with Fig. 4(b). Nonetheless, it still has a nonvanishing value at all temperatures. The zero-temperature gap for TTF-TCNQ has a value of $2\Delta(0) \sim 450 \pm 50$ K, and still exhibits the same ratio

TABLE I. Some experimental data on the conductivity of quasi-one-dimensional systems considered in the text.

Compound	T_c (K)	T_{peak}[a] (K)	$2\Delta(0)$ (K)	$2\Delta(0)/T_c$	No. of samples
TTF-TCNQ	53	58–60	450	8.5	16
TSeF-TCNQ	29	38–42	230	8.0	17
DSeDTF-TCNQ	~45	60–64	~360	~8	8
$(\text{TSeF})_{0.03}(\text{TTF})_{0.97}(\text{TCNQ})$	50	60–64	420	8.4	4
$\text{TTF-Br}_{0.76}$ (Ref. 20)	175	275–325	1400	8	4
NMP-TCNQ (Ref. 21)	~90	~230	860	~9.6	
KCP (Ref. 22)	~125	~250	1300	~10	

[a] T_{peak} is the temperature at which the peak in the conductivity occurs.

$2\Delta(0)/T_c \sim 8.5$ as does TSeF-TCNQ (see Table I.) The consistency in the value of $2\Delta(0)/T_c$ for TTF-TCNQ and TSeF-TCNQ indicates the first transition at 53 K is closely related to the activation energy below the second transition. The zero-temperature gap in $(\text{TSeF})_{0.03}(\text{TTF})_{0.97}(\text{TCNQ})$ has a value of ~420 ± 50 K (see Table I).

Aside from other complications, a nonvanishing gap is inconsistent with the recent magneto-resistance measurement which indicates that the gap goes to zero at ~53 K in TTF-TCNQ.[24] Forcing the activation energy to go to zero at the M-I transition leads to two other possible alternatives equally problematical. One could assume that the mobility, contained in ρ_c, is not the same below and above the M-I transition and changes suddenly at the transition. The activation energy determined by a choice of ρ_c to fit the low-temperature data could then go to zero along the solid line in Fig. 4(b). Such a situation corresponds to a considerably more resistive scattering mechanism in the metallic regime than in the semiconducting one, contrary to the expected behavior. Alternatively one could choose ρ_c so that the activation energy goes to zero at the M-I transition.[25] Using the same data, we show the temperature variation of the resulting activation energy in Fig. 4(d). As expected from Eq. (2) the zero-temperature activation energy is unchanged, but the interpolation between zero temperature and T_c is quite different. In fact, the gap parameter goes to zero almost linearly with temperature, with the exception of the two sharp drops at the two transitions. Such behavior is clearly inconsistent with the prediction of mean-field theory and rules out the possibility of long-range order in TTF-TCNQ. We emphasize that there is no intrinsic disorder in TTF-TCNQ to create ambiguity about the transition range as in KCP.[22] In KCP the gap parameter has been forced to go to zero at the conductivity peak. As a result it qualitatively looks like Fig. 4(c) with the exception of the two sharp drops.[22]

The activation energy in DSeDTF-TCNQ has a qualitatively similar behavior to that of TTF-TCNQ shown in Figs. 4(b) and 4(d) with exception of the two sharp drops. The smeared transition in DSeDTF-TCNQ indicates that the cation chains are probably disordered. The smeared transition region in the conductivity of DSeDTF-TCNQ is, in many ways, the same as in KCP.[22] This similarity suggests that a comparative study of the other experimental data on DSeDTF-TCNQ with those on TTF-TCNQ and TSeF-TCNQ may resolve the role of disorder in KCP and in the other pseudo-one-dimensional systems.[26] Table I summarizes a comparative study of the different parameters related to the conductivity in these quasi-one-dimensional systems which undergo metal-insulator transition.

In Sec. II we pointed out that temperature of the peak in the logarithmic derivative of the conductivity relates more closely to the M-I transition temperature than the temperature where the conductivity peaks. The reason for this is the fact that the activation energy and not the conductivity is the more basic physical parameter. In the mean-field approximation the gap parameter goes to zero with infinite slope at the M-I transition temperature. As a result the conductivity peaks at the same temperature as the peak in the rate of change of the gap parameters, $d\Delta(T)/dT$. In the presence of fluctuation, for example, the two temperatures can be quite different. It has been shown then the temperature of the peak in $d\Delta(T)/dT$ is closer to the thermodynamic transition temperature than the temperature at which $\Delta(T)$ goes to zero.[27] For a fairly sharp transition the peak in $d\Delta(T)/dT$ occurs at the same temperature at which a peak in the derivative of $\ln R$ with respect to T^{-1} occurs, which is the same temperature as the peak in the logarithmic derivative of the conductivity. We may point out that for a smeared transition the peak in the logarithmic derivative of the conductivity could occur at slightly different temperature from the peak in $d\Delta(T)/dT$.

V. MODEL

We would now like to interpret the experimental evidence regarding the two transitions in TTF-TCNQ in terms of a phenomenological model in which the transitions are driven by a two- or three-dimensional ordering of the fluctuation distortions along the chain. The belief that the *M-I* transition as well as the transition at ~ 38 K should be two or three dimensional is a consequence of their sharpness. In this model, the *M-I* transition is due to the formation of a static gap related to the ordering.

A band-structure calculation,[28] a recent comparative study of the thermoelectric power measurements in TTF-TCNQ and TSeF-TCNQ,[29] and nuclear spin-lattice relaxation measurements[15] indicate that above the *M-I* transition both TTF and TCNQ chains are metallic. The evidence presented in Sec. III then shows that the 53-K transition corresponds to the opening of two unequal gaps on the two chains. The presence of the larger gap on the TCNQ chains suggests that a two- or three-dimensional ordering of the TCNQ chains drives the first transition. This is not an unreasonable assumption in light of a stronger coupling between TCNQ chains due to their larger size in the closely-packed crystal.[18] The idea that the 53-K transition envolves primarily the TCNQ chains has also been developed independently by a careful study of the electron-spin-resonance *g* shift.[30] The TTF chains are now placed in the field of ordered TCNQ sheets and show some kind of induced order reflected in their smaller gap. The transtion at 38 K, which was shown to involve primarily the TTF chains, then corresponds to a development of full three-dimensional order on TTF chains.

The fact that there is a single transition at lower temperature in TSeF-TCNQ can be explained by the following considerations. All the lattice parameters in TSeF-TCNQ are larger than in TTF-TCNQ.[4] The first transition, which is driven by a two- or three-dimensional ordering of the TCNQ chains, is then lowered because of a decrease in the coupling between the TCNQ chains. In light of the relative insensitivity of the *M-I* transition temperature to the *b*-axis separation[9,11,12] we do not feel that the intrachain coupling in the TCNQ chains plays a major role in determining the transition temperature. The replacement of the sulfur atoms in TTF by the larger selenium atoms, on the other hand, increases the coupling between the donor and acceptor sheets in TSeF-TCNQ over TTF-TCNQ. As a result of the strong intersheet coupling the two transitions then occur simultaneously.

VI. CONCLUSION

We have reported a comparative study of the dc conductivity in the semiconducting state of TTF-TCNQ and its selenium analogs. Our measurements have revealed the presence of a second transition in TTF-TCNQ at ~ 38 K at atmospheric pressure. We have explained that the observed anomaly at ~ 38 K is the cause of a second peak in the anisotropy σ_b/σ_a and not vice versa. The two anomalies have a two-dimensional nature consistent with sheets of donors separated by sheets of acceptors as seen in the crystal structure. The sharpness of the two anomalies indicates that the underlying transtions are two or three dimensional. Our measurements on the selectively doped system $(\mathrm{TSeF})_{0.03}(\mathrm{TTF})_{0.97}(\mathrm{TCNQ})$ show that the transition at 38 K involves primarily the TTF chains. Also below the first transition the conductivity is dominated by the TTF contribution as a result of a smaller gap on TTF chains. Below ~ 38 K the conductivity has a farily constant activation energy of ~ 230 K. We have noted that this is about three times larger than the activation energy in the susceptibility at the same temperature range.

TSeF-TCNQ has a single transition at ~ 29 K. This is ~ 10 K lower than the peak in the conductivity. A comparison of these systems indicates that the position of the peak in the logarithmic derivative of the conductivity and not the peak in the conductivity itself is more closely related to the thermodynamic transition. DSeDTF-TCNQ has been found to be different, showing no anomaly in its conductivity. This behavior has been attributed to the random arrangement of *cis/trans*-DSeDTF molecules in the cation chains.

The conductivity data were used to study the temperature variation of the activation energy related to the gap parameter. It was observed that the ratio of the zero-temperature gap to the transition temperature is the same in TTF-TCNQ and TSeF-TCNQ and in many, if not all, other quasi-one-dimensional systems which undergo a *M-I* transition. The invariance of this ratio hints at a common mechanism driving the *M-I* transition in the quasi-one-dimensional systems, and its magnitude indicates that this mechanism is different from the mean-field theory of the transition. A detailed comparison of the activation energy in TTF-TCNQ and TSeF-TCNQ revealed differences which remain to be understood.

We have suggested a phenomenological model which is consistent with our observations of the transitions in these systems. In this model two- or three-dimensional ordering of fluctuating distortions gives rise to a metal-insulator transition. It is suggested that the ordering of TCNQ chains drives the first transition in TTF-TCNQ and induces a gap on the TTF chains. The transition at ~ 38 K is then due to a further ordering of the TTF chains. The lowering of the transition temperature in TSeF-TCNQ is due to a decrease in the interchain coupling of TCNQ chains. The absence of a second transition is, however, due to stronger coupling between donors and acceptors which has resulted in simultaneous occurrence of the two transitions.

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[1] F. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Am. Chem. Soc. 95, 948 (1973).

[2] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 13, 1125 (1973).

[3] For synthetic details see E. M. Engler and V. V. Patel, J. Am. Chem. Soc. 96, 7376 (1974); E. M. Engler and V. V. Patel, J. Chem. Soc. Chem. Commun. (to be published).

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

[5] R. A. Craven, M. B. Salamon, G. DePasquali, R. M. Herman, G. Stucky, and A. Schultz, Phys. Rev. Lett. 32, 769 (1974).

[6] S. Etemad, T. Penney, and E. M. Engler, Bull. Am. Phys. Soc. 20, 496 (1975).

[7] (a) A. J. Berlinsky (private communication); (b) A. J. Berlinsky, T. Tiedje, J. E. Carolan, L. Weiler, and W. Friesen, Bull. Am. Phys. Soc. 20, 465 (1975).

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

[9] S. Etemad, E. M. Engler, B. A. Scott, T. Penney and T. D. Schultz (unpublished).

[10] J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 3131 (1974).

[11] C. W. Chu, J. M. E. Harper, and T. H. Geballe, Phys. Rev. Lett. 31, 1491 (1973). They observed a shoulder in their data at ~45 K.

[12] D. Jérome, W. Müller, and M. Weger, J. Phys. (Paris) 35, L77 (1974). A refinement of this work is to be published by J. R. Cooper, D. Jérome, M. Weger, and S. Etemad; J. Phys. (Paris) 36, L219 (1975).

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

[14] P. I. Perov and J. E. Fischer, Phys. Rev. Lett. 33, 521 (1974).

[15] E. F. Rybaczewski, A. F. Garito, A. J. Heeger, and E. Ehrenfreund, Phys. Rev. Lett. 34, 524 (1975). The significance of the change at 38 K in the nuclear spin-lattice relaxation time of the protons on TTF molecules was not mentioned by the authors.

[16] M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, G. Stucky, and A. Schultz, Phys. Rev. B 11, 619 (1975).

[17] J. M. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1298 (1974).

[18] T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, Acta Crystallogr. B 30, 763 (1974).

[19] See, for example, M. J. Rice, and S. Strässler, Solid State Commun. 13, 125 (1973).

[20] B. A. Scott, J. B. Torrance, S. J. LaPlaca, P. Corfield, D. C. Green, and S. Etemad, Bull. Am. Phys. Soc. 20, 496 (1975). The data presented show the presence of a *M-I* transition at ~175 K and a zero-temperature gap of ~1400 K.

[21] L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, Phys. Rev. B 7, 2122 (1973). In the light of our present understanding their data must be reanalyzed. In particular the *M-I* transition does not occur at the temperature at which the conductivity peaks. Their conductivity data are then consistent with a *M-I* transition at ~90 K and not at ~200 K. The zero-temperature gap is ~860 K. We note that there is an error in their evaluation of the slope of lnσ vs T^{-1}. As a result the temperature variation of the gap parameter is incorrect. The gap parameter derived through a correct analysis of the data is very similar to that shown for TSeF-TCNQ. The correct analysis will be detailed by L. B. Coleman Ph.D. thesis (University of Pennsylvania, 1975) (unpublished).

[22] H. R. Zeller, *Festkörperprobleme*, edited by H. J. Queisser (Pergamon, New York, 1973), Vol. 13, p. 31. The zero-temperature gap parameter is ~1200 K. The transition temperature in this compound is smeared and centered about 120 K.

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

[24] T. Tiedje, J. F. Carolan, A. J. Berlinsky, and L. Weiler, Can. J. Phys. (to be published).

[25] It was pointed out to us by J. B. Torrance and A. J. Berlinsky (unpublished) that the activation energy should go to zero at the temperature of the conductivity peak.

[26] E. Ehrenfreund, S. Etemad, L. B. Coleman, E. F. Rybaczewski, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 29, 269 (1972).

[27] D. J. Scalapino, M. Sears, and R. A. Ferrell, Phys. Rev. B 6, 3409 (1972).

[28] A. J. Berlinsky, J. F. Carolan, and L. Weiler, Solid State Commun. 15, 795 (1974).

[29] P. M. Chaikin, R. L. Greene, S. Etemad, and E. M. Engler (unpublished).

[30] Y. Tomkiewicz and A. Taranko (unpublished).