

Thermopower of an isostructural series of organic conductors

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The thermoelectric power of a series of isostructural organic charge-transfer salts has been measured. The compounds consist of a tetracyanoquinodimethane (TCNQ) anion with cations of tetrathiafulvalene, *cis/trans*-diselenadithiafulvalene, and tetraselenafulvalene. The salts are metallic at high temperatures with a sharp transition to a low-temperature insulating state clearly indicated by these measurements. In addition, the systematics of this study show the relative conductivities on the cation and anion chains and indicate similar scattering processes in all of these crystals.

I. INTRODUCTION

The charge transfer salts based on the tetracyanoquinodimethane TCNQ anion [Fig. 1(a)] have shown many exciting solid-state phenomena. They are the highest conducting organic salts and have highly anisotropic (quasi-one-dimensional) electronic properties and several different types of phase transitions.¹⁻⁴ The detailed study of which interactions are most important in determining the various behaviors has been hampered by the lack of a system in which the molecular constituents can be varied in a controlled fashion. The TCNQ salts of tetrathiafulvalene [TTF, Fig. 1(b)], tetraselenafulvalene [TSeF, Fig. 1(c)], and *cis/trans*-diselenadithiafulvalene [DSeDTF, Figs. 1(d) and 1(e)] provide a unique series of highly conducting "metalliclike" charge transfer salts in which the crystal structure remains essentially constant as the molecular properties of the cation are changed.⁵

Previous experiments have already demonstrated a remarkable similarity in their dc conductivities which peak at 58, 64, and 40 K as one goes from TTF to DSeDTF to TSeF-TCNQ (Table I). It was therefore concluded that the same process must govern their conduction mechanism in spite of their varying molecular properties.⁶

Measurements of the thermoelectric power of TTF-TCNQ have been reported elsewhere.⁷ It was found that in the metallic state (at temperatures considerably above the transition) the Seebeck coefficient had a linear temperature dependence extrapolating through zero at zero temperature, a textbook example of metallic behavior.⁸ There appeared a sharp transition at 58 K (close to the temperature at which the conductivity was maximum), and below 40 K the thermopower was large,

impurity dependent, and increasing as temperature decreased, characteristics of a semiconductor. The thermoelectric study of the selenium derivatives was undertaken in order to study systematically the effect of changing the electronic parameters such as disorder, density of states, band structure, and ionization potential of the cation on the conduction process of these fulvalinium systems. We also hoped to confirm that the conduction process was similar throughout the series as well as to clear up the thermopower of TTF-TCNQ in the nonideal region between 140 and 60 K and between 58 and 40 K.

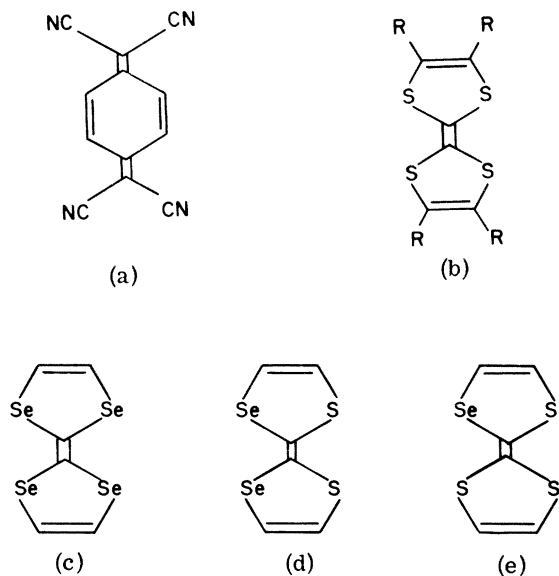


FIG. 1. Molecular diagrams of (a) TCNQ₁, (b) TTF (where R=H), (c) TSeF, (d) *cis*-DSeDTF, and (e) *trans*-DSeDTF.

TABLE I. Comparative values of the transport properties of TCNQ salts. T_p is the temperature of the conductivity peak, $\sigma(300\text{ K})$ is the 300 K conductivity (Ref. 17), $s(300\text{ K})$ the room-temperature thermopower, and E_{gap} is determined from activated conductivity (Refs. 17 and 18) and thermopower below the metal-insulator transition.

	TTF-TCNQ	DSeDTF-TCNQ	TSeF-TENQ
T_p	58–60 K	62–64 K	39–40 K
$\sigma(300\text{ K})$ ($\Omega\text{ cm})^{-1}$	500	550	800
$S(300\text{ K})$ ($\mu\text{V/K}$)	-28	-10	+3
E_{gap} (conductivity)	500 K		300 K
E_{gap} (Thermopower)	200 K		100 K

II. EXPERIMENTAL RESULTS

In Fig. 2 we show the experimentally determined thermopower for TSeF-TCNQ.⁹ The data shown were taken on three separate crystals but are representative of over ten crystal measurements made in the three different laboratories of the authors. In Fig. 3, we show the low-temperature thermopower for TSeF-TCNQ and in Fig. 4 we have plotted the thermopowers, through their transitions, of TTF-TCNQ, TSeF-TCNQ, and DSeDTF-TCNQ for comparison.

In spite of their varied appearances (Fig. 4), our data show an over-all similarity in the temperature dependence of the thermoelectric power. This is seen by considering three distinct temperature regions. At the highest temperatures, the dominant contribution is small in magnitude and linear in temperature indicative of a metallic state. In the intermediate temperature, nonideal metallic region, just above the temperature where the conductivity peaks (T_p), a second contribution is present which is uniformly increasing (positively) with decreasing temperature. In the low-temperature region, the thermoelectric power is (approximately) inversely proportional to temperature, characteristic of a semiconducting state (Fig. 3).

From Fig. 4 we see that the temperature dependence of thermoelectric power in the metallic

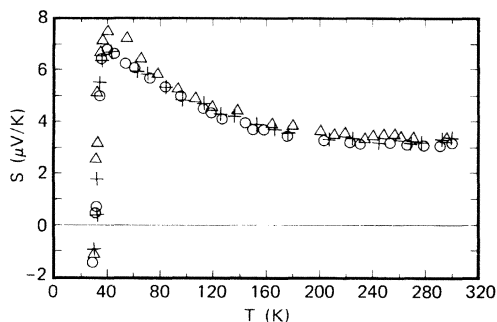


FIG. 2. Absolute thermopower of TseF-TCNQ.

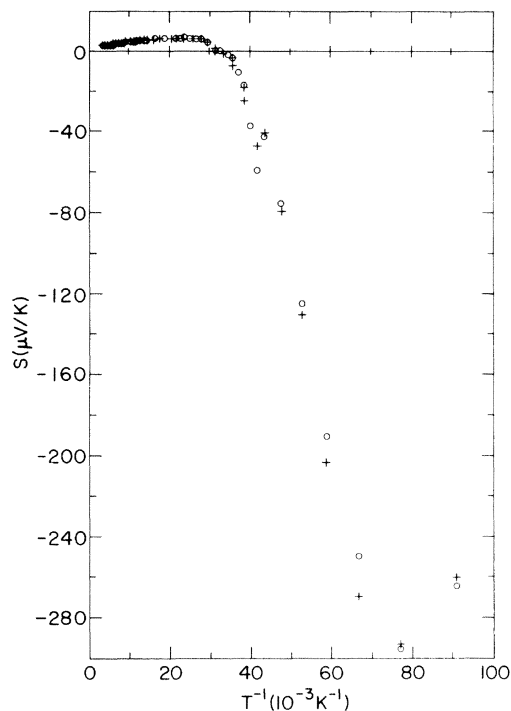


FIG. 3. Low-temperature thermopower of TseF-TCNQ.

and semiconducting regions is quite smooth, whereas the transition between them is quite abrupt in the cases of TTF-TCNQ and TSeF-TCNQ. The “break” in the curves occurs at 58 and 40 K, respectively, within two degrees of the conductivity

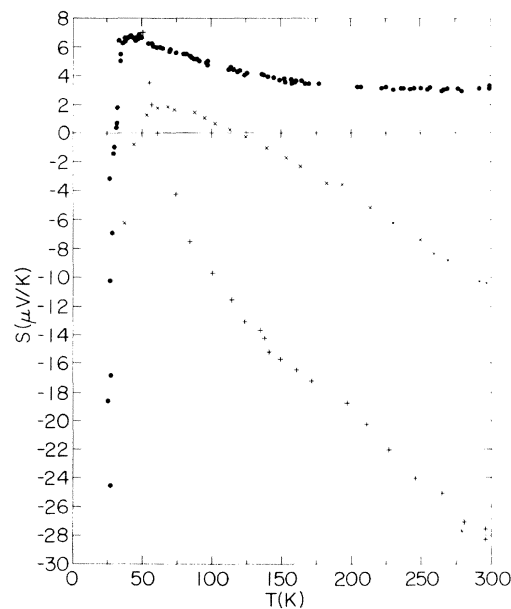


FIG. 4. Absolute thermopower of TSeF-TCNQ (solid dots), DSeDTF-TCNQ (x's), and TTF-TCNQ (+'s).

maxima reported previously.⁶ We note that recent experiments on the low-temperature conductivity, and specific heat indicate that the thermodynamic transition occurs at lower temperatures than the conductivity peak and thermopower break.¹⁰

The potentially disordered compound DSeDTF-TCNQ has a more gradual transition indicated in Fig. 4. This compound has cations which form with the selenium atoms either on the same side of the molecule (*cis*-configuration) or on opposing sides (*trans*-configuration) (see Fig. 1). It is worth noting that *cis*-configuration has a permanent electrical dipole moment because of its lack of inversion symmetry. The crystal contains a mixture of *cis*- and *trans*-DSeDTF cations which we assume is a random array. The potential and structural disorder caused by this stacking appears to have noticeable consequences for the transport properties. In particular the phase transition is "smeared" as measured both by thermopower and by conductivity.⁶ The transition region from the thermopower is about 65 K, in good agreement with the conductivity peak.

III. ANALYSIS

For an uncorrelated degenerate Fermi gas, the thermopower can be obtained from the Boltzmann equation

$$S = -K_1/|e|TK_0, \quad (1)$$

$$\sigma = e^2 K_0, \quad (2)$$

where S is the thermoelectric power (Seebeck coefficient), σ is the conductivity, e is the electron charge, and T is the temperature. The generalized transport coefficients are given by

$$K_n = -\frac{1}{3} \int v_k v_k \tau_k (\epsilon_k - \mu)^n \frac{\partial f_0(k)}{\partial \epsilon_k} d^3K, \quad (3)$$

with band velocity v_k , scattering time τ_k , energy ϵ_k , Fermi-Dirac distribution function $f_0(k)$, and chemical potential μ .⁸

For a single one-dimensional band we can solve the above equations with the result

$$S = \frac{-\pi^2 k_B^2 T}{3|e|} \left(\frac{\epsilon_k''}{(\epsilon_k')^2} + \frac{\tau'(\epsilon)}{\tau(\epsilon)} \right)_{\epsilon=\epsilon_F}, \quad (4)$$

where ϵ_k' and ϵ_k'' are, respectively, the first and second derivative of the one-electron band energies with respect to crystal momentum. The primary assumption in the derivation of Eq. (4) is that none of the quantities vary appreciably on the energy scale of order of the thermal energy (usually stated as $kT \ll \epsilon_F$).

The band structure should be temperature independent whereas the scattering time should be temperature dependent. A linear thermopower term therefore gives an indication as to the band structure. The deviation from linear behavior is to be associated with the scattering and hence is indicative of the conduction mechanism.

For two conducting bands, the Boltzmann equation yields the following more complicated form for the thermopower:

$$S = \frac{-\pi^2 k_B^2 T}{3|e|} \left(\frac{\tau_1(\epsilon) \epsilon_{k_1}'' / \epsilon_{k_1}' + \tau_2(\epsilon) \epsilon_{k_2}'' / \epsilon_{k_2}' + \tau_1'(\epsilon) \epsilon_{k_1}' + \tau_2'(\epsilon) \epsilon_{k_2}'}{\tau_1(\epsilon) \epsilon_{k_1}' + \tau_2(\epsilon) \epsilon_{k_2}'} \right)_{\epsilon=\epsilon_F}. \quad (5)$$

This can be reduced to the more general form usually seen for any number of bands

$$S = \left(\frac{\sum_i \sigma_i S_i}{\sum_i \sigma_i} \right), \quad (6)$$

where the thermopowers are weighted by their respective conductivities.¹¹

The bands with which we are dealing are formed by π electron overlap at relatively large distances so that tight-binding bands are appropriate. This is corroborated by calculations of Berlinsky *et al.*¹² who derive values of $t \sim 0.1$ eV for the transfer integrals. The band-structure contribution to the thermopower for a single band is then

$$S = \frac{-\pi^2 k_B^2 T}{6|e|t} \frac{\cos \frac{1}{2} \pi \rho}{1 - \cos^2 \frac{1}{2} \pi \rho}, \quad (7)$$

where ρ is the electron density in the band ($\rho=1$ for one electron per site) and t is the transfer integral ($4t$ is the bandwidth). For $\rho < 1$ (a less than half-filled band) the thermopower is negative or electronlike. For $\rho > 1$, S is positive or holelike as might be expected from simple arguments.

In the present case we must consider the two bands formed by the TTF (or derivative) cations and the TCNQ anions. As the electron concentrations are determined by charge transfer, the sum of ρ (TTF) and ρ (TCNQ) must be two. Photoemission¹³ and more recently low-temperature x-ray diffraction measurements¹⁴ indicate an electron density of 0.6 for TCNQ. Hence we expect negative thermopower from the TCNQ chain and positive from the TTF.

If we take equal scattering times τ_1 and τ_2 on the two chains, Eq. (5) becomes

$$S = \frac{-\pi^2 k_B^2 T}{3|e|} \left(\frac{\cos \frac{1}{2} \pi \rho / \sin \frac{1}{2} \pi \rho + \cos \frac{1}{2} \pi (2-\rho) / \sin \frac{1}{2} \pi (2-\rho) + \tau'(\epsilon) / \tau(\epsilon)}{2t_1 \sin \frac{1}{2} \pi \rho + 2t_2 \sin \frac{1}{2} \pi (2-\rho)} \right) = \frac{-\pi^2 k_B^2 T}{3|e|} \frac{\tau'(\epsilon)}{\tau(\epsilon)}. \quad (8)$$

Independent of either of the bandwidths (or the sign of the transfer integrals) or of the amount of charge transfer, the band-structure term is zero (for $\tau_1 = \tau_2$).

A. Ideal metallic region

The scattering term involving $\tau'(\epsilon)/\tau(\epsilon)$ appears to fall off as temperature is increased. Typically elemental metals exhibit a linear term only at high temperatures.¹¹ We therefore take the thermopower at the highest temperature as being most representative of the linear band-structure term.

The fact that the room-temperature thermopower varies from $-28 \mu\text{V/K}$ for TTF-TCNQ to $-10 \mu\text{V/K}$ for DSeDTF-TCNQ, to $+3 \mu\text{V/K}$ for TSeF-TCNQ can be interpreted in several ways. Using a single-band model as in Eq. (7), one would associate a change of charge transfer with the cation variation, going from approximately $\rho = 0.6$ for TTF to $\rho = 1$ for TSeF (all of the conductivity being on the TCNQ chain). Gas-phase ionization energy determinations for the TTF and TSeF cations show that TTF is a better donor, therefore making this interpretation less viable.¹⁵

In a two-band model, the large change in room-temperature thermopower comes from the *relative* scattering times on the two chains. In TTF-TCNQ, the room-temperature conductivity is dominated by the TCNQ chain. The scattering time is large on TCNQ as its bandwidth is larger than TTF.¹⁶ In TSeF-TCNQ, both chains conduct comparably as the cation bandwidth has increased, the total conductivity is increased¹⁷ (see Table I), and the scattering times are nearly equal, producing near-zero thermopower as in Eq. (8). The DSeDTF-TCNQ case is in between, the disorder having a small effect at 300 K.

Preliminary measurements on the alloy system $\text{TTF}_{1-x}\text{TSeF}_x\text{TCNQ}$ strongly favor the second interpretation.¹⁸ For $x = 0.68$, the room-temperature thermopower goes to the TTF-TCNQ value of $-28 \mu\text{V/K}$. The cation chain has been selectively disordered so that the conductivity is almost entirely on TCNQ, giving a large negative value as in TTF-TCNQ.

B. Semiconductor regime

The thermopower for a semiconductor can be approximated in Boltzmann theory by

$$S = \frac{-k_B^2}{|e|} \left(\frac{b-1}{b+1} \frac{E_g}{kT} + \ln \frac{m_h}{m_e} \right), \quad (9)$$

where b is the ratio of electron-to-hole mobility

($b = \mu_e/\mu_h$), and m_h and m_e are, respectively, the effective mass of the holes and electrons.⁸

In the temperature range directly below the metal-insulator transition, there appears a characteristic difference between TTF-TCNQ and the two other salts studied. In the previously published data on TTF-TCNQ there appears a plateau in the thermopower from 40 to 58 K which was sample independent.⁷ At temperatures below 40 K, the thermopower became more characteristically semiconducting. It has been noted in several experiments that a second transition may take place in TTF-TCNQ at 40 K. Conductivity data along the highly conducting axis shows a well defined exponential behavior only below 40 K,¹⁷ the anisotropy shows a second maximum at 40 K,¹⁹ and the thermal conductivity also shows structure at this temperature.²⁰

From 40 to 58 K, the thermopower of TTF-TCNQ is positive. In light of the two transitions and a double-chain model, we suggest that at 58 K the TCNQ chain forms an energy gap and becomes insulating. The conductivity is then dominated by the TTF chain producing the positive thermoelectric power. Additional support for this suggestion comes from the preliminary study of the alloy series $\text{TTF}_{1-x}\text{TSeF}_x\text{TCNQ}$.^{18,21} For $x = 0.03$, the thermopower is very similar to that of pure TTF-TCNQ down to about 100 K. There is a transition at ~ 58 K but the thermopower never becomes positive. The TSeF doping has altered the cation chain so that it never dominates the conductivity. The thermopower therefore remains negative.

In contrast to TTF-TCNQ, conductivity studies on the TSeF and DSeDTF salts show no anomalous behavior below the metal-insulator transition.¹⁷ In agreement with those measurements, the thermopower shown in Figs. 3 and 4 shows no region below the respective transition temperatures in which the thermopower levels off or shows nonsemiconducting behavior.

In the semiconducting state the thermopower is strongly impurity dependent, as has been shown for TTF-TCNQ. This is due to the strong dependence of the position of the chemical potential in the gap on the presence of donors or acceptors. In an extrinsic semiconductor, the thermopower measures the difference in energy between the Fermi level and the edge of the band responsible for the conduction. Therefore, the effective gap $E_g(b-1)/(b+1)$ in the thermopower [Eq. (9)] will generally be a fraction of the gap as measured by a conductivity experiment.

Just below the transition temperature of the TSeF

salt we find an inverse T dependence with ϵ_{gap} effective ≈ 100 K, in reasonable accord with the conductivity, measurement of $\epsilon_{\text{gap}} \approx 300$ K.¹⁷ For TTF-TCNQ we can look just below 40 K in both thermopower and conductivity. We find from thermopower, ϵ_{gap} effective ≈ 200 K and from conductivity, $\epsilon_{\text{gap}} \approx 500$ K.¹⁷

C. Nonideal metallic regime

The understanding of the strong deviation from linear behavior in the nonideal metallic regime is by itself very important. The fact that the deviation is semiquantitatively the same for TTF-TCNQ and TSeF-TCNQ and qualitatively the same for DSeDTF-TCNQ is indicative of a common mechanism for transport in these crystals. In the following we would like to propose two distinct possibilities.

Under the assumption that electron-phonon scattering can be ignored with respect to phonon-phonon scattering. i. e., no phonon drag, in the metallic state we see from Eq. (4) that two terms contribute to the thermopower. The first, $\epsilon_k''/(\epsilon_k')^2$ is a band-structure term which we expect to be temperature independent in the metallic regime. The second $\tau'(\epsilon)/\tau(\epsilon)|_{\epsilon_F}$ involves the scattering process and can have considerable temperature dependence. If the band-structure term is reduced the scattering term will dominate and the thermopower will be smaller and nonlinear. Experimentally this could be the situation as we go from TTF-TCNQ to TSeF-TCNQ.

A comparison of the deviation from linearity (Fig. 4) in the three salts implies that the scattering processes are the same through the series with the DSeDTF compound having a smaller effect due to the intrinsic disorder mentioned previously [which would smear out the energy dependence of $\tau(\epsilon)$]. The similarity in scattering processes is also shown in the previously published conductivity study.⁶

From Eq. (4) we see that the positive sign of the scattering term is caused by a negative value of $\tau'(\epsilon)$ or a scattering rate with positive energy derivative. The data clearly show that the energy dependence is sharpening up as temperature is decreased. The scattering rate associated with acoustic phonons has the opposite energy dependence. Possible mechanisms for the implied scattering-rate derivative are optical phonons or a gap forming in the electronic density of states.²²

The observation of smaller energy derivative of the scattering rate for DSeDTF-TCNQ is not unexpected. Intuitively faster electrons are expected to be scattered less efficiently by the static disorder than the slower electrons.¹¹

In terms of the two-band model [Eq. (5)], the

deviation from linearity also corresponds to the temperature dependence of τ . One can envision the scattering time decreasing on the TCNQ chain, so that the positive contribution of the cation chain becomes more dominant, resulting in an increase in the thermopower as temperature is lowered toward the transition.

It is also possible that phonon drag plays a role in these compounds evidenced by the characteristic $1/T$ deviation from linearity (which fits only approximately in the region $140 > T > 60$). However, phonon drag is only a sizeable effect at temperatures small compared to the Debye temperature (≈ 100 K) and for defect and impurity-free samples. Neither of these conditions is fulfilled in our crystals as a strong deviation from linearity appears below ≈ 140 K.

IV. CONCLUSION

A two-chain model seems most appropriate for a discussion of conductivity in this series of organic conductors. Within this model, the thermoelectric power reveals a good deal of information as to which chains are dominating the conductivity. However, a detailed transport theory for the relative scattering times on the two chains is necessary for quantitative analysis of this data. Such a theory has been proposed by V. Shante using dynamic disorder.²³

The thermopower data presented here suggests that the TCNQ chain dominates the conductivity (has a larger scattering time) in TTF-TCNQ above the 58 K transition. From 58 to 40 K the conductivity is dominated by the TTF chain (implying that the 58-K transition involves primarily the TCNQ chains). A comparison of the conductivity of TTF-TCNQ and TTF_{0.97}TSeF_{0.03}TCNQ in this temperature range has shown that this is in fact the case.¹⁷ In TSeF-TCNQ, the two chains contribute approximately equally to the conductivity at room temperature probably due to the increased bandwidth of the cation. Strong support for this argument as to relative cation-anion bandwidths is found in the EPR g -shift analysis of Tomkiewicz and Taranko.¹⁶

DSeDTF-TCNQ has some contribution to conductivity from both chains but at room temperature is dominated by the TCNQ chain. Its transition is "smeared" by the slight static cation disorder.

The temperature dependence of the thermopower in the metallic state shows deviations from linearity which can be associated with the scattering processes. The fact that these deviations are similar for TTF-TCNQ and TSeF-TCNQ indicates that there is a common mechanism for transport in these crystals in confirmation of earlier conductivity measurements.

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