Because of spin degeneracy, any level into which it goes will be partially filled. Thus we may apply this model to $(V, \mathrm{Ti})_2O_3$ by assuming that the lowest Ti level, whatever its symmetry, slightly penetrates the V_2O_3 host valence or conduction band, whatever their symmetries.

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Thermoelectric Power of Tetrathiofulvalinium Tetracyanoquinodimethane*

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Measurements of the thermopower of the organic conductor tetrathiofulvalinium tetracyanoquinodimethane have been made in the region 10–300°K. At high temperatures ($T > 140$°K) the samples are metallic showing increased electron correlations as the temperature is lowered to about 56°K. At this point the thermopower is zero and a discontinuity marks the transition to the insulating state.

In a recent Letter Coleman *et al.*[1] reported the observation of a high conductivity maximum in the organic charge-transfer salt tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ). The magnitude and temperature dependence were interpreted in terms of superconducting fluctuations preceding a transition to a Peierls insulating ground state. The extraordinary conductivity maximum has been observed in only a few of the many samples tested. The remaining samples show a qualitatively similar conductivity, but with much smaller maxima of magnitude varying from 5 to 25 times the room-temperature value, in general agreement with the results of Ferraris *et al.*[2]

The structure of TTF-TCNQ[3] consists of alternating chains of TCNQ anions and TTF cations, creating strong anisotropy in the electronic properties and a quasi-one-dimensional conductivity similar to many of the other highly conducting TCNQ salts.[4] The one-dimensional chains are extremely sensitive to imperfections, defects, and impurities as a conductivity measurement on a highly conducting chain would be limited by the resistance of any interruptions. It is therefore plausible that the measurement of an extremely high conductivity would only be observed in near-perfect crystals. The thermoelectric power, however, is a *zero-current* transport measurement and would not be limited by breaks in the chains assuming that most of the temperature drop occurred across the unbroken regions (which of necessity for the high conductivity are much longer than the insulating regions). We would therefore expect, and indeed observe, only one type of behavior for the samples measured (about 15 so far).

The thermopower was measured by mounting the samples on 1- or 0.5-mil gold wires with silver paint contacts and alternately heating the wires while measuring their temperature difference and the voltage generated across them. The temperature gradient was varied and reversed at each sample temperature. The temperature gradient and drift during each measurement could be controlled so that the Seebeck coefficient measured was typically an average over 1°K in all regions except near the transition at $\approx 56°$K where it is an average over less than 0.5°K. Absolute temperature was determined to better than 1°K by a combination of platinum and germanium temperature resistors and a copper-Constantan thermocouple. Details of the experimental apparatus will be published elsewhere.[5]

The absolute thermoelectric powers for a series of crystals are shown in Fig. 1. In Fig. 2 we have plotted the data from one crystal for clarity. The thermopower of the gold leads has been subtracted throughout the plot. This is only of importance just at the temperature of the transition where $-S_{\mathrm{Au}} = 1.1\ \mu\mathrm{V}/°\mathrm{K}$. In other regions S_{Au} is very small compared with the thermopower of the TTF-TCNQ. (In many measurements on organic samples the metal leads are not subtracted as their contribution is negligible.)

At high temperature, $140°\mathrm{K} < T < 300°\mathrm{K}$, the Seebeck coefficient is linear with temperature extrapolating through zero to within 0.5 μV/°K. The linear temperature dependence is characteristic of a degenerate electron gas and metallic conduction. The most sensitive electron transport property of a metal is its thermopower. A simple calculation assuming free electrons and energy-independent scattering yields the result[6]

$$S = \pi^2 k^2 T / 6 e \epsilon_{\mathrm{F}}. \tag{1}$$

The slope of the linear portion of our data can then be used to obtain the Fermi energy. Our result of $\epsilon_{\mathrm{F}} = 0.14$ eV is in agreement with an estimate obtained from the high-temperature (Pauli) susceptibility.[7]

In fact, the agreement between the thermopower and the susceptibility is surprising. From the Boltzmann equation we find that the thermopower is given by

$$\begin{aligned} &S = K_1 / e T K_0, \\ &K_n \equiv -\tfrac{1}{3} \int v_K^2 \tau_K (\epsilon_K - \mu)^n (\partial f_{0K} / \partial \epsilon_K)\, dK, \\ &\sigma \equiv e^2 K_0, \end{aligned} \tag{2}$$

which reduces to Eq. (1) for free electrons with energy-independent scattering. We expect tight binding to be more appropriate for the energy bands in the TCNQ salts.[8] For a one-dimensional half-filled tight-binding band with τ_K independent of ϵ the thermopower is rigorously zero from Eq. (2). The assumption which is obviously least appropriate is the form of $\tau(\epsilon)$.

Alternatively, one might argue that the bands in question are not half filled as a result of incomplete charge transfer. However, the molecular bond lengths suggest significant charge transfer,[3] and it has been argued theoretically that the charge transfer to the ionic configuration should

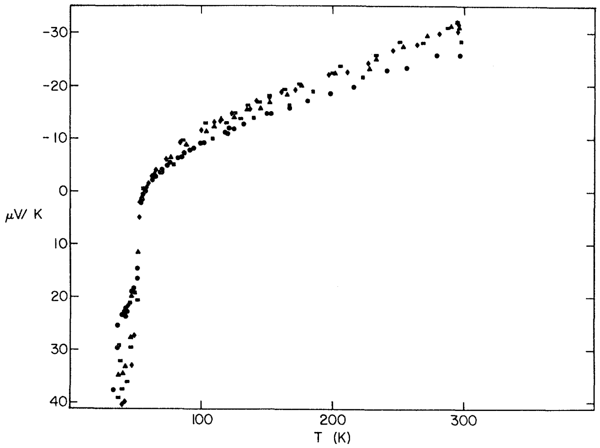

FIG. 1. Absolute thermoelectric power of several single-crystal samples of TTF-TCNQ.

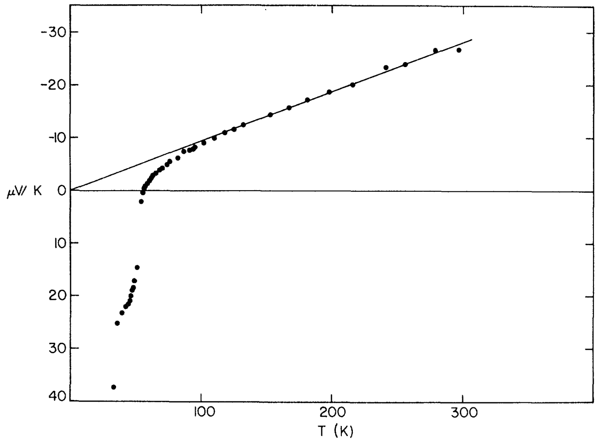

FIG. 2. Absolute thermopower of one single crystal of TTF-TCNQ.

be complete.[9]

We emphasize that a linear temperature dependence of the thermopower is a general result for a degenerate Fermi gas independent of the dimensionality of the sample. The coefficient of the linear term depends on the band structure and the scattering processes. For one dimension Eq. (2) can be approximated as

$$S=\frac{\pi^2k^2}{3e}\left[\frac{\epsilon_K''}{(\epsilon_K')^2}+\frac{\tau'(\epsilon)}{\tau(\epsilon)}\right]T\bigg|_{\epsilon=\epsilon_F}. \qquad (3)$$

It should be noted that the high-temperature thermopower of these samples is very different from that found in other highly conducting quasi-one-dimensional solids, none of which show an appreciable temperature range with linear S extrapolating to zero.[10] These results are probably the best evidence to date that TTF-TCNQ is metallic at high temperature. (We would not expect large deviations from the linear term from phonon drag effects at high temperatures.)

The most interesting temperature region is from 140 to 57°K, where Coleman *et al.* claim to have observed superconducting fluctuations preceding a transition to a distorted state or Peierls instability. It is clear from our data that there is phase transition at about 56°K. It is not yet possible to determine whether the thermopower or its temperature derivative is discontinuous at this point. Below 140°K there is a deviation from the linear T dependence with S decreasing to zero at the transition temperature. At this point the absolute thermopower of the TTF-TCNQ is zero to a precision of better than 0.2 μV/°K. (During the experiment the reading near this point was about 1 μV/°K, corresponding to the Au leads.)

The gradual appearance of a semiconducting gap as temperature is lowered is not a reasonable explanation of the data. In this region (140°K $> T >$ 57°K) the conductivity in all samples is still increasing. In addition, a variety of other measurements also indicate that the samples are metallic above the transition.[1,7] The thermopower itself indicates that the transition is sharp rather than gradual and hence that we are not merely following a smooth transition from electron to hole conductivity.

Since the thermopower is a measure of the entropy per carrier it is most reasonable to ascribe the tendency toward zero as the transition is approached from above to the formation of strong electron-electron correlations. Such correlations might be explained by either of the present theories, namely, fluctuations into the superconducting state with the formation of pairs as suggested in Ref. 1, or fluctuations into the dynamically distorted state as suggested by Bardeen[11] from the earlier work of Fröhlich.[12] It is well known that when measured statically (low frequency) the thermopower of a superconductor is zero.[13] However, there has been no theoretical or experimental work on the effect of superconducting fluctuations on the thermopower, such as has been available for conductivity. To prompt such work we mention that above the transition the Seebeck coefficient is fairly well described by $(T-56°\text{K})^{3/4}$ over a decade in S, and up to about $T-56°\text{K}\approx 50°\text{K}$. However, from different plots the data can be fitted by $(T-T_c)^\alpha$, $0.6<\alpha<0.8$, as T_c is changed from 55 to 58°K.

Other interpretations of the phase transition in TTF-TCNQ are also possible, but the vanishing of the thermopower at the transition, independent of small impurity doping, must be accounted for in forthcoming theories.

Below the transition the thermopower becomes positive and increases as the temperature is lowered (Fig. 3). The positive sign implies that the conductivity is dominated by holes. The large nonlinear (with T) thermopower indicates we are no longer dealing with a degenerate electron gas and thus a metal-insulator transition has taken place very sharply at 56°K.

Recently, we obtained large samples of TTF-TCNQ prepared using a different synthesis by IBM Research Laboratory in San Jose. These samples were prepared from TTF and TCNQ starting material which was at an early stage in the purification process and hence the resulting

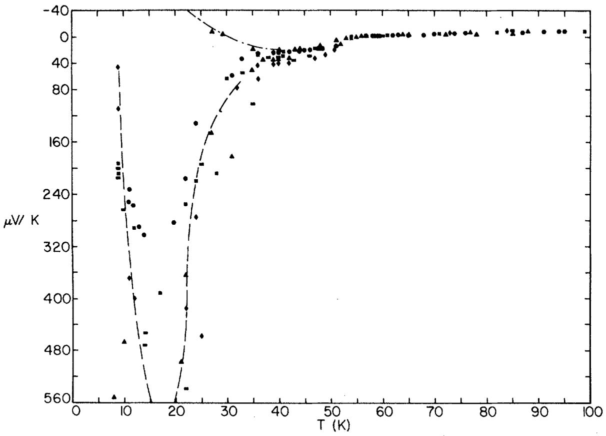

FIG. 3. Absolute thermopower of several single crystals of TTF-TCNQ. Dashed line, temperature dependence of the "Penn" samples; Dash-dotted line, temperature dependence of the IBM samples.

TTF-TCNQ salt was known to be less pure than the samples prepared at the University of Pennsylvania. Their room-temperature conductivity was approximately a factor of 5 less than the best reported in Ref. 1. However, their larger size permitted four-probe conductivity along with themopower to be measured on the same crystals during the same run. The temperature dependence of the conductivity was the same as the "normal" samples reported in Refs. 1 and 2.

Above the transition the thermoelectric power of the two sets of samples is identical. Just below the transition both sets of samples have positive thermopower. However, the Penn samples continue to a large positive value whereas the IBM samples quickly cross zero again and go to a large negative value (≈ -500 μV/°K). This behavior indicates that above 56°K the Seebeck coefficient is determined by the degenerate electron distribution and metallic conductivity which is insensitive to excess electrons or holes. Below 56°K the thermopower is determined by the number and position of the donor and acceptor states. We would expect this behavior from impurities in an insulator.

One might argue that the fact that the thermopower goes to zero is not significant since at low temperature it is of opposite sign and therefore must cross zero. However, what is important is the way in which it goes to zero and the particular temperature at which $S = 0$. The transition from negative to positive is not smooth but rather tends to zero from high temperature and reaches zero just at the point where the curve breaks, corresponding to the temperature of the transition. The low-temperature thermopower does not extrapolate to zero at the same point.

Again it is useful to compare these results with other one-dimensional systems, in particular NMePh$^+$-TCNQ$^-$.[10] From the thermopower data of Ref. 10 one can see that at high temperature the Seebeck coefficient for NMePh$^+$-TCNQ$^-$ is small and negative, gradually changing over to a large positive contribution as temperature is lowered. The thermopower passes smoothly through zero at 150°K and fits a T^{-1} dependence nicely at lowest temperatures. The NMePh salt illustrates the behavior we would expect for a gradual metal-insulator transition with a temperature-dependent gap. It is qualitatively different from the observations reported in this paper.

From Eq. (2) it is clear that the thermopower is not unrelated to the conductivity so that one would expect a reduction in S where σ increases. That this does not account completely for the thermopower can be seen by noting that only a few samples reported previously have a sufficient increase in σ to reduce S as drastically as we find in all samples. Moreover, we would then expect S to vary as $(T - T_c)^{3/2}$ rather than a much lower power.

In conclusion, we have demonstrated that TTF-TCNQ is metallic at high temperatures, undergoes a sharp metal-insulator transition at about 56°K, and exhibits strong electron correlations as it approaches the transition from the metallic state. We plan to continue these measurements on samples prepared in other laboratories to check the consistency of the results and to probe the four-lead conductivity simultaneously.

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