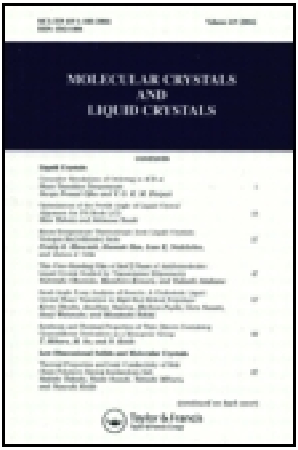

Molecular Crystals and Liquid Crystals

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Transport Studies of Several Novel Organic Conductors

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TRANSPORT STUDIES OF SEVERAL NOVEL ORGANIC CONDUCTORS

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Abstract We present the results of conductivity and thermopower measurements on several new conducting organic compounds. $(BEDT\text{-}TTF)_2BrO_4$ is isomorphous with the superconducting ReO_4 salt; our data show it to be metallic above 200K and semiconducting below 100K, although without any clear transition. In $(TMTSF)_2SiF_5$ the anion is neither octahedral nor tetrahedral; however, our results suggest behavior very like the octahedral salts. $(BEDT\text{-}TTF)_2InBr_4$ is semiconducting at room temperature with an activation energy of .12 eV. Low-temperature conductivity measurements on $(BEDT\text{-}TTF)_2I_3$ at 0.5 kbar show suppression of the known ambient-pressure superconducting state to below 1K, and an anomaly at 7K reminiscent of the CDW transition in $NbSe_3$.

INTRODUCTION

The two families of organic compounds based on tetramethyltetraselenafulvalene (TMTSF)[1] and bis(ethylenedithio)tetrathiofulvanene (BEDT-TTF or ET for short)[2] have recently drawn a great deal of attention. Since there are many other papers in these proceedings dealing with the various properties of these materials, we will dispense with the provision of a general background and concentrate on those points relevant to the present work.

$(TMTSF)_2X$ family

Most Bechgaard salts $(TMTSF)_2X$ can be divided into two groups based on the symmetry of the anion X - either octahedral or tetrahedral. The salts with octahedral anions (e.g., PF_6) typically have a spin density wave (SDW) ground state at ambient pressure, but superconduct under pressure, usually above 6 kbar.[3] The salt with the tetrahedral anion ClO_4, on the other hand, exhibits superconductivity at ambient pressure if it has been cooled slowly; if it is cooled quickly (quenched), it also has a SDW ground state. The sensitivity to cooling rate is due to the occurrence of a sluggish anion-ordering transition at 24K.[4] It is therefore interesting to look at the salt with X=SiF_5, since that anion has neither of the usual symmetries and is intermediate in size, and relate its behavior to that of the other salts. Such information could be useful in discovering the important parameters determining the ground state of these materials.

(BEDT-TTF)$_2$X family

The (BEDT-TTF)$_2$X (or (ET)$_2$X) family of organic compounds includes the first sulfur-based organic superconductor (ET)$_2$ReO$_4$, which superconducts under pressure.[5] (ET)$_2$BrO$_4$ is isomorphous with the ReO$_4$ salt[6] and thus on past experience could be expected to show similar behavior. Any significant differences in behavior should raise questions regarding our understanding of these materials.

Like the (TMTSF)$_2$X salts, most ET compounds are divided into two groups based on the symmetry of the anion. The group with tetrahedral anions are generally metallic, while the group with octahedral anions have all thus far been insulators at low temperature. $InBr_4$ is tetrahedral, but much larger than ReO_4 or ClO_4. Structural studies show the degree of bonding in (ET)$_2$InBr$_4$ to be intermediate, in a sense, between the bondings in the tetrahedral and octahedral salts,[7] so that its behavior provides a measure of the importance of the bonding pattern in determining the ground state.

(ET)$_2$I$_3$ is the first sulfur-based ambient-pressure organic superconductor, with a transition temperature near 1.5K.[8,9] We undertook measurements of the low-temperature conductivity under pressure in order to investigate an anomaly seen in electron spin resonance measurements at 0.5 kbar and 7K and to study the effect of pressure on the superconducting transition.

EXPERIMENTAL DETAILS

The crystals were prepared according to published procedures.[1-9]. The conductivity was measured in each case with a linear four-probe arrangement along the highly conducting crystal axis by applying a constant low-frequency ac current to the outer two probes and measuring the voltage on the inner two probes with a lock-in amplifier. Thermopower measurements were made using a low-frequency cycling technique which eliminates stray thermal voltages.[10] All contacts were made using conductive gold paint and gold pads evaporated onto the samples; the contact resistances were generally less than one ohm. Ambient-pressure studies were done in a closed-cycle refrigeration system capable of temperatures from 10K to 300K. Pressure studies were done in a conventional magnet dewar system using He^4 to obtain essentially hydrostatic conditions.[11]

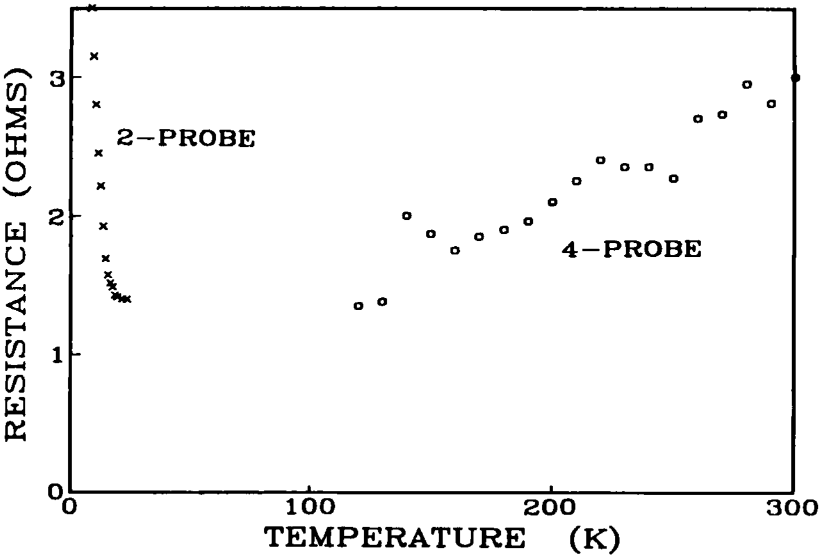

FIGURE 1. Resistance versus temperature of a typical $(TMTSF)_2SiF_5$ crystal. The scale for the 2-probe data is arbitrary).

RESULTS AND DISCUSSIONS

$(\underline{TMTSF})_2\underline{SiF_5}$

Figure 1 shows the resistance of a typical sample versus temperature. The room-temperature conductivity was about 1000 $(\Omega\text{-cm})^{-1}$. Note that the four-probe data stop at 120K. This is due to the fact that almost all the samples, with amazing consistency, broke in two very near that temperature. Thus only two-probe data, as shown in figure 1, could be obtained at low temperatures. Those data, however, clearly show the occurrence of a metal-insulator transition at about 12K. The thermopower versus temperature is shown in figure 2. Again, all the samples tested broke near 120K.

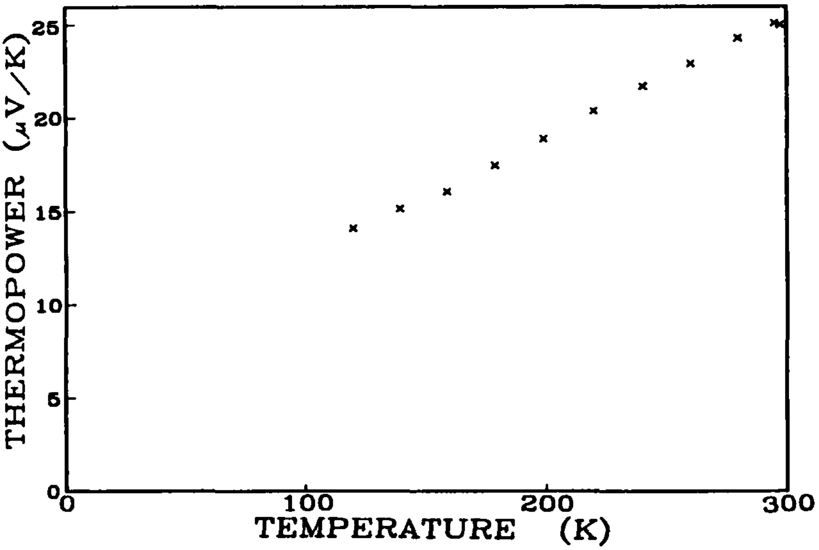

FIGURE 2. Thermopower of $(TMTSF)_2SiF_5$

The present conductivity and thermopower data are very similar to the data for the other TMTSF salts. The presence of a sharp transition near 12K, however, is reminiscent of several of the octahedral salts and would seem to imply that there is no anion disorder as in quenched ClO_4 and no ambient pressure superconductivity. One may argue that the odd symmetry of SiF_5 and its relatively large size cause it to affect the crystal like the octahedral anions. The perverse tendency of the samples to break near 120K is actually quite intriguing. The SiF_5 salt is, if anything, even more brittle and fragile than the other TMTSF salts. If there is a structural phase transition at that point, it would not be surprising that the crystals, which are subjected to stress by the gold paint contacts, fall apart. Actually, the same transition may be present in the other salts, which also tend to break in the same temperature region. To support this conjecture, we merely note the change in slope of the thermopower versus temperature of most of the family near 120K.[1]

$(ET)_2BrO_4$

The conductivity of $(ET)_2BrO_4$ versus temperature is shown in figure 3a. Note that, on cooling, the conductivity increases slightly from its room-temperature value of about 600 $(\Omega\text{-cm})^{-1}$. There is a broad maximum around 180K below which the conductivity decreases

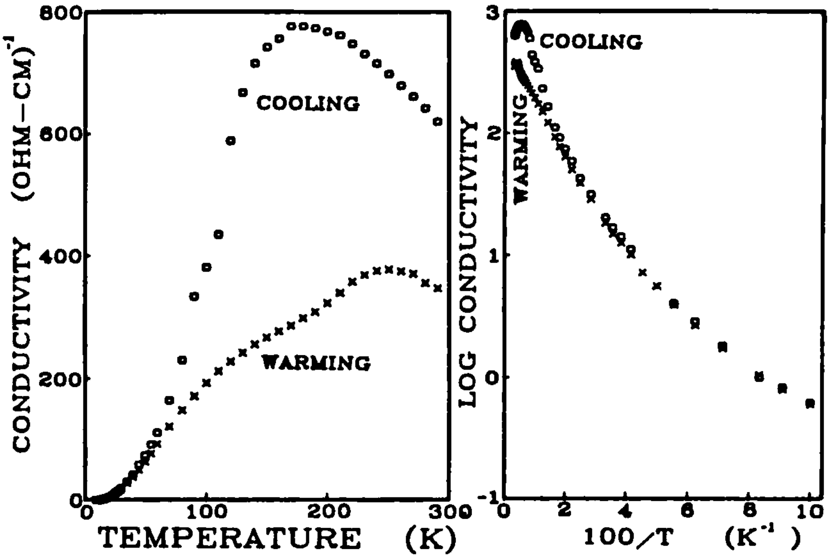

FIGURE 3. (a) The conductivity of $(ET)_2BrO_4$ versus temperature. (b) Log conductivity versus inverse temperature.

gradually toward zero, with no apparent anomaly to indicate a phase transition. Note also that on subsequent warming the conductivity is reduced and the position of the maximum shifted, presumably due to the series of small breaks encountered while cooling. The conductivity is plotted versus inverse temperature in figure 3b. The thermopower of a typical crystal is plotted in figure 4.

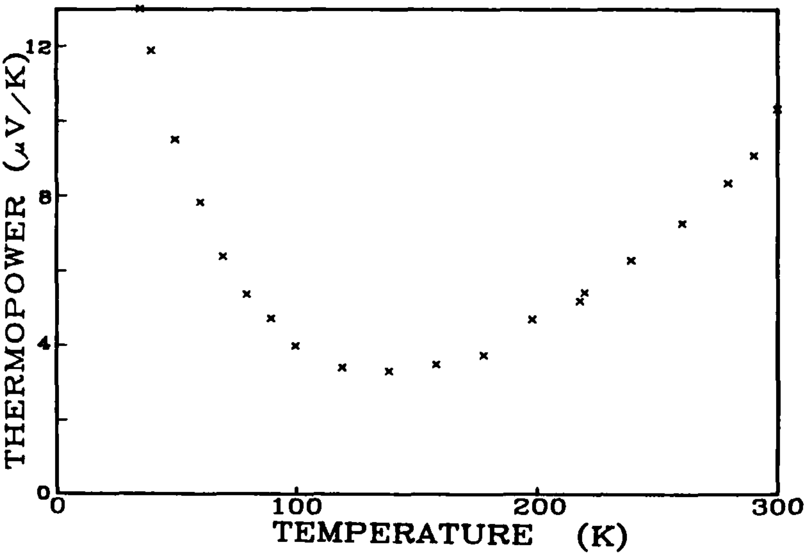

FIGURE 4. Thermopower of a typical $(ET)_2BrO_4$ crystal.

Both the conductivity and thermopower indicate a metallic state at high temperature (the thermopower is even smaller than for most organic metals) and a semiconducting state at low temperatures. But neither shows any sign of a phase transition: The changed position of the conductivity maximum during warming indicates that the maximum is extrnsic in origin. An interpretation consistent with the transport data is that of a disordered semiconductor, similar to quinolinium-$(TCNQ)_2$[12]. However, the structural[6] and ESR[13] data on $(ET)_2BrO_4$ both indicate low disorder. An alternative possible interpretation is that there is a narrow band gap, steric in origin, which is simply overcome by thermal energy at the higher temperatures.

It is difficult to reconcile the present data with the strikingly different behavior of $(ET)_2ReO_4$, which has an extremely sharp metal-insulator transition near 180K, since the compounds are isomorphous. The disorder idea is attractive, but as pointed out above, the direct evidence argues against disorder. Moreover, for the disorder to be itself responsible for nonmetallic behavior requires the system to be more one-dimensional than it is.

$(\underline{ET})_2\underline{InBr_4}$

This material is semiconducting even at room temperature, where $\sigma \simeq .1\ (\Omega\text{-cm})^{-1}$ and $E_a = .12$ eV, despite having a tetrahedral anion. The reason, apparently, is that $InBr_4$ is a very large tetrahedral anion, so that the S-S bonding is not as good as in the other tetrahedral salts.[7] The bonding is not as poor, however, as in the octahedral salts, so one might have expected an intermediate conductivity type. As it is, this compound may be regarded as an example of the fragility of the metallic state in the whole ET family.

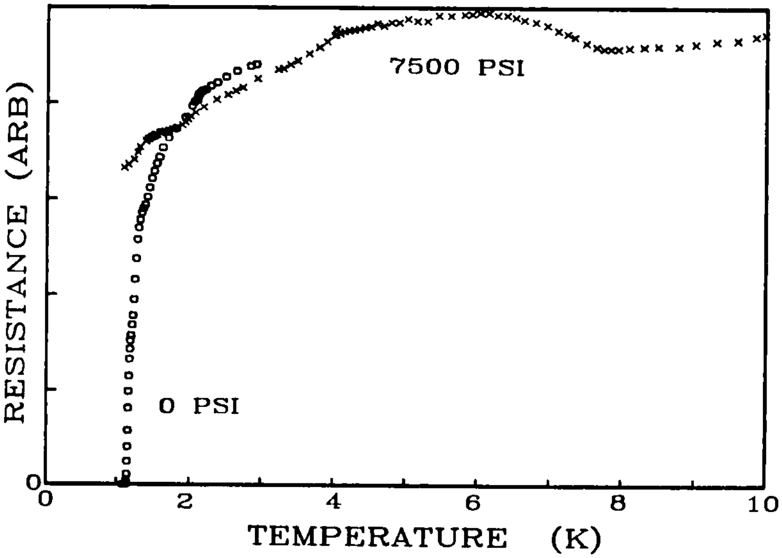

FIGURE 5. Resistance at low temperature of a typical $(ET)_2I_3$ crystal, at zero and 7500 psi pressure.

$(\underline{ET})_2\underline{I}_3$

Figure 5 shows the resistance of a typical crystal at low temperatures under both zero and 7500 psi pressures. Two significant effects of pressure are apparent from the figure. First, the superconductivity, which has T_c= 1.5K at ambient pressure, is suppressed to below one degree at 7500 psi (1/2 kbar), or $dT_c/dP \approx -1$ K/kbar. Thus the superconductivity in $(ET)_2I_3$ is even more strikingly sensitive to pressure than that of the TMTSF salts. Second, there is an anomaly in the 7500 psi resistance at 7K which is reminiscent of the charge density wave anomalies in $NbSe_3$.[14] Although the P=0 data shown in the figure go up only to 3K, we have uncalibrated cool-down data with no anomaly apparent. In $NbSe_3$, the many-body correlations act to destroy part of the Fermi surface, so the system is still metallic at lower temperatures. In the present case it seems reasonable to surmise that the application of pressure (perhaps by inducing disorder like that in quenched $(TMTSF)_2ClO_4$) tends to favor the formation of a weak spin density wave and hence the suppression of superconductivity. We note that the sample was cooled at the same speed in either pressure (about 1K per minute), so that cooling rate is not a relevant factor.

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