Structureless transition and strong localization effects in bis-tetramethyltetrathiafulvalenium salts [(TMTTF)₂X]

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(Received 28 September 1984)

We find a new "structureless anomaly" in several salts in the family of compounds of the form $(TMTTF)_2X$ (for $X = ReO_4$, SbF_6, AsF_6, and alloys of the latter anions). This anomaly is seen very clearly through thermopower studies and less clearly in conductivity data: In both cases it appears as a change in derivative of the corresponding transport property. There is no change in the magnetic susceptibility of the material at the anomaly, and no change in structure has been observed. We suggest that the presence of an anomaly of such description indicates that the electronic system is highly correlated and that this must be taken into account when modeling these materials, making such models rather complicated.

I. INTRODUCTION

Over the past few years the bis-tetramethyltetrathiafulvalenium salts [(TMTTF)₂X] and bis-tetramethyltetraselenafulvalenium salts [(TMTSF)₂X] have been widely studied[1] because among the many known organic compounds these are the only ones to show antiferromagnetic ground states and with the exception of the recently discovered [(bis-ethylenedithiolene)-tetrathiafulvalene] (BEDT-TTF) salts,[2,3] the only ones to show superconducting states. Another feature that distinguishes these salts from the other highly conducting organic charge-transfer salts is the highly localized charges of the commensurate anion array. The anions form sheets separating planes of conducting organic molecular stacks.[4,5] Close contacts between the anions and cations suggest an important interaction between these species.[6] In previous work, this interaction has largely been ignored. The anions in these compounds can be disordered or ordered[7,8] depending on the temperature and pressure range but in both cases will influence the charge carriers on the organic stacks. When disordered, the anions form scattering sites and when ordered, the long-range potential may introduce a gap in the charge excitation spectrum.

A comparison of the electrical properties of the TMTTF and TMTSF salts suggest that localization effects, if present, are more important in the TMTTF salts than in their selenium analogous: the sulfur compounds are typically 20 times less conducting than the TMTSF salts at 300 K and their resistivities increase on cooling below some broad minimum near 250 K.[9,10] Recently a comparative study of the electrical behavior of $(TMTTF)_2X$ compounds containing the octahedral anions, MF_6 ($M = P, As, Sb$) has been published and an unexpected high-temperature anomaly has been reported in some of these materials, in which the temperature coefficient of resistance (TCR) abruptly increases.[11] We present in this paper additional data on the transport properties of these compounds and compare them with those obtained for salts of anions of different symmetries.

II. EXPERIMENTAL

The samples were prepared by standard electrochemical techniques from 1,1,2-trichloroethane or dichloromethane.[12] Two series of samples containing octahedral and tetrahedral anions, respectively, were studied. The $(TMTTF)_2(SbF_6)_{1-x}(AsF_6)_x$ samples were taken from the same batches as those used in the earlier work of Laversanne *et al.*[11] For these samples, the value of x was checked by x-ray energy dispersive fluorescence methods and was found to be in good agreement with the starting concentration of anions in solution. This is a general result which occurs because of the high solubility of the tetrabutylammonium salts of the anions. Consequently we have a high degree of confidence that for the $(TMTTF)_2(ReO_4)_{1-x}(ClO_4)_x$ alloys prepared for this study, the value of x is that of the anion concentration in solution.

The conductivity measurements were made using standard four-in-line probe ac lock-in techniques with silver paint contacts. Pressure was applied using a small Be-Cu clamp cell with the samples contained in a teflon cell using heptane as the pressure fluid. Thermopower was measured with a standard 2 contact arrangement. The voltage versus temperature loops were collected in a digital form and analyzed using an IBM/PC personal computer.

III. RESULTS

A. Resistivity $\rho(T,P)$ of various $(TMTTF)_2X$ salts

The $(TMTTF)_2X$ salts are moderate conductors at ambient pressure $[\sigma \sim 30 \ (\Omega \ cm)^{-1}]$. Their resistivities exhibit broad minima at temperatures near 200 K and in-

crease at even lower temperatures. We will refer to this behavior descriptively as "electronic localization" and give evidence for this later. For most of these salts electronic localization occurs continuously as the temperature is reduced. However, in certain cases a more rapid change in conductivity is found in a narrow temperature range. In particular one finds such behavior for the $X=$SCN, SbF$_6$, and ReO$_4$ salts. For the $X=$SCN salt, this anomaly is the signature of an ordering of the anions which are disordered in all these salts at room temperature. At this phase transition, a $(a, 2b, 2c)$ superstructure in established.[13] For the $X=$SbF$_6$ salt there is a sharp anomaly in σ near 155 K (see Fig. 1) but unlike the $X=$SCN salt no evidence has been found for a change in structure below the anomaly. The $X=$ReO$_4$ salt (see Fig. 2) shows both the behavior of the $X=$SCN and SbF$_6$ salts, in that there are two anomalies in σ. The lower temperature anomaly shown in Fig. 2 at 160 K has been shown to be associated with an anion ordering into a $(2a, 2b, 2c)$ superstructure below this temperature;[14] x-ray studies at a second anomaly around 225 K have failed to reveal any structural distortion at this temperature as is also the case for the 155-K transition in (TMTTF)$_2$SbF$_6$.[11,15]

Pressure has been shown to have an important effect on the electrical properties of the (TMTTF)$_2X$ salts: Extensive work has been carried out on various salts including the $X=$Br,[16] PF$_6$,[16] ClO$_4$,[16] and SCN (Ref. 17) salts. To help understand the unusual electrical properties of these two salts we have extended these measurements to higher pressures. The results are given in Figs. 1 and 2. Since random jumps in resistance often occur when applying pressure the measured absolute value is not very meaningful but the variation of resistivity with temperature is found to be less sample dependent. For this reason we have normalized the data. For (TMTTF)$_2$SbF$_6$ the anoma-

FIG. 2. Normalized resistivity versus temperature of (TMTTF)$_2$ReO$_4$ at 1 bar and 5 kbar.

ly, as detected by the maximum in the slope of the resistivity curve, becomes less obvious when the pressure is increased and the application of moderate pressure appears to suppress the anomaly. Thus, at 5 kbar the resistivity versus temperature curve of the SbF$_6$ salt is close to that of the ambient pressure behavior of (TMTTF)$_2$AsF$_6$. The 225-K anomaly of (TMTTF)$_2$ReO$_4$ is also quickly suppressed under pressure. At 3 and 5 kbar the resistivity curve only shows one anomaly near 160 K suggesting that only anion ordering occurs at these low pressures. At higher pressures we find a single anomaly near 160 K indicating that the anion order-disorder transition is much less sensitive to pressure.

B. Thermopower $S(T)$ of various (TMTTF)$_2X$ salts

Thermopower data for several compounds are given in Fig. 3. Data for several other salts in this series have been published by Mortensen et al.[18] As shown in Fig. 3 the thermopower for all these materials exhibits a weak tem-
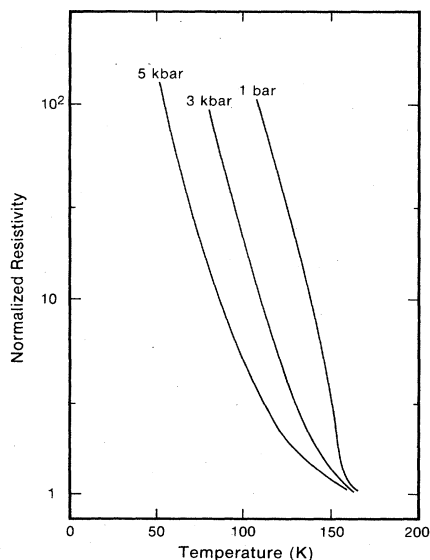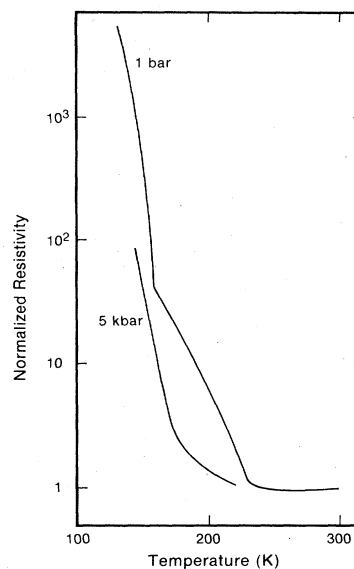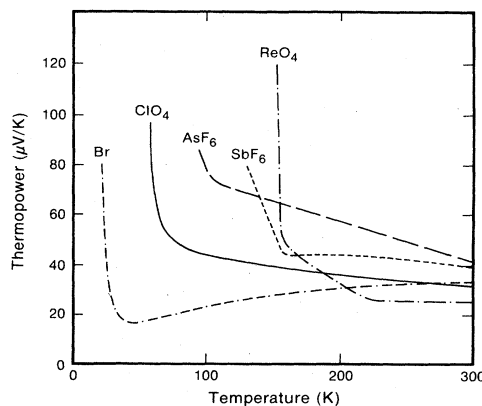

FIG. 1. Normalized resistivity versus temperature of (TMTTF)$_2$SbF$_6$ at 1 bar and 3 and 5 kbar. The data at 1 bar is from Ref. 11.

FIG. 3. Thermopower versus temperature curves of several (TMTTF)$_2X$ salts.

perature dependence near room temperature: With the single exception of the Br salt the slope of the S versus T curve is slightly negative. At lower temperatures below some characteristic temperature the thermopower curve shows a more marked temperature dependence. In most cases this behavior can be correlated with anomalies in conductivity at similar temperatures. In certain cases [X=ClO$_4$, ReO$_4$ (at 160 K), SCN] these anomalies can be identified with anion order-disorder transitions but in the majority of cases no corresponding structural transition has yet been observed. Our data is in good agreement with that reported by Mortensen et al.[18] near room temperature but there are some differences in these data at lower temperatures which may reflect some differences in extrinsic behavior or quality of the samples. Note particularly the position of the minimum for the Br salt which we find near 40 K but Mortensen et al. find near 70 K and the slope of the thermopower curve for the X=ClO$_4$ salt near 75 K. In the latter case S can become very negative or very positive depending on sample batch: We find that for our best samples S becomes positive at low temperatures in contrast to the data presented by Mortensen et al.

C. Alloys with mixed anions

As discussed above, S data confirm the presence of a "structureless anomaly" (SA in the X=SbF$_6$ and ReO$_4$ salts near 160 and 225 K, respectively. To investigate these transitions in more detail we have prepared alloys of these salts with corresponding anions of the same symmetry.

We present in Fig. 4 thermopower versus temperature data for a series of alloys of the form (TMTTF)$_2$(SbF$_6$)$_{1-x}$(AsF$_6$)$_x$. The absolute value of S at 300 K (40–50μV/K) is approximately the same within this series and is also similar to values obtained for other (TMTTF)$_2X$ salts (see Fig. 1). The most noticeable feature
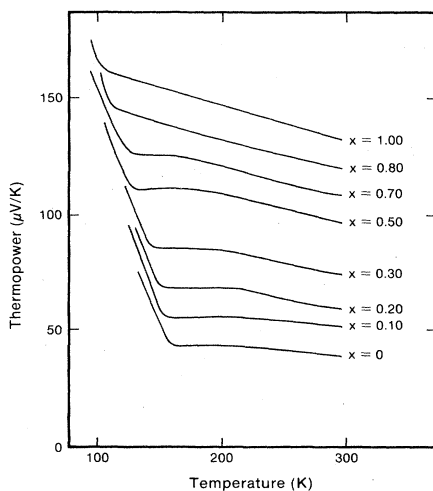
of Fig. 4 is the abrupt change in slope of all the thermopower curves at temperatures varying from $T_{SA} \sim 155$ K in the X=SbF$_6$ salt (x=0) to ~ 95 K in the X=AsF$_6$ salt (x=1). As x is varied from 0 to 1 the temperature of this anomaly varies monotonically. These results are in agreement with previous conductivity studies[11] although the anomaly is observed much more clearly in these thermopower data, particularly at high x. Above these anomalies S is weakly temperature dependent. However, the slope of the S-T curve is significantly larger for alloys containing more than 20% of AsF$_6$. Indeed there appears to be a crossover from behavior characteristic of SbF$_6$ to that of AsF$_6$ for $x \sim 20$%. The behavior of S in this temperature regime appears to be rather complicated: Note the presence of a plateau in S just above T_{SA} for $x < 80$% whose origin is unclear.

We have also studied a second series of alloys containing tetrahedral anions of the form (TMTTF)$_2$(ReO$_4$)$_{1-x}$(ClO$_4$)$_x$ (x=3% and 5%). The resistivity thermopower and EPR properties of these systems as a function of temperature are shown in Figs. 5

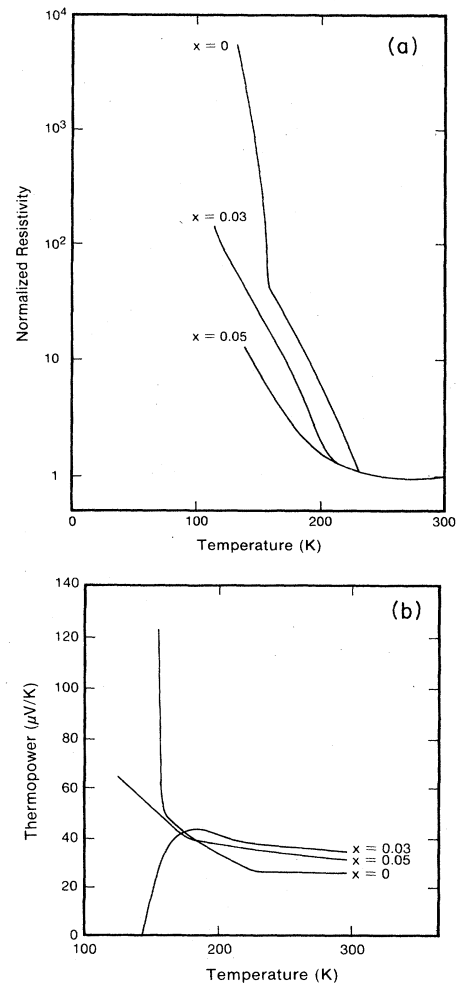FIG. 4. Thermopower of the (TMTTF)$_2$(SbF$_6$)$_{1-x}$(AsF$_6$)$_x$ alloys. For clarity, the origin of several curves has been shifted ($+5$ μV/K, $+20$ μV/K, $+30$ μV/K, $+40$ μV/K, $+60$ μV/K, $+65$ μV/K, and $+85$ μV/K for z=0.1, 0.2, 0.3, 0.5, 0.7, 0.8, 1, respectively). However, the absolute value of S at 300 K is similar for all the salts.

FIG. 5. Temperature dependence of (a) the resistivity and (b) the thermopower of (TMTTF)$_2$(ReO$_4$)$_{1-x}$(ClO$_4$)$_x$ salts for x=0, 3%, and 5%.

and 6. Below the 160-K transition in $(TMTTF)_2ReO_4$ the EPR susceptibility goes to zero [see Fig. 6(b)] indicating that a gap is opened in the magnetic excitation spectrum in agreement with the observation of a $(2k_f, \frac{1}{2}, \frac{1}{2})$ distortion from x-ray experiments.[14] Note in contrast that the EPR susceptibility is unaffected at the anomaly at $T_{SA} \sim 225$ K. ESR data for the $x = 5\%$ alloy shows that the susceptibility for this compound goes to zero below about 100 K indicating T_{OD} is substantially depressed by the introduction of a small amount of ClO_4. Conductivity and thermopower data which probe the upper anomaly show that T_{SA} is less affected by alloying with ClO_4. T_{SA} occurs at about 200 and 180 K for the 3% and 5% doped samples, respectively, as shown by both σ and S data. Note that doping $(TMTTF)_2ReO_4$ with small amounts of ClO_4 considerably modifies the behavior of S below the anion ordering: a change in sign of S is shown in Fig. 5(b) for the 3% doped sample as compared with $x = 0$, and we find similar behavior for doping levels of $\sim 1\%$. However, for the 1% case the conductivity behavior is almost identical to that of the undoped material. These results are not inconsistent with our earlier remarks concerning the sensitivity of the thermopower data to crystal quality.

The jump of both the ESR linewidth and susceptibility at T_{OD} in $(TMTTF)_2ReO_4$ confirms the first-order character of this phase transition inferred from detailed x-ray studies.[14] In contrast ESR data for the 5% salt (see Fig. 6) indicates that the ordering which now occurs around 100 K is probably a second-order phase transition since both the temperature dependence of the linewidth and the susceptibility are continuous.

IV. CONCLUSIONS

In order to understand the transport properties of the $(TMTTF)_2X$ salts, it would be useful to decide on the importance of various energy terms. This might seem to be a simple problem but is a subject of long-standing contro-

versy in the field of organic metals because of the complexity of these molecular systems.[1,19] One might describe this controversy in the following terms. On the one side there are those who consider electron-electron interaction energies to be of paramount importance, so much so that the properties of these salts cannot be rationalized without first determining the magnitude of these energies, which are typically proposed to be in the range of 1—2 eV.[1,20,21] On the other hand, there are those who effectively use a renormalized Drude-type model in which these large energies are irrelevant when considering properties in the temperature range of a few meV. For many materials this latter approach is very effective but the nature of the quasiparticles is not examined. For many systems neither model is able to give a complete description of the electronic properties of the material and a more general approach is required. The materials of interest here fall into this category and we shall not attempt to model in detail the data presented above.

The most important result of these experiments has been to show the presence of what we have termed a structureless anomaly in several $(TMTTF)_2X$ salts, namely, the $X = AsF_6$ and SbF_6 salts and their alloys and in the $X = ReO_4$ salt. No corresponding change in crystal structure has yet been observed at these anomalies although careful x-ray measurements as a function of temperature to study a possible formation of superstructures or changes in symmetry of the crystal lattice at the structureless anomalies in $(TMTTF)_2SbF_6$ (Refs. 11 and 15) and $(TMTTF)_2ReO_4$ (Ref. 15) have been made. These anomalies are characterized by an increase in thermopower and resistivity and an unchanging magnetic susceptibility. The latter implies that the structureless anomalies cannot be described with a model lacking correlation terms: Without correlation effects, a gap in the charge excitation spectrum cannot be accommodated without affecting the magnetic susceptibility.

The origin of the observed anomalies is not clear. There are several possibilities to explain this behavior, including the effect of the anions. One possibility is an increase of the anion potential seen by the electrons due to either a reduced anion-molecular distance or a reduced anion disorder [note that NMR data have been interpreted as implying such an effect in $(TMTSF)_2PF_6$ (Ref. 22)]. A second possibility is a subtle change in the crystal structure. Alternative explanations not involving the anions directly are not excluded.

In summary we have discovered a new structureless anomaly in a number of $(TMTTF)_2X$ salts which cannot be understood without invoking correlation effects. An important remaining question is whether or not there is a condensation of a new long-range order of some order parameter at the structureless anomaly which would indicate a phase transition.
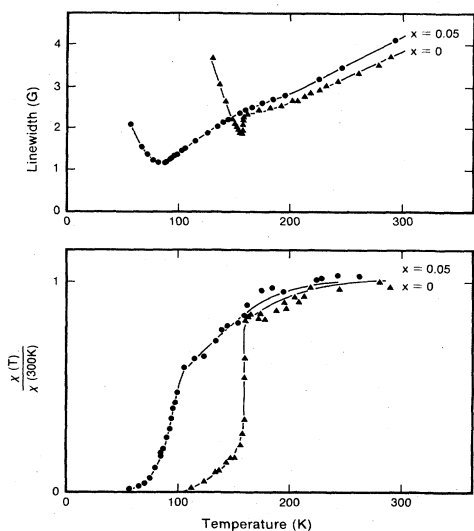

FIG. 6. Temperature dependence of (a) the EPR linewidth and (b) the normalized EPR susceptibility of the $(TMTTF)_2(ReO_4)_{1-x}(ClO_4)_x$ salts for $x = 0$ and 5%.

ACKNOWLEDGMENTS

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