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Structureless Anomaly in the $TMTTF_2X$ Family

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STRUCTURELESS ANOMALY IN THE $TMTTF_2X$ FAMILY

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Abstract A new type of high temperature anomaly, seen as an abrupt change in slope of thermopower and conductivity in the temperature range 100-200 K, is observed in several $(TMTTF)_2X$ salts. This anomaly is different from anion ordering phase transitions in several respects: at the anomaly no structural change has been found and the anomaly decreases much more rapidly with pressure. We suggest these anomalies may reflect some sort of electron localisation process.

I-INTRODUCTION

Phase transitions which have been found in the $TMTTF_2X$ and $(TMTSeF)_2X$ families may be divided into two classes- those labelled as anion ordering transitions and those related to the formation of antiferromagnetic or spin-Peierls instabilities[1]. Recently[2] an anomaly in conductivity has been observed in several salts of TMTTF containing anions of the form MF_6 which appears to be a signature of a 'phase transition' belonging to neither of these two classes. We present thermopower data which confirms the existence of such a transition and we show the same type of anomaly is seen in salts containing tetrahedral anions thus suggesting the need for a new class of ' phase transitions' in the $(TMTTF)_2X$ salts.

II-RESULTS

Crystals were prepared using standard electrochemical techniques. The $(TMTTF)_2SbF_6$ samples used in this study were taken from the same batch as those used in ref. 1.

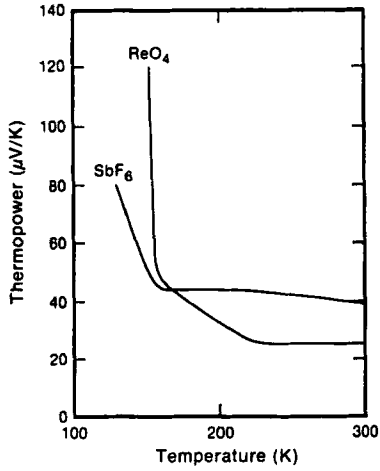

Figure 1: Thermopower versus temperature curves for $(TMTTF)_2ReO_4$ and $(TMTTF)_2SbF_6$.

Thermopower versus temperature curves are shown in figure 1 for $(TMTTF)_2ReO_4$ and $(TMTTF)_2SbF_6$. There is an abrupt change in slope near 155 K for the SbF_6 salt which is the same temperature at which a change in the gradient of the conductivity versus temperature curve has earlier been reported (these data are reproduced in figure 3). X-ray studies indicate no change in crystal structure[2,3].

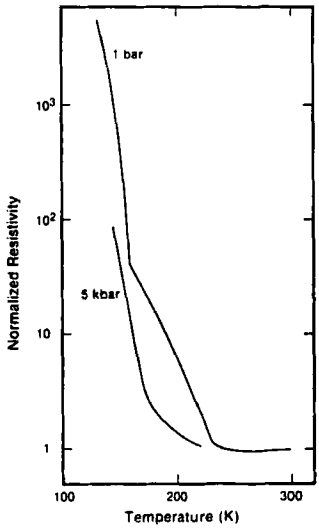

Figure 2: Normalised resistivity versus termperature curves for $(TMTTF)_2ReO_4$ at ambient pressure and 5 kbar.

Figure 1 shows there are two anomalies in the thermopower curve for the ReO_4 salt near 225 K and 160 K respectively. The low temperature anomaly

at 160 K is associated with ordering of the ReO_4 anions[4] which as found for all the $(TMTTF)_2X$ compounds are disordered at high temperatures[1]. No significant structural change (symmetry, lattice parameters) was detected near 225 K where the second anomaly is observed[3]. Conductivity data for $(TMTTF)_2ReO_4$ are shown in figure 2: two changes in slope are clearly visible at temperatures similar to those indicated by the thermopower data. Figure 2 also includes conductivity data under pressure for the ReO_4 salt: these data suggest that a moderate pressure will suppress the upper transition but has little effect on the anion order-disorder transition temperature. We have checked the reliability of these pressure experiments by repeating the ambient pressure measurement following the high pressure studies and reproducing the ambient pressure curve.

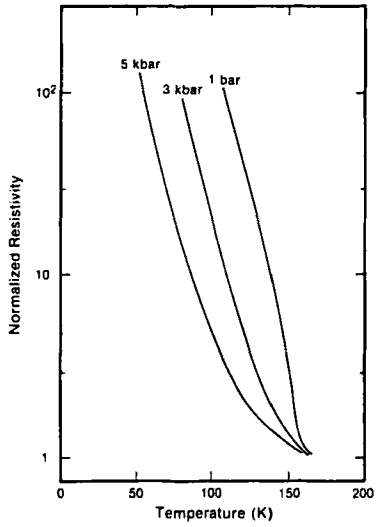

Figure 3: Normalised resistivity versus termperature curves for $(TMTTF)_2SbF_6$ at 1 bar, 3 and 5 kbar.

Data under pressure for $(TMTTF)_2SbF_6$ are shown in figure 3 and suggest that the 155 K anomaly is washed out at low pressures in agreement with the ReO_4 data. However even though no transition is indicated by conductivity data, we have found through extensive studies on TMTTF systems containing mixture of anions, that the transition may still be detected through thermopower studies. The pressure data must therefore be treated circumspectly. A detailed description of these data is given elsewhere.

We have summarised in table 1 temperatures of different types of phase transitions observed in a number of $(TMTTF)_2X$ compounds: we have also indicated in the table where anomalies are seen in susceptibility, conductivity/thermopower and in x-ray studies.

Table 1: Transition Temperatures in the $(TMTTF)_2X$ Family

	Anion Ordering	Magnetic/ Spin-Peierls	Structureless Anomaly	Anomaly in χ	Anomaly in σ/S	Anomaly in X-ray
SCN	160			N	Y	Y
		AF9		Y	†	*
NO_3	40			Y	†	Y
BF_4	40			Y	†	Y
ClO_4	75			Y	Y	Y
ReO_4			225	N	Y	N
	160			Y	Y	Y
Br		AF11		Y	Y	N
SbF_6			160	N	Y	N
		AF8		Y	†	*
AsF_6			95	N	Y	N
		SP15		Y	†	*
PF_6			85	N	Y	N
		SP15		Y	†	Y

AF and SP correspond to antiferromagnetic and spin-Peierls instabilities

† sample too resistive to make σ or S measurements at low T.

* no data available at the transition temperature-precursor effects seen in some cases[1,2]

III-CONCLUSIONS

We have shown the existence of a new class of 'phase transitions' in the $TMTTF_2X$ materials. This transition is characterised by abrupt changes in slope of conductivity and thermopower curves with no corresponding change in crystal symmetry or structure. Application of moderate pressure seems to suppress this transition. We have shown the transition is a general phenomenon found in various $(TMTTF)_2X$ salts containing anions of different symmetries.

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