PROPERTIES OF ORGANIC SALTS OF TMTSF AND TMTTF

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The transport properties (σ and S) of the two groups of organic salts $(TMTSF)_2X$ and $(TMTTF)_2X$ as well as the solid solutions $(TMTSF_{1-x}TMTTF_x)_2X$ are reviewed. Analysis of the data gives evidence of significant Coulomb repulsion (Hubbard U) only on TMTTF salts. On that basis the influence of anion ordering on transport properties is discussed for respectively TMTSF and TMTTF salts.

1. INTRODUCTION

Much of the recent interest in the study of organic metals has been focused upon the tetramethyltetraselenafulvalene salts $(TMTSF)_2X$ where X is PF_6, ClO_4, ReO_4, H_2F_3 etc. [1]. These materials have shown a variety of novel features including ground states ranging from the superconducting state [2] to magnetic or non-magnetic insulators. The closely related tetramethyltetrathiafulvalene salts $(TMTTF)_2X$ where selenium is replaced by sulphur exhibit also a variety of behavior [1]. The two classes of salts are isostructural, belonging to the $P\bar{1}$ space group [3]. The nearly planar TMTSF or TMTTF molecules, which form zig-zag stacks along the a-direction are slightly tilted relative to the stacking axis, thereby resulting in dimerization. Charge transfer to the anions results in half-filled bands. If we were to neglect the dimerization gap the bands would be three-quarter filled.

The physical properties of $(TMTSF)_2X$ and $(TMTTF)_2X$ salts are in spite of their chemical and structural similarities very different. $(TMTSF)_2X$ sals are generally quite good conductors with metallic characteristics over wide temperature ranges (Fig. 1). $(TMTTF)_2X$ salts show on the contrary basically semiconducting be-

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havior (Fig. 2). Both classes of materials exhibit examples of transitions induced by changes in the anion-lattice. However, the related effect on the electronic properties differs distinctly. Antiferromagnetic ordering is also seen in both TMTSF and TMTTF salts, but while the magnetic ordering occurs in a highly conducting state of the former salts, it occurs in an insulating state of the latter. Superconductivity is found in most $(TMTSF)_2X$ salts, when treated under hydrostatic pressure [1,2], whereas none of the $(TMTTF)_2X$ salts have shown indications of such behavior [11].

In order to understand which physical properties are decisive for the differencies between $(TMTSF)_2X$ and $(TMTTF)_2$ salts, and thereby also learning more about both TMTSF and TMTTF, we have studied a series of solid solutions: $(TMTSF_{1-x}\text{-}TMTTF_x)_2PF_6$, $0<x<1$ [5]. In this paper we summarize some of these results as well as results on pristine salts [2-10]. Discussions about the SDW and superconducting states are very important, but beyond the purpose of this paper.

2. ROLE OF THE HUBBARD U

Conductivity (σ) and thermopower (S) of $(TMTSF)_2PF_6$ is shown in Figs. 1 and 3. $(TMTSF)_2PF_6$ can in the metallic region be treated as a quasi-ID conductor, with

$$\sigma = \sigma_o\ T^{-\alpha} \tag{1a}$$

$$S \approx (2\sqrt{2}\pi^2/3)(k/e)(kT/4t) \tag{1b}$$

with $\alpha \approx 2$ [12]. $(TMTTF)_2PF_6$, Figs. 2 and 3, shows semiconducting behavior

$$\sigma = ne\mu \tag{2a}$$

$$S = k/e\ (bE_a/kT + cst) \tag{2b}$$

with the number of carriers activated, $n \propto T^{\frac{1}{2}} \exp(-E_a/kT)$ $E_a \approx 50$ meV and the mobility $\mu \propto T^{-\alpha}$, $\alpha \approx 3.5$ [5]. b is a function of the electron and hole mobility-ratio. The changes in slope of S vs. 1/T reflect cross-over to dominance by specific impurity or defect levels. (This is even more marked in several of the other $(TMTTF)_2X$ salts, Fig. 2b, which show dramatic changes near 100K due to transition from intrinsic to extrinsic dominance [5]). Since $(TMTSF)_2PF_6$ and $(TMTTF)_2PF_6$ are isostructural and have the same degree of bandfilling, the distinct differencies in electronic behavior can be only due to marked differencies in molecular overlap (t) or differencies in electron correlations.

The metallic thermopower, Eq. 1b, gives information on t. It appears from Fig. 3b that the TEP remains basically unchanged for as much as 25% of TMTSF molecules substituted with TMTTF [4]. Thus t of TMTTF must be approximately equal to that of TMTSF, i.e. 0.2-0.25 eV. This is further supported by recent optical studies [13]. The semiconducting properties of $(TMTTF)_2PF_6$ (and other $(TMTTF)_2X$ salts) can therefore only be understood as a result of strong electron correlations, i.e. Coulomb repulsion for a second electron on a site larger than the band-width, 4t. This doubles the Fermi wave vector and brings thereby E_F to midband in coincidence with the gap due to dimerization.

If the U/4t-ratio was much larger than unity, the TEP should at high-T approach $k/e \cdot \ell n2$, assuming symmetry between upper and lower Hubbard subbands [5]. All investigated $(TMTTF)_2X$ salts (with theexception of $TMTTF)_2Br$) show however $S_\infty \approx 35 \mu V/K$ (Fig. 2b). This imply that although $U/4t > 1$, U is not much larger than 4t. It has been speculated that the $U/4t > 1$ relation is closely related to the small overlap of S atoms on adjacent chains [4]. In $(TMTTF)_2Br$ this overlap is markedly enhanced due to the small anion and the Coulomb repulsion is accordingly smaller. This explains why a number of properties of $(TMTTF)_2Br$ are intermediate between those of $(TMTTF)_2X$ ($U/4t > 1$) and those of $(TMTSF)_2X$ salts ($U/4t < 1$).

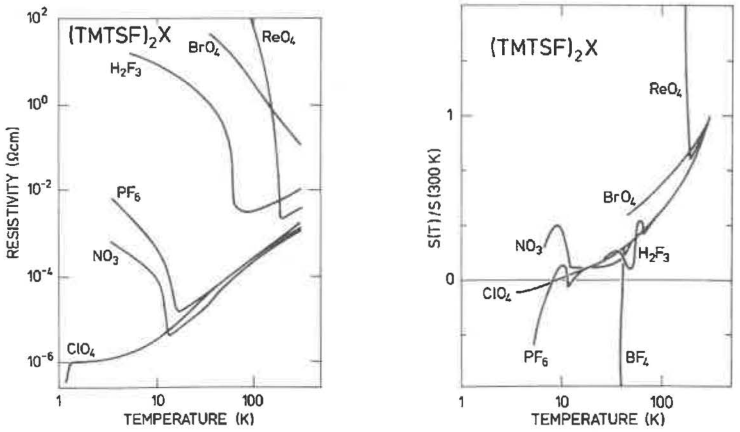

Figure 1. Resistivity (a) and thermopower (b) of representative $(TMTSF)_2X$ salts [3,6,8-10].

When TMTTF molecules are introduced in the TMTSF-chains, the relative large U/4t ratio on the TMTTF sites prevents electrons to pass. Therefore the mobility is dramatically reduced already at dilute concentrations of TMTTF, as observed experimentally (Fig. 3a).

3. ANION ORDERING

The role of the anions of $(TMTSF)_2X$ and $(TMTTF)_2X$ has been the subject of several recent papers. Many of the anions are at room temperature disordered over two possible orientations, and undergo at a specific temperature, T_c, a transition into an ordered ground state. On the basis of the discussion above it is now clear why superstructure induced by the anion-ordering can have distinct different influence on the electronic properties of $(TMTSF)_2X$ and $(TMTTF)_2X$ salts. Doubling of the stacking axis parameter, f.ex., is expected to transform a $(TMTSF)_2X$ salt from a metal to a non-metal, as it induces a gap at E_F, whereas it is expected only to change the properties of $(TMTTF)_2X$ slightly, since the effect near E_F of the new anion potential is to modify the already existing dimerization gap. An example is $(TMTSF)_2ReO_4$, where ReO_4-ions form a new unit cell (2a, 2b, 2c) at 182K [14], resulting in a gap at E_F [6] (see Fig. 1). The same unit cell formed at 70K by the ClO_4-ions in the TMTTF-salt has only minor effect on σ and S (Fig. 2) [5,7]. Doubling of stacking axis parameter leads correspondingly to non-metallic behavior of $(TMTSF)_2BF_4$ below 40K [3], of $(TMTSF)_2H_2F_3$ below

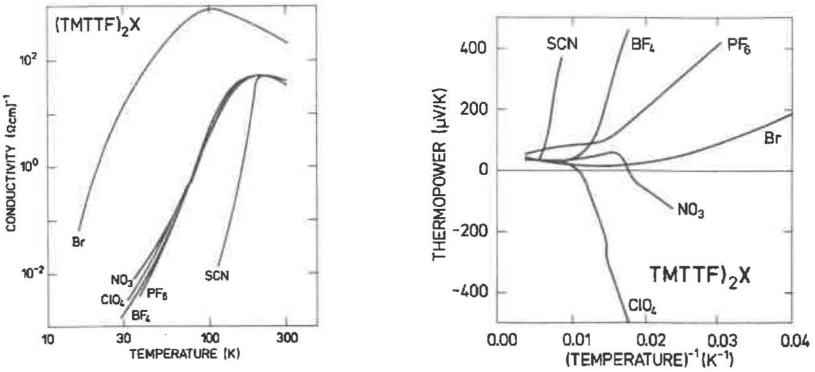

Figure 2. Conductivity (a) and thermopower (b) of representative $(TMTTF)_2X$ salts [5,7].

63K [8] and $(TMTSF)_2BrO_4$ already at room temperature [9,14]. In the ReO_4 and BF_4 salts, the anions are ordered over long range, thus leading to well defined gaps and typical semiconducting properties. In $(TMTSF)_2BrO_4$, however, the anions are ordered only over short range, thus leading to a finite density of states near the Fermi level. The charge transport in the BrO_4-salt is therefore not activated, but via variable range hopping among localized carriers [9] (Fig. 1).

$$\log \sigma \propto T^{1/4} \tag{3a}$$

$$S \propto T^{1/2} \tag{3b}$$

The low-T properties of $(TMTSF)_2H_2F_3$ may be similar. In contrast to expectations, the (2a,b,c)-ordered anions of $(TMTSF)_2NO_3$ below 41K do not lead to semiconductivity (Fig. 1). In $(TMTTF)_2NO_3$ the anions order similarly at 50K without any significant change in σ and S (Fig. 2).

Anion ordering which retains the a-parameter should only have minor influence on σ and S of $(TMTSF)_2X$ salts, since it only modifies the dimerization gap. This is confirmed from studies of $(TMTSF)_2ClO_4$, in which the anions give rise to a (a,2b,c) unit cell below 24K [15]. (This ordering is, though, cruzial for superconductivity [2].) In TMTTF-salts, on the contrary, such anion-ordering can still be important if it gives rise to marked change in the dimerization gap. Such example is $(TMTTF)_2SCN$, in

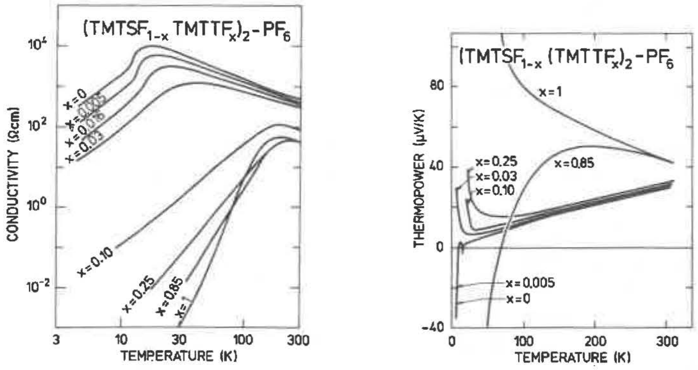

Figure 3. Conductivity (a) and thermopower (b) of $(TMTSF_{1-x}TMTTF_x)_2PF_6$, $0 < x < 1$ [4].

which a (a,2b,2c) unit cell formation at 160K causes marked changes in σ and S (Fig. 2) [5,7,16].

It has been speculated that even the hexafluoro-anions, PF_6, AsF_6, SbF_6 and TaF_6, which all show properties similar to the PF_6-salt shown in Fig. 1, may exhibit properties which reflect changes in the anions [17]. F.ex. the rather sharp change in slope of various parameters at approximately 100K (e.g. S vs T), which reflects the 1D-2D cross-over [10], may be coupled to a structural transition.

4. CONCLUSION

In conclusion we have shown that the different behavior of typical TMTSF and TMTTF salts to a large amount can be attributed to different Hubbard U.

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