

Ditetramethyltetraselenafulvalenium fluorosulfonate: The effect of a dipolar anion on the solid state physical properties of the $(\text{TMTSF})_2\text{X}$ phase

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The solid state properties of the title compound are described. The material undergoes a metal to insulator transition at 86 K which is *not* driven by spin density waves. The metal to insulator transition is reflected by very sharp changes in conductivity and magnetic susceptibility.

After Bechgaard discovered the family of organic superconductors $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{PF}_6^-$, AsF_6^- , SbF_6^- , TaF_6^- , BF_4^- , ClO_4^- , NO_3^-),¹⁻³ it was accepted that the metal-to-insulator transition (T_{MI}) which at least three of these salts undergo at ambient pressure and low temperature (PF_6^- , 11.5 K; AsF_6^- , 11.5 K; ClO_4^- , 5 K) is due to pinning of spin density waves (SDW).^{4,5} A hypothesis to explain why these salts did not have their low temperature phase transitions driven by pinning of charge density waves (CDW) was recently put forth.^{6,7} Central to that interpretation is the role of the anion lattice. To date, all the anions that have been incorporated into the $(\text{TMTSF})_2\text{X}$ phase are *symmetric* and either octahedral or tetrahedral.⁸

We decided to introduce FSO_3^- in the above-mentioned "Bechgaard phase" because this anion is approximately the same size as perchlorate and is also tetrahedral but has a *permanent* dipole moment. In this paper we describe the profound effect on the physical properties of $(\text{TMTSF})_2\text{X}$ resulting from the incorporation of a small, dipolar, tetrahedral anion.

RESULTS

Crystal growth

Crystals of $(\text{TMTSF})_2\text{FSO}_3$ were grown electrochemically in H cells of ~25 ml capacity using tetrabutylammonium fluorosulfonate as electrolyte. The latter was prepared from fluorosulfonic acid and tetrabutylammonium hydroxide and was recrystallized three times from ethyl acetate. The electrolysis solvent was 1, 1, 2-trichloroethane,⁹ the electrodes were platinum wire, and the current was ~0.3 μA at constant 9 °C. No special precautions were taken during har-

vesting but the TMTSF was gradient sublimed onto Teflon before use.

Transport properties

Single crystal conductivity

The low frequency conductivity measurements were performed using a standard four-probe technique with silver paint contacts aligned along the needle axis (*a* axis). For some samples, the silver paint was applied to evaporated gold pads, but little difference was observed with contacts directly on the crystal surface. In the metallic region the measurement involved either a lockin detector at 103 Hz or dc, while high dc resistance measurements were made with an electrometer.

For the ac conductivity determination, crystals were measured using microwave cavity perturbation techniques at 9.35 GHz. The samples were suspended in He exchange gas at the electric field maximum of a cylindrical TE_{011} cavity. The cavity temperature was measured with a calibrated silicon diode and a carbon resistance thermometer. The electric field strength in the skin-effect region of the cavity samples was approximately 1 mV/cm at a power input to the cavity of 1×10^{-6} W.

Figures 1 and 2 show plots of the resistivity as a function of temperature for low and high frequencies, respectively. The room temperature conductivity was found to be $1600 (\Omega \text{ cm})^{-1}$ at low frequency and $300 (\Omega \text{ cm})^{-1}$ at microwave frequencies. A very sharp transition at 86 K (T_{MI}) is the most striking feature of these plots. Below this transition the conductivity is thermally activated and decreases by more than six orders of magnitude before, at about 30 K, it begins a more gradual temperature dependence. Thus, at very

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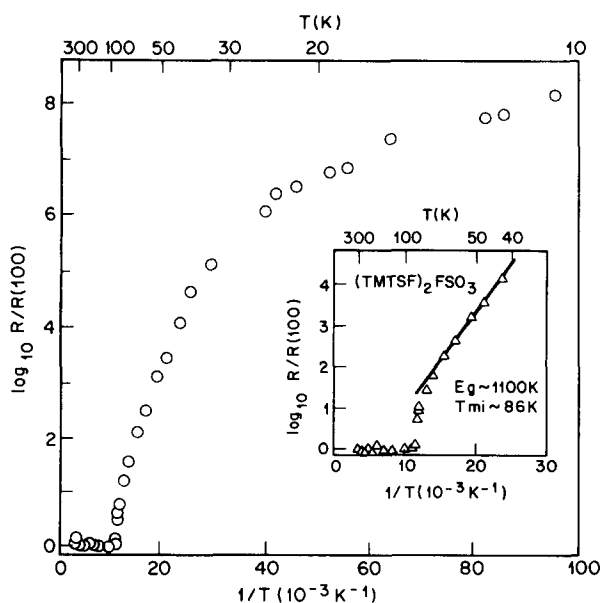


FIG. 1. Resistivity of $(\text{TMTSF})_2\text{FSO}_3$ single crystals as a function of temperature. Inset; magnification of the temperature region 100–40 K.

low temperatures the conductivity is not dominated by thermal excitation across the energy gap and is either extrinsic or related to some low energy collective charge carriers.

The inset in Fig. 1 shows the resistivity in the region of the metal insulator transition. For conventional semiconductors the slope of the $\log(R)$ versus $1/T$ plot

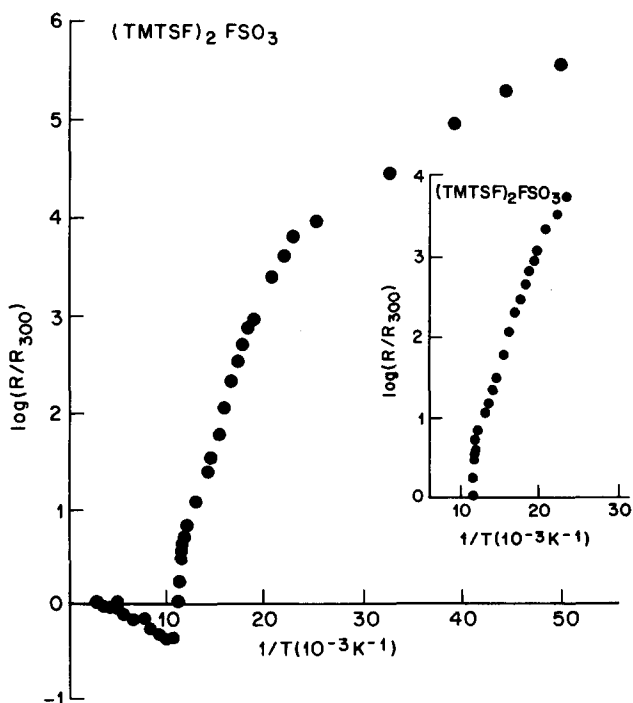


FIG. 2. Microwave resistivity of a single crystal of $(\text{TMTSF})_2\text{FSO}_3$ as a function of temperature. Inset is a magnification between 100 and 40 K.

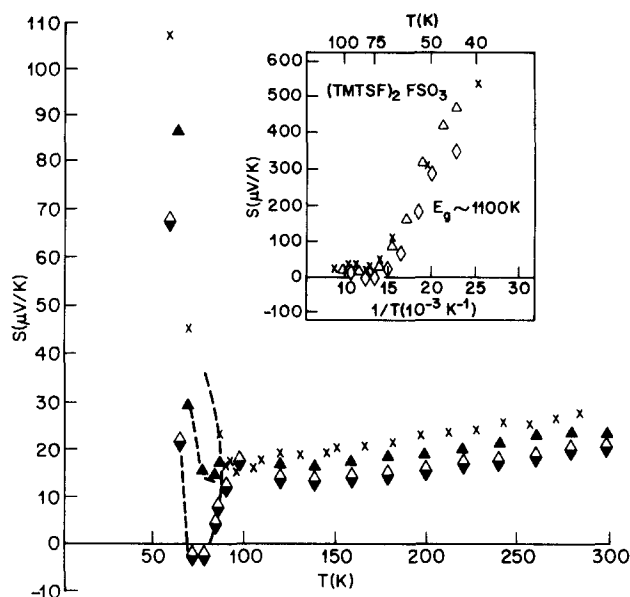


FIG. 3. Thermopower of single crystals of $(\text{TMTSF})_2\text{FSO}_3$. \times , Δ , Δ ; individual crystals.

gives a measure of the carrier activation energy and hence the energy gap. However, just below the metal insulator transition temperature, the gap should be temperature dependent and this contributes to the slope of the curve. If the transition is BCS-like, this correction to the analysis is significant down to $\sim 0.7 T_c$ or 60 K. The region over which we can confidently determine the gap is thus limited. Taking the slope of the curve in the inset in Fig. 1 literally we arrive at a gap of ~ 1100 K (0.1 eV).

It is worth pointing out that the ratio of the gap to the transition temperature is ~ 12.5 , as compared to 3.5 which would be predicted from the BCS theory or the value of ~ 8 that has previously been found for the metal-insulator transition in other organic salts. The unusually high value suggests that either this material is more one-dimensional than the previously studied compounds in the same class, (so that its three-dimensional ordering temperature is even further below the mean field temperature) or that the transition is not simply an electronically driven Peierl's transition but may involve coupling of the electronic transition to a structural transition such as might result from anion ordering.

Another unusual observation is the high degree of reproducibility between data taken on different samples as can be seen in Fig. 1.

Preliminary measurements indicate that the room temperature conductivity anisotropy between the a^* and b^* directions is several thousand and that the conductivity at 77 K is ohmic up to electric field strengths of at least ~ 10 V/cm.

Thermopower

The thermoelectric power is plotted as a function of temperature in Fig. 3. From room temperature down

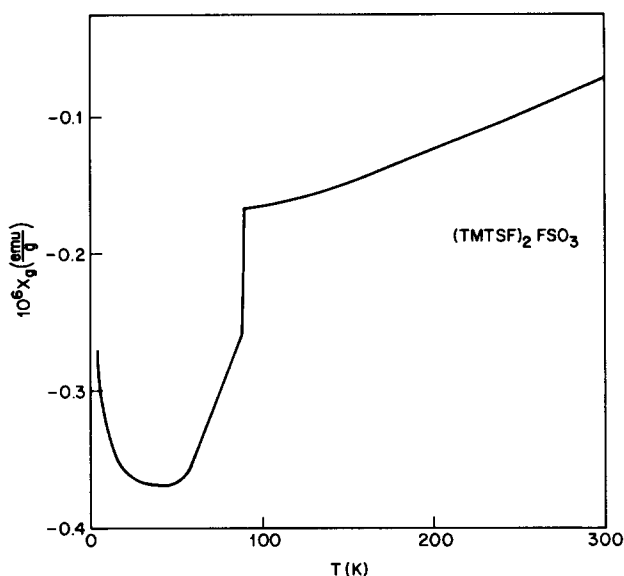


FIG. 4. Magnetic susceptibility of single crystals of $(\text{TMTSF})_2\text{FSO}_3$.

to the transition at 86 K, the thermopower is small and decreasing with decreasing temperature, behavior characteristic of a metal. These results for the metallic region are quite similar to those found for the other "Bechgaard phase" salts and lead us to the conclusion that there is a similar bandwidth of ~ 1 eV and that the metallic carriers are holes. The inset in Fig. 3 shows the low temperature thermopower plotted as a function of $1/T$. The slope of the latter curve ideally indicates the energy gap ($S = K_B E_g / 2eT$) to be ~ 1100 K, in excellent agreement with the evaluation from the resistivity.

The low temperature thermopower differs in sign from that which has been observed in other Bechgaard phase salts. Holelike carriers are dominant in the present material whereas electronlike carriers were seen at low temperatures previously. Normally the sign of the thermopower in a semiconductor is very sensitive to shifts in the chemical potential caused by small concentrations of impurities. The sign difference is thus probably an extrinsic effect that reflects differences in chemical synthesis. However, it is unusual that in most of the materials studied the thermopower just below T_{MI} starts to change in one direction and then turns around and diverges with the opposite sign. In the present case this can be seen in Fig. 3 as a sample dependent drop, which sometimes crosses zero, followed by the large positive increase. In previously studied salts the thermopower just below the transition increased positively, in a sample-dependent manner, before eventually becoming large and negative. In an as yet unknown way this behavior may be reflecting some of the dynamics of the transition.

Magnetic properties

Magnetic susceptibility

The static magnetic susceptibility of ~ 40 mg of crystals lined up roughly with their long axes (a axis) per-

pendicular to the external field (12 kG) was measured with a Faraday balance over the temperature range of 4–300 K. The result is depicted in Fig. 4. The shape of the curve is similar to the magnetic susceptibility of $\text{TTF} \cdot \text{TCNQ}$ except that in this case the slope of the susceptibility above T_{MI} is shallow and the transition occurs at 89 K and is sharper. In contrast to the present compound, $(\text{TMTSF})_2\text{PF}_6$ shows only a small, field dependent dip in the susceptibility at 11.5 K.¹⁰

Electron spin resonance

Experiments were performed at 12 GHz in the temperature range 1.5–300 K. At room temperature, a broad, somewhat asymmetric resonance with the anisotropy characteristic of the conducting $(\text{TMTSF})_2\text{X}$ salts was observed. On cooling, the resonance narrows and becomes more asymmetric consistent with increasing conductivity (more pronounced skin effect) down to ~ 80 K. At liquid helium temperatures (4.1–1.5 K), however, the microwave loss essentially vanishes and the ESR signal is weak, narrow ($\Delta H_{pp} \sim 8$ G) and symmetric (as observed in organic insulators or nearly insulating semiconductors). The g tensor may then be accurately determined ($g_{\parallel} = 1.9915 \pm 0.0005$, $g_{\perp} = 2.0426 \pm 0.0005$). No anisotropy of g_{\perp} in the b^*c^* plane could be measured which is unusual in the Bechgaard phase salts. Signal intensity versus microwave power revealed no nonlinearity of the sort observed below the SDW transitions of the PF_6^- AsF_6^- , and most recently the ClO_4^- salt.⁵

Solid state structure

Crystal data for $(\text{TMTSF})_2\text{FSO}_3$ shown in Table I¹¹ were obtained using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The same table contains data for $(\text{TMTSF})_2\text{ClO}_4$.⁹ It is clear that the compounds are isostructural (triclinic, space group $P\bar{1}$) and have practically identical unit cell volumes. The FSO_3^- salt, from a unit cell dimensions point of view is slightly different from the ClO_4^- salt ($a_{\text{FSO}_3} < a_{\text{ClO}_4}$, $b_{\text{FSO}_3} = b_{\text{ClO}_4}$, $c_{\text{FSO}_3} > c_{\text{ClO}_4}$). A study of the structure of $(\text{TMTSF})_2\text{FSO}_3$ as a function of temperature¹¹ with emphasis on the changes in Se–Se contacts in the a – b plane revealed that these distances contract (with decreasing temperature) *more in the b direc-*

TABLE I.

$(\text{TMTSF})_2\text{FSO}_3^a$
$a = 7.255(1)$, $b = 7.680(1)$, $c = 13.313(2)$, $V = 695.3(2)$
$\alpha = 84.40(1)$, $\beta = 86.68(1)$, $\gamma = 70.42(1)$ at $T = 298$ K
2271 independent data, 1747 with $F^2 > 3\sigma(F^2)$
$4.0^\circ \leq 2\theta \leq 50.0^\circ$, $\mu_c = 105.1 \text{ cm}^{-1}$ $R(F^2 > \sigma F^2) = 0.056$
$(\text{TMTSF})_2\text{ClO}_4^b$
$a = 7.266$, $b = 7.678$, $c = 13.275$, $V = 694.3$
$\alpha = 84.58$, $\beta = 86.73$, $\gamma = 70.43$

^aReference 11.

^bReference 9.

TABLE II.

Contact	Symmetry operation ^a	Distance (Å)		Distance (Å)	
		X = $(\text{FSO}_3)^-$ (298 K)	X = $(\text{FSO}_3)^-$ (123 K)	Δ Å	Δ/σ
Se1-Se3	i	3.866(1)	3.829(4)	-0.037(4)	-9 ^b
Se1-Se4	ii	3.868(1)	3.782(2)	-0.086(2)	-43 ^c
Se-Se2	iii	4.023(1)	3.981(3)	-0.042(3)	-14 ^b
Se1-Se3	iii	4.028(1)	3.962(3)	-0.066(3)	-22 ^b
Se1-Se2	i	4.120(1)	4.083(3)	-0.037(3)	-12
Se2-Se2	iv	3.782(1)	3.684(4)	-0.098(4)	-25 ^c
Se2-Se4	i	3.927(1)	3.884(4)	-0.043(4)	-11 ^b
Se2-Se4	iii	3.960(1)	3.901(4)	-0.059(4)	-15 ^b
Se2-Se4	v	4.188(1)	4.225(2)	+0.037(2)	+19
Se2-Se3	i	4.982(1)	4.962(3)	-0.020(3)	-7
Se4-Se4	ii	3.952(1)	3.871(4)	-0.081(4)	-20 ^c

^aSymmetry operations: (i) $2-x\ 1-y\ 1-z$; (ii) $1-x\ 2-y\ 1-z$; (iii) $1-x\ 1-y\ 1-z$; (iv) $2-x\ -y\ 1-z$; (v) $x\ y\ -1\ z$.

^bIntermolecular intrastack Se-Se contact.

^cIntermolecular interstack Se-Se contact.

tion (interstack) than in the a direction (Table II). Closer examination of Table II reveals that the three interstacks Se-Se distances decrease by 0.081–0.098 Å (20–43 Δ/σ) while the five Se-Se intrastack contacts contract by only 0.0370–0.066 Å (9–22 Δ/σ).

DISCUSSION

The above results indicate that the mechanism responsible for the metal to insulator transition in $(\text{TMTSF})_2\text{FSO}_3$ is not one driven by pinning of spin density waves because of the following: (1) The transition occurs at too high a temperature. SDW driven transitions are not expected to be nearly as strong energetically as those driven by CDW's.⁷ (2) The compound does not exhibit nonlinear electric field effects below T_{MI} in its ESR behavior or its conductivity. It is characteristic of CDW pinned systems that some residual spins are observable well below T_{MI} , whereas our limited experience with organic SDW systems indicates *no* spins below T_{MI} . (3) The temperature dependence of the magnetic susceptibility corresponds to that observed in typical CDW-driven phase transitions; e.g., TTF-TCNQ, TSF-TCNQ, etc.¹²

A comparison of the crystal structures of the ClO_4^- and FSO_3^- salts shows that aside from slight lengthening of the c length of the unit cell of the latter, the unit cells are the same; indicating that the profound differences in physical properties between these salts (ClO_4^- , T_{MI} 5 K, T_c 1.3 K; FSO_3^- , T_{MI} 86 K, no SC T_c at atmospheric pressure) is attributable only to the anions. Both anions are identical in shape and approximately the same size [$r_{\text{ClO}_4^-} \sim 3.06$ Å; $r_{\text{FSO}_3^-} \sim 3.09$ (S–O), 3.01 (S–F)].¹³ The only difference is that ClO_4^- has no permanent dipole moment whereas FSO_3^- should have one.¹³

The transition observed in the transport and magnetic properties could be due to ordering of the FSO_3^- anions. Unfortunately, the x-ray structure determination could not be performed below 123 K to test this suggestion.

It could also be that the FSO_3^- sublattice undergoes a distortion¹⁴ without ordering of the dipoles. The latter hypothesis could be tested by diffuse x-ray scattering techniques; such experiments are in progress.¹⁵

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