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# Physical properties of the new organic conductor series di(tetramethyl-dithiadiselenafulvalene) X; X=BF<sub>4</sub>, ClO<sub>4</sub>, ReO<sub>4</sub>, PF<sub>6</sub>, AsF<sub>6</sub>, SbF<sub>6</sub>

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PHYSICAL PROPERTIES OF THE NEW ORGANIC CONDUCTOR SERIES  
DI(TETRAMETHYL-DITHIADISELENAFULVALENE) X; X=BF<sub>4</sub>, ClO<sub>4</sub>, ReO<sub>4</sub>, PF<sub>6</sub>, AsF<sub>6</sub>,  
SbF<sub>6</sub>

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#### ABSTRACT

We have investigated a new series of organic conductors based on the mixed sulfur-selenium molecule tetramethyl-dithiadiselenafulvalene: (TMDTDSF)<sub>2</sub>X with different anions X = BF<sub>4</sub>, ClO<sub>4</sub>, ReO<sub>4</sub>, PF<sub>6</sub>, AsF<sub>6</sub> and SbF<sub>6</sub>. Transport measurements under pressure and a preliminary study of magnetic properties were performed in order to establish a general temperature-pressure phase diagram for this family.

The PF<sub>6</sub> salt has been studied extensively. At ambient pressure, spin-Peierls (SP) and spin density waves (SDW) states establish successively on cooling as shown by ESR and <sup>1</sup>H NMR, respectively. The metallic ground state is stabilized above P=20kbar but no sign of superconductivity can be detected down to T=0.56K. The SDW ground state is also observed for the other compounds between P=9 and 16 kbar except for the ReO<sub>4</sub> salt. The latter compound is the only one which undergoes the metal to insulator phase transition driven by anion ordering whose pressure dependence is very similar to the equivalent salt in the (TMTSF)<sub>2</sub>X series.

These properties and the absence of a superconducting state could be related to the possible disorder in the stacking of the asymmetric organic molecules which has been observed by X-rays diffuse scattering at all temperatures. Furthermore, this disorder could prevent anion ordering at low temperature for tetrahedral anions at least for the smallest ones.

#### INTRODUCTION

The instabilities occurring in a quasi 1-D electron gas at low temperature have been investigated in the (TMTTF-TMTSF)<sub>2</sub>X series either via application of high pressure or by magnetic properties study [1] [2]. The investigation of the (TMTTF)<sub>2</sub>X salts has revealed the competition between the SP and the SDW ground states under pressure for instance in (TMTTF)<sub>2</sub>PF<sub>6</sub> around 10 kbar [3]. However, the P-T diagram of the all-selenium series has shed light on the cross-over between SDW and superconductivity [4]. Therefore, the synthesis of a new series based on the hybrid molecule, TMDTDSF, provides us a prototype for the physical properties. Moreover, the disorder introduced along the organic stack modifies ordering conditions for tetrahedral anions at low temperature.

## EXPERIMENTAL RESULTS

Single crystals of  $(\text{TMDTDSF})_2\text{X}$  with  $\text{X} = \text{BF}_4, \text{ClO}_4, \text{ReO}_4, \text{PF}_6, \text{AsF}_6$  and  $\text{SbF}_6$  were obtained by electrocrystallization [5]. The determination of the crystal structure [6] on  $(\text{TMDTDSF})_2\text{PF}_6$  provides a triclinic structure  $\text{P}\bar{1}$  with two donors per unit cell as for the  $(\text{TMTTF-TMTSF})_2\text{X}$  series. Unit cell parameters at  $T = 295 \text{ K}$  are  $a = 7.206 \text{ \AA}$ ,  $b = 7.632 \text{ \AA}$ ,  $c = 13.374 \text{ \AA}$ ,  $\alpha = 83.23 \text{ (deg)}$ ,  $\beta = 85.59 \text{ (deg)}$ ,  $\gamma = 71.63 \text{ (deg)}$ , with interplanar distances 3.61 and 3.59  $\text{\AA}$ . These values are nearly midway between those of all-sulfur and all-selenium compounds. At first sight the structure is disordered in terms of the heteroatoms stacking.

We performed resistivity measurements under pressure for the six compounds. The conductivity values at room temperature are intermediate between the all-sulfur and the all-selenium salts:  $\sigma(300 \text{ K}) = 200 \text{ \Omega}^{-1}\text{cm}^{-1}$ . The transport data for  $(\text{TMDTDSF})_2\text{ClO}_4$  are reported in fig. 1, as they are representative of all the series except the  $\text{X}=\text{ReO}_4$  salt. The results are very similar to those obtained in the TMTTF series. At ambient pressure, Coulomb-induced localization is observed below  $T_p = 165 \text{ K}$ . The ground state at lower temperature has been identified only for  $(\text{TMDTDSF})_2\text{PF}_6$  [5]. A spin-Peierls state establishes around 20K, as shown by an exponential decreasing of the ESR spin susceptibility whereas an upturn of the proton relaxation rate is noticed below  $\approx 18 \text{ K}$  giving rise to a  $T_1^{-1}$  maximum at 7 K, which is the signature of SDW ordering [7].

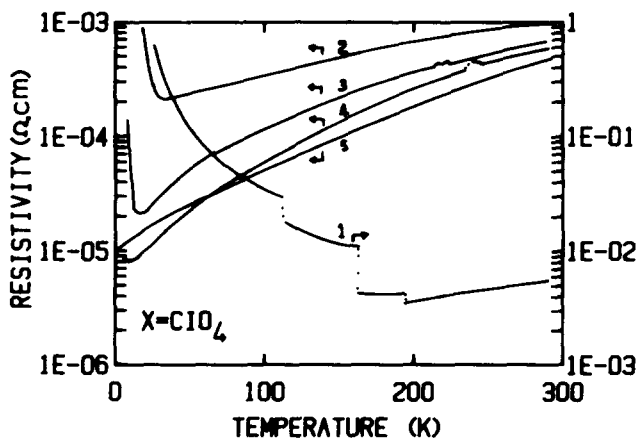


Fig. 1. Temperature dependence of the resistivity of  $(\text{TMDTDSF})_2\text{ClO}_4$  at  $P = 1 \text{ Bar}$  (1),  $P = 9.5 \text{ kBar}$  (2),  $P = 13 \text{ kBar}$  (3),  $P = 15.5 \text{ kBar}$  (4) and  $P = 20 \text{ kBar}$  (5).

Charge localization is rapidly removed under pressure. Above  $P \approx 9 \text{ kbar}$  a large regime in temperature exhibiting metallic-like conductivity extends down to the sharp phase transition at  $\approx 15 \text{ K}$  and even lower temperatures, down to 5K at higher pressures. By comparison with TMTTF and TMTSF salts, we attribute this sharp transition to the SDW state stabilization. As for  $(\text{TMTTF})_2\text{Br}$  under very high pressure, the insulating ground state is fully suppressed above 19 kbar. At pressures higher than 20kbar  $(\text{TMDTDSF})_2\text{PF}_6$  remains metallic down to the lowest temperature

reached(0.56K)[5]. These transition temperatures slightly vary with the anion X(table 1). However, for the  $\text{BF}_4$  salt the ground state could be different from SDW as anion ordering has just been identified at ambient pressure, below 22K by X-rays diffraction experiments ( $q=(1/2,1/2,1/2)$ ) [8].

For the  $(\text{TMDTDSF})_2\text{ReO}_4$  salt, the same anion ordering induced phase transition is observed at  $T_{\text{AO}} = 163$  K for  $P = 1$  Bar. This temperature is intermediate between the two transition temperatures of  $(\text{TMTSF})_2\text{ReO}_4$  (180 K) and  $(\text{TMTTF})_2\text{ReO}_4$  (156 K) [9]. It is observed both by a first-order transition on the resistivity and by X-rays diffraction [8]. This latter experiment gives the same wave vector of the superstructure,  $q=(1/2,1/2,1/2)$ , as in  $(\text{TMTTF-TMTSF})$  family. The temperature of this transition decreases with applied pressure as shown in table 2 and Fig.2.

TABLE 1

Pressure dependence of the metal-spin density waves (SDW) transition temperature for all  $(\text{TMDTDSF})_2$  X salts studied except the  $X = \text{ReO}_4$  compound .M is for metallic and means that the compound remains metallic down to the lowest temperature reached, indicated in the brackets .

TABLE 2

Pressure dependence of the anion ordering transition temperature  $T_{\text{AO}}$ , for  $(\text{TMDTDSF})_2\text{ReO}_4$ .

PRESSURE (kBar)	0.001	9	12.5	15.5	20	PRESSURE (kBar)	$T_{\text{AO}}$ (K)
(K)	$T_{\rho}$	$T_{\rho} = T_{\text{SDW}}$	$T_{\text{SDW}}$	$T_{\text{SDW}}$		ANION X	= $\text{ReO}_4$
$\text{PF}_6$	180	17.5	11.9	9.3	M(0.5K)		
$\text{AsF}_6$	180		13.5	9.8		0.001	163
$\text{SbF}_6$	172		13	10		10	146
$\text{BF}_4$	150	15.5	13.5	9		12.5	49
$\text{ClO}_4$	165	15	11	5	M(4.2K)	15	34.5

TABLE 1

TABLE 2

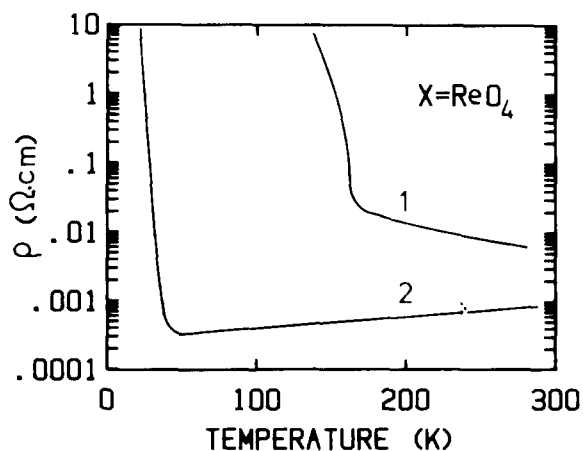


Fig. 2. Temperature dependence of the resistivity of  $(\text{TMDTDSF})_2\text{ReO}_4$  at  $P = 1$  Bar (1) and  $P = 15$  kBar (2) showing the anion ordering transition for  $T_{\text{AO}} = 163$  K and 34.5 K respectively .

#### DISCUSSION:

X-rays diffuse scattering and diffraction structure suggest that the organic stacks are disordered concerning the orientation of the asymmetric molecules. However diffuse lines are the

weakest for the salts with the biggest anions i.e.  $X = \text{ReO}_4$  and  $\text{SbF}_6$  [8]. For the compounds with tetrahedral anions, too much disorder along the conducting chains could prevent from the possibility of anion ordering at low temperature except if the anions have so big volume that they impose at least a partial alternate stacking of (TMDTDSF) molecules. So the  $X = \text{ReO}_4$  compound is the better candidate for a search for superconductivity at higher pressure as it is the most ordered system and as disorder on organic stacks is likely to decrease the superconducting transition .

For the other salts, transport measurements under pressure complete the (T,P) phase diagram obtained for  $(\text{TMDTDSF})_2\text{PF}_6$  [5]. The modifications deduced from this study are shown in fig. 3. More ESR susceptibility measurements are in progress in order to investigate the low temperature ground state at ambient pressure, and confirm the successive stabilization of SP and SDW states observed on the  $X = \text{PF}_6$  salt, at ambient pressure.

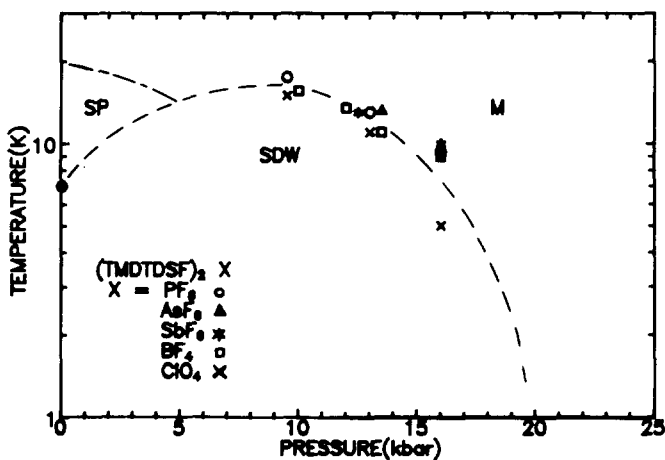


Fig. 3. Pressure dependence of the metal-spin density waves (SDW) transition temperature for all  $(\text{TMDTDSF})_2\text{X}$  salts studied except the  $X = \text{ReO}_4$  compound .The dashed lines indicates the other phase transitions detected on the  $X = \text{PF}_6$  salt and identified at ambient pressure.

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