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Structural and electrical properties of $(\text{TMTTF})_2\text{MF}_6$ salts ($\text{M} = \text{P}, \text{As}, \text{Sb}$). Rôle of the anions

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Résumé. — Les propriétés structurales et électriques de différents sels $(\text{TMTTF})_2\text{MF}_6$ sont décrites et le rôle de la taille de l'anion est étudié, à partir du comportement du sel de SbF_6 pour lequel un accroissement critique de la résistivité est vu à 154 K.

L'effet du dopage de $(\text{TMTTF})_2\text{SbF}_6$ par AsF_6 ou PF_6 est étudié et nous montrons que cette anomalie persiste pour de faibles taux de dopage. Enfin, l'existence d'instabilités structurales impliquant des anions centrosymétriques est brièvement discutée.

Abstract. — The structural and electrical properties of different $(\text{TMTTF})_2\text{MF}_6$ compounds are described and the rôle of the anion size is investigated through the behaviour of the SbF_6 salt for which a critical increase of the resistivity occurs below 154 K.

The effect of alloying $(\text{TMTTF})_2\text{SbF}_6$ with AsF_6 or PF_6 is also studied and we show that this electrical anomaly still exists for small amount of doping. Finally the existence of structural instabilities involving centrosymmetrical anions is briefly discussed.

Introduction.

The discovery of the superconducting properties of the tetramethyltetraselenafulvalene (TMTSF) radical cation salts [1-3] was the precursor of an intensive study of this series of compounds. The sulphur analogues of these salts, the tetramethyltetrathiafulvalene (TMTTF) salts were shown to be isomorphous and isostructural with these compounds [4] and thus belong to the same group of conductors. Actually some similarities were found between the physical properties of the two series. For example, low temperature antiferromagnetic ground states are observed for both TMTSF and TMTTF salts [5-7]. Another common feature concerns the possibility of anion ordering. Because of the « zig-zag » structure of these compounds [8] the anions are in cavities at a centre of symmetry of the room temperature $\text{P}\bar{1}$ crystallographic structure. When they are non-centrosymmetrical, the symmetry has to be restored by a statistical disorder of the anions and order-disorder phase transitions are generally observed at low temperature associated with the formation of superstructures [9]. The situation for centrosymmetrical anions (like octahedron) is less clear : a statistical disorder is no longer necessary to keep the inversion centre of the high temperature structure; however, some disorder of the anions was reported in recent structural

refinement [10]. At low temperature, NMR and EPR studies have shown the freezing of some degrees of freedom [11, 12] but the rôle of the anions in these processes is not completely clarified.

We compare in this paper the structural and electrical properties of the $(\text{TMTTF})_2\text{MF}_6$ compounds ($M = \text{P, As, Sb}$) and show that an unexpected result is found for the SbF_6 salt. To evaluate the influence of the anion we will also describe the effect of alloying $(\text{TMTTF})_2\text{SbF}_6$ with AsF_6 or PF_6 . Finally a discussion of the results will be given.

1. Synthesis and characterization of the samples.

All the compounds described in this paper were obtained with the usual electrochemical method with 1, 1, 2-trichloroethane as solvent. A very weak constant current ($2 \mu\text{A}$) allows the growth of good quality samples. To prepare the alloys described in the third part of the paper the corresponding proportion of tetrabutylammonium salts was introduced in the electrochemical cell. A dispersive energy fluorescence method allowed us to prove that the composition of the crystals was close to the nominal values with an accuracy of 5%. Furthermore by X-ray diffraction all samples studied showed well defined Bragg reflections and must be considered well crystallized.

2. Comparison of the physical properties of the $(\text{TMTTF})_2\text{MF}_6$ salts ($M = \text{P, As, Sb}$).

2.1 CRYSTAL STRUCTURE AT ROOM TEMPERATURE. — $(\text{TMTTF})_2\text{SbF}_6$ crystallizes in the space groupe $\text{P}\bar{1}$. Lattice parameters are reported in table I. A single crystal with dimensions $0.5 \times 0.05 \times 0.003 \text{ mm}^3$ was selected for the structural investigation which will be published in detail elsewhere. The structural packing of this salt is similar to that of other $(\text{TMTTF})_2\text{MF}_6$ compounds already described [14-16]. In particular the intra and interstack distances are not very different from those found in the PF_6 [14] or AsF_6 [15] salts. Nevertheless it is of interest to note that the shortest S-F distance (Fig. 1) is observed for $(\text{TMTTF})_2\text{SbF}_6$: $d_{\text{S-F}} = 3.21 \text{ \AA}$ (Table I). Therefore interactions between organic and anion stacks are certainly more significant in this latter salt, the $d_{\text{S-F}}$ distance being smaller than the sum of the sulphur and fluorine Van der Waals radii (3.27 \AA).

Table I. — Room temperature structural and electrical data for $(\text{TMTTF})_2\text{MF}_6$: $M = \text{P, As, Sb}$.

$(\text{TMTTF})_2$	Unit cell parameters						Shortest S-F distances (\AA)	Room temperature conductivity $\Omega^{-1} \text{ cm}^{-1}$	$T_C(\text{K})$
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$			
PF_6	7.154	7.576	13.208	82.65	95.26	107.62	3.30	40	—
AsF_6	7.178	7.610	13.317	82.03	95.75	107.11	3.27	25	105
SbF_6	7.195	7.622	13.450	81.19	96.56	106.19	3.21	10	154

A second important result of these comparative data is given by the thermal motion associated with the fluorine atoms. The SbF_6 salt shows a statistical disorder more significant than the PF_6 [16] and AsF_6 [15] compounds. Electron density maps in the bc plane reveal distinctly two equivalent statistically occupied positions of the F atoms. This last observation recalls the disordered anion model recently described for $(\text{TMTSF})_2\text{AsF}_6$ at 125 K [10].

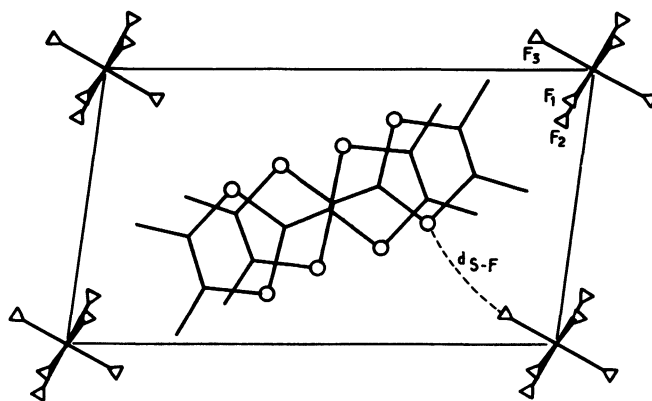


Fig. 1. — Projection in the *bc* plane of (TMTTF)₂SbF₆, showing the shortest S-F distance (○ : sulphur atoms ; △ : fluorine atoms).

2.2 ELECTRICAL PROPERTIES. — The electrical conductivity of the AsF₆ and SbF₆ salts was measured using the standard four probe method in order to compare the data with those of the PF₆ salt already published [18]. The room temperature values (σ_{RT}) are given in table I. It is found that σ_{RT} is a decreasing function of the anion size. The temperature dependences of the resistivity (ρ_T) of the three salts are given in figure 2. The behaviours of the PF₆ and AsF₆ salts are quite similar, however with a more pronounced minimum of ρ_T for the AsF₆ compound. A different behaviour is observed for the SbF₆ salt. The resistivity decreases more strongly at high temperature up to about 154 K where a sharp increase of ρ_T is observed leading to an insulating ground state at lower temperatures. This anomaly is more clearly observed in the behaviour of the quan-

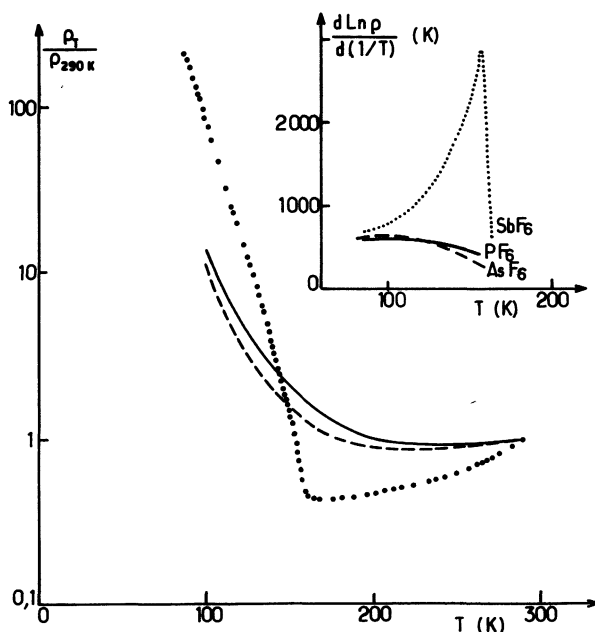


Fig. 2. — Temperature dependence of the normalized resistivity of (TMTTF)₂SbF₆ (TMTTF)₂AsF₆ ---, (TMTTF)₂PF₆ — (the data have been normalized at room temperature). In insert plot of the logarithm derivative of the resistivity.

tity $\Delta = d \ln \rho / d(1/T)$ versus T . The insert of figure 2 shows a sharp maximum of Δ around 154 K. On the other hand only a broad and very weak maximum remains for the AsF_6 salt and a monotonic decrease of Δ with T is obtained for the PF_6 salt. Finally it should be noted that the extrapolated value of Δ at low temperature is almost the same for the three compounds ($\Delta \simeq 600$ K).

2.3 LOW TEMPERATURE X-RAY DATA. — The first purpose of the X-ray investigation, combining the « Laue monochromatic » and the Weissenberg methods already used for the study of $(\text{TMTTF})_2\text{SCN}$ [7] was to check if the electrical anomaly found at 154 K in $(\text{TMTTF})_2\text{SbF}_6$ was accompanied by a structural phase transition. Laue monochromatic X-ray patterns as well as oscillating crystal X-ray patterns fail to detect any $2 k_F = 1/2 a^*$ and $4 k_F = a^*$ superstructure reflections below 154 K.

Likewise, Weissenberg photographs of the $[0 k l]$ reciprocal planes taken at 120 K give no evidence of $4 k_F$ superstructure reflections of intensity comparable to that observed in $(\text{TMTTF})_2\text{SCN}$ [7]. In addition no noticeable change in the intensity of the main Bragg reflections of the $[0 k l]$ and $[2 k l]$ reciprocal planes can be detected between 170 K and 120 K.

After the observation of a $2 k_F$ diffuse scattering below 60 K and its condensation in $(1/2, 1/2, 1/2)$ superstructure reflections around 10 K in $(\text{TMTTF})_2\text{PF}_6$ [17] we undertook a low temperature X-ray diffuse scattering investigation of $(\text{TMTTF})_2\text{SbF}_6$ and $(\text{TMTTF})_2\text{AsF}_6$. In $(\text{TMTTF})_2\text{SbF}_6$ no evidence of $2 k_F$ diffuse scattering was found down to 15 K. On the contrary in the same conditions a very weak quasi one dimensional $2 k_F$ diffuse scattering can be detected below about 40 K in $(\text{TMTTF})_2\text{AsF}_6$, recalling that found in $(\text{TMTTF})_2\text{PF}_6$. However in the present investigation it has not been possible to cool the sample to 10 K in order to check if the $2 k_F$ scattering condenses in superstructure reflections. Surprisingly $(\text{TMTTF})_2\text{AsF}_6$ also exhibits in the same temperature range a quasi one dimensional $4 k_F$ scattering which sharpens strongly as the temperature decreases. This observation needs further investigation.

3. Effect of alloying $(\text{TMTTF})_2\text{SbF}_6$ with AsF_6 or PF_6 .

To deepen the previous study and specify the rôle of the anion size we have prepared $(\text{TMTTF})_2(\text{SbF}_6)_{1-x}(\text{AsF}_6)_x$ and $(\text{TMTTF})_2(\text{SbF}_6)_{1-x}(\text{PF}_6)_x$ alloys.

The room temperature resistivity is a monotonic function of x for the two series of alloys. Upon cooling a metallic behaviour is first observed as shown in figures 3a and 4a. It becomes less and less pronounced when the amount of PF_6 or AsF_6 increases. At lower temperature an insulating ground state appears. The anomaly of the quantity $\Delta = d \ln \rho / d(1/T)$ already mentioned for the SbF_6 salt weakens upon doping (Figs. 3b and 4b). This effect is more pronounced for the PF_6 alloys, for which the maximum of Δ disappears when $x > 50\%$, than for the AsF_6 alloys where a maximum in Δ can be always detected.

The temperature T_c at which Δ presents its maximum value is given in the figure 5 for the different salts. For the two series of alloys T_c first decreases linearly when x increases. For the AsF_6 alloys the maximum becomes very broad for $x > 70\%$ and only a rough estimation of T_c can be given for the higher x values (dashed line in Fig. 5).

4. Concluding remarks.

The resistivity of $(\text{TMTTF})_2\text{SbF}_6$ shows clear evidence of an anomaly around 154 K. This behaviour which gradually disappears by alloying with AsF_6 or PF_6 recalls that found for $(\text{TMTTF})_2\text{SCN}$ [18]. The similarity between the two salts also concerns the low temperature magnetic properties. Preliminary EPR studies indicate an increase of the linewidth of the resonance line below 154 K and the stabilization of an antiferromagnetic ground state at $T \simeq 8$ K for $(\text{TMTTF})_2\text{SbF}_6$ [19] exactly as previously reported for the SCN salt [7].

For the latter compound, the anomaly of resistivity is the signature of a structural phase transition involving the ordering of the SCN anions in a $(a^* = 4 k_F, b^*/2, c^*/2)$ superstructure. Howe-

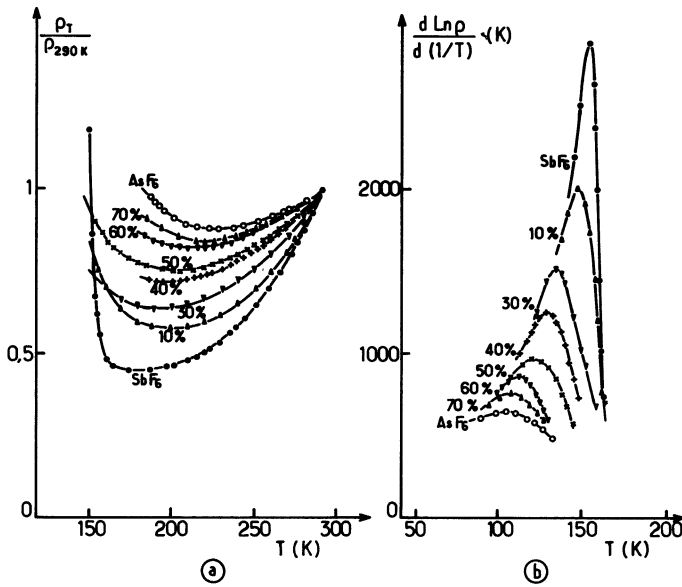


Fig. 3. — a) Temperature dependence of the normalized resistivity of some alloys $(\text{TMTTF})_2(\text{SbF}_6)_{1-x}(\text{AsF}_6)_x$ (the data have been normalized at room temperature). b) Logarithm derivative of the resistivity.

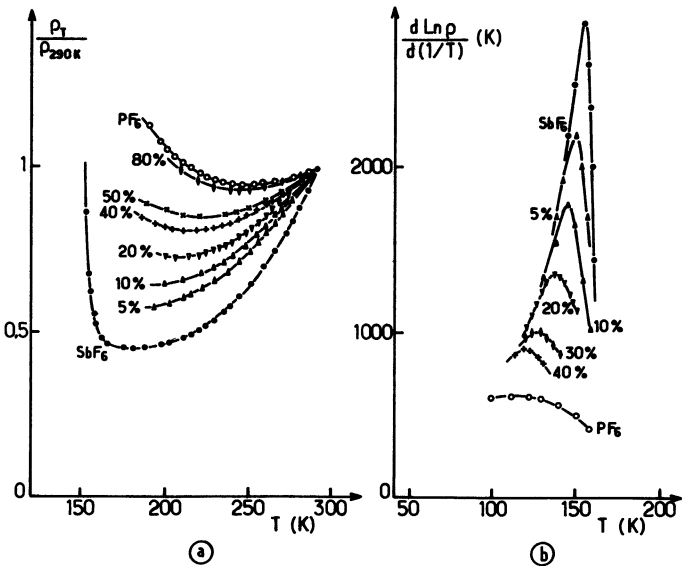


Fig. 4. — a) Temperature dependence of the normalized resistivity of some alloys $(\text{TMTTF})_2(\text{SbF}_6)_{1-x}(\text{PF}_6)_x$ (the data have been normalized at room temperature). b) Logarithm derivative of the resistivity.

ver up to now no sign of $4 k_F$ or $2 k_F$ superstructure reflections has been found for the SbF_6 salt, in spite of the structural refinement, suggesting from the occurrence of two statistically occupied positions at 300 K for the SbF_6 anion, a possible ordering at lower temperature. Nevertheless one should consider that an ordered ground state below 154 K may be hard to detect. The difficulty in this detection is either because of very weak superstructure reflection intensities or because of the

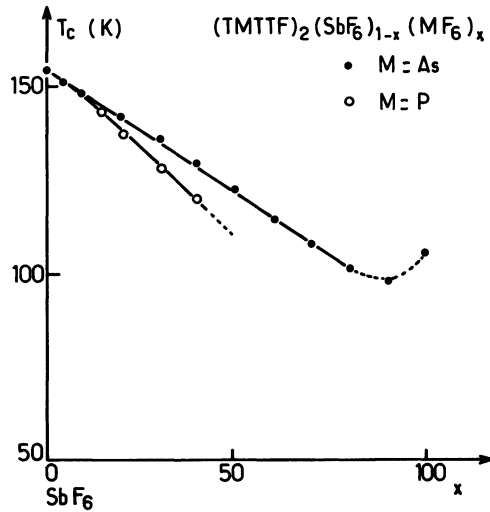


Fig. 5. — Concentration dependence of the temperature T_c defined by the maximum of $d \ln \rho / d(1/T)$ in figures 3b and 4b, for the alloys $(\text{TMTTF})_2(\text{SbF}_6)_{1-x}(\text{MF}_6)_x$ with $M = \text{As}$ and P .

occurrence of an ordering without any change of the crystal symmetry allowing for the centrosymmetrical anions. Further low temperature X-ray studies would be useful to clarify this point.

The rôle of the anions as a driving force of the 154 K anomaly of $(\text{TMTTF})_2\text{SbF}_6$ is still questionable and other explanations for the unexpected behaviour of this salt may be proposed. For example the unit cell parameter in the z direction has been shown to be relevant to describe the low temperature behaviour of the $(\text{TMTSF})_2\text{X}$ salts [3, 12]. Structural data of table I show clearly an increase of the c parameter and the decrease of the shortest S-F distance along the sequence PF_6 , AsF_6 , SbF_6 . The increase of the c parameter along which sheets of TMTTF and anions alternate leads to a decrease of the coupling between organic molecules. On the other hand the decrease of the S-F contact distance leading to an increase of the chemical bonding between the MF_6 and the TMTTF molecule may favour the localization of a hole in the vicinity of this bond as has been suggested recently by Bruinsma and Emery [20]. The origin of the observed anomalies of resistivity may be related to these structural parameters. The evolution of these parameters is being investigated in the alloys and will be published elsewhere.

Whatever is the origin of the electrical anomalies reported in this letter it is important to know if they are the result of a true phase transition. At least for the pure SbF_6 compound which displays a sharp anomaly reminiscent of that for $(\text{TMTTF})_2\text{SCN}$ the condensation of a new kind of long range order below 154 K is not excluded. It should be noted that the temperature dependence of the resistivity of $(\text{TMTTF})_2\text{PF}_6$ was explained by a continuous localization of the electrons without any phase transition [18, 21], which might be driven by the $4 k_f = a^*$ potential of the anion lattice. The continuous decrease of the room temperature electrical conductivity and the enhancement of the electrical anomaly when the amount of SbF_6 increases in the alloys, may suggest that the explanation is still valid for all the compounds including $(\text{TMTTF})_2\text{SbF}_6$. For this last salt the sharp anomaly would simply indicate the vicinity of a critical point. Further experimental investigations are in progress to try to distinguish between these possibilities.

Finally it is noteworthy that an antiferromagnetic ground state is found below 10 K for the SbF_6 and SCN salts in contrast with the condensation of a non magnetic ground state around 15 K for the AsF_6 and PF_6 compounds [15, 18]. In this respect a $2 k_F$ diffuse scattering is only found for the two latter salts and the condensation of the $2 k_F$ scattering in $(1/2, 1/2, 1/2)$ superstructure reflections in $(\text{TMTTF})_2\text{PF}_6$ proves that the non magnetic ground state, generally viewed as the

result of a spin Peierls instability, has a structural component. Therefore it may be suggested, as already proposed for (TMTTF)₂SCN [7], that the process giving rise to the high temperature electrical anomaly is, quite generally in the TMTTF series, the first step to get an antiferromagnetic ordering of the spins in the localized state. This point will be discussed in more detail elsewhere [19].

In conclusion our results indicate that the classification of the TMTTF salts in distinct groups according to the symmetry of the anions may be irrelevant. A detailed analysis of the interaction between the organic stacks and the anions is probably necessary to understand the behaviour of the (TMTTF)₂MF₆. Quite generally this may be an important asset in describing the competition between the low temperature ground states as already suggested by Bruinsma *et al.* [21].

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