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Physical properties and phase transitions in the (tTTF)₂X series of organic conductors

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Abstract. — The electrical, magnetic and structural properties of several (tTTF)₂X salts with X = PF₆, AsF₆, SbF₆, ClO₄, ReO₄, Br have been investigated. In each case, low temperature phase transitions are found corresponding to the stabilization of various ground states. In the case of salts with the octahedral anions (X = AsF₆, SbF₆), the antiferromagnetic ground state observed below T_N = 25 K and 19 K respectively has been characterized by resonance measurements. In the case of the ClO₄ salt a structural distortion, probably relaxing the Coulomb repulsions between localized charges, is observed at 137 K. An unusual phase transition affecting both the charge and spin degrees of freedom is observed in the PF₆ salt around 50 K. A comparison is made with the properties of the TMTTF salts and related series in order to rationalize these results. Finally the role of the interchain coupling in the competition between the spin-Peierls and antiferromagnetic ground states is emphasized.

Introduction.

It is now well established that many organic salts deserve a unified description of their structural and physical properties [1]. Among these compounds there are the TMTSeF salts which are also known as « Bechgaard salts » for which organic superconductivity was first discovered [2]. A common characteristic of these salts is their stoichiometry, namely two organic molecules for one counterion and a crystallographic structure in which organic layers alternate with planes of anions. Moreover, the stacking of the organic molecules in the planes allows a classification of these salts into two groups [3]:

- in many compounds, the molecules are stacked in weakly dimerized chains. The TMTTF salts belong to this category which is labelled as type I in the following;
- other salts like (DIMET)₂SbF₆ present a much larger dimerisation and the organic layers are better described as a 2D lattice of dimers. In this case we talk of salts of type II.

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The physical properties are reminiscent of the structural organisation. The electrical resistivity of samples of type I ranges from a strongly metallic to a semiconducting behavior (i.e. an activated resistivity). Intermediate behaviors with a minimum of resistivity at a temperature T_p below room temperature are also found. These different situations, all corresponding to the same paramagnetic phase, show a weakly temperature dependent spin susceptibility. In other words, there is a decoupling between charge and spin degrees of freedom. An activated resistivity reveals an electronic localization which is a 1D effect and does not correspond to a phase transition. This localization has been explained by the $4k_F$ charge density wave response function of the organic chain to the anionic potential [4]. Samples of type II which present a stronger dimerisation also show a stronger electronic localization. These materials can be described in the strong coupling limit (where Coulomb interactions are dominant) and their magnetic susceptibility is characteristic of 1D (or 2D) spin lattices in the paramagnetic phase [3, 5].

A few years ago the molecule tTTF (trimethylenetetrafulvalene) was synthesized combining one half of the TTF molecule with one half of the HMTTF molecule and 2 : 1 salts were prepared.

The physical properties of these materials were briefly described in [6]. This first study was limited by the poor quality of the samples then prepared. However, because of the activated behavior of their electrical resistivity, these salts also offer the opportunity to study the role of charge localization in the physics of quasi-one dimensional conductors.

We present in this paper a more complete study of these effects by combining structural, electrical and magnetic measurements for samples of better quality obtained with octahedral (PF_6^- , AsF_6^- , SbF_6^-), tetrahedral (ClO_4^- , ReO_4^-) and spherical (Br^-) anions. In particular, special care has been devoted to the study of low temperature phase transitions exhibited by these materials.

Experimental.

The samples have been prepared as already described in [6]. Special care has been taken for the separation of the tTTF molecule from the mixture containing also TTF and HMTTF. This is certainly an important condition to obtain good quality samples.

Electrical conductivity has been measured along the needle axis (a direction) of the samples with a low frequency lock-in equipment. Contacts were made with platinum paste in the standard four-in-line configuration. ESR measurements were made with a Varian X band spectrometer operating at fixed frequency (9.3 GHz). The same equipment was used for antiferromagnetic resonance measurements.

As in previous studies of structural instabilities of organic conductors, the X-ray diffuse scattering experiments have been performed with the so-called fixed film-fixed crystal method using a monochromatised $\text{CuK}\alpha$ X-ray source as incident radiation. Temperatures regulated from 25 K to room temperature were obtained with a closed circuit cryostat. The photographic study was completed by quantitative measurements using a position sensitive linear detector.

Fig. 1. — Electrical conductivity of tTTF salts (note the semi-log plot). The logarithm derivative for the PF₆ and ClO₄ salts is given in the inset.

Electrical conductivity.

The room temperature conductivity is about $10 \Omega^{-1} \text{ cm}^{-1}$ for the PF₆, AsF₆ and SbF₆ salts. It is about 30 times smaller for the ClO₄ salt. These numbers are in agreement with the preliminary results given in [6]. The temperature dependence of the resistivity of these compounds is given in figure 1. Three different behaviors can thus be deduced from these measurements.

1) (tTTF)₂ClO₄ shows a semiconducting behavior. An anomaly in the temperature dependence of its resistivity is observed at 137 K. This is illustrated in the inset of figure 1 where the logarithmic derivative of the resistivity has a sharp peak at this temperature. The corresponding gap Δ defined by the extrapolation at low temperature of this derivative has the same order of magnitude (~ 900 K) above and below the anomaly.

2) The behavior in temperature of the AsF₆ and SbF₆ salts is very similar. For this reason only the data for SbF₆ is given in figure 1. Moreover, the conductivity of (tTTF)₂AsF₆ was already given in reference [6]. No minimum of resistivity is observed when cooling in contrast with the (TMTTF)₂X compounds [7] however the observed temperature dependence suggests a minimum of resistivity above room temperature. Thus these salts should belong to the group of materials of type I previously defined. Below room temperature the resistivity is roughly activated with a gap of about 1 000 K, a value similar to that shown by the ClO₄ salt.

3) When cooling, the temperature dependence of the resistivity of the PF₆ salt is at first very small, then after a broad minimum around 200 K shows an increase at low temperatures. The inset of figure 1 shows a clear increase of the gap Δ around 60 K. Δ is almost saturated

below 40 K with a value close to 300 K. Finally it should be noted that the samples are very brittle around 230 K (dashed region shown in Fig. 1) and the incorporation of the crystals into grease was necessary to prevent their degradation around this temperature. This has probably to be correlated with the poor X-ray quality of the samples (most of them are a collection of misoriented crystals with a common a direction) or with a possible freezing of the solvent included in the structure (see next part).

The poor crystal quality of the ReO_4 salt did not allow any electrical measurements. Preliminary results were obtained for the Br salt which has a conductivity similar to that of the SbF_6 or AsF_6 compounds. However because of their irregular shape, the determination of the conductivity along the stack direction would require an X-ray orientation of the crystals.

X-ray measurements.

Table I gives the lattice symmetry and lattice parameters of some crystals considered in this study. $[0, k, \ell]$, $[1, k, \ell]$ and $[2, k, \ell]$ Weissenberg photographs show that the PF_6 salt belongs to the $\text{P}_{21/n}$ space group. The lattice parameters have been determined both from rotating crystal, Weissenberg photographs and by the measurement of the position of $25(h, k, \ell)$ reflections on a 4 circle diffractometer. Surprisingly the cell volume obtained is about $200 \text{ \AA}^3$ larger than that for the ClO_4 salt ($Z = 2$) or twice that of the AsF_6 salt ($Z = 1$). This suggests that two molecules of the solvent (trichloroethane) used in the electrocrystallization (each of them with a volume of about $100 \text{ \AA}^3$) are incorporated in the structure. The lattice parameters of the SbF_6 salt have been determined from rotating crystal and $[h, k, \ell]$ with $h = 0, 1, 2, 3$ Weissenberg photographs, according to the procedure developed in reference [8].

Then we have performed a low temperature X-ray diffuse scattering investigation of the ClO_4 and PF_6 salts in order to detect possible structural phase transitions.

a) In the ClO_4 salt, X-ray patterns clearly reveal the occurrence of a structural phase transition at about 137 K (T_c), temperature at which an anomaly of resistivity is observed (see Fig. 1). The structural transition below T_c consists in

Table I. — *Structural parameters of some $(\text{tTTF})_2\text{X}$ salts at room temperature.*

X	ClO_4	PF_6	AsF_6	SbF_6
a ($\text{\AA}$)	14.42	7.13	7.376	7.56
b ($\text{\AA}$)	6.45	11.76	6.398	6.56
c ($\text{\AA}$)	13.35	17.08	12.811	13.06
α (deg)	96.0	90	83.52	83.9
β (deg)	104.9	90.8	86.36	88.6
γ (deg)	81.9	90	85.88	86.5
V ($\text{\AA}^3$)	1 163	1 433	598.2	643
Z	2	2	1	1
Space group	P_1	$\text{P}_{21/n}$	P_1	P_1
Reference	[22]	This work	[6]	This work

Fig. 2. — Temperature dependence of the intensity of a superlattice reflection (a) and of a main Bragg reflection (b) of (tTTF)₂ClO₄.

i) the onset of superlattice Bragg reflections at the reduced wave vector $(0, 1/2, 1/2)$ with respect to the main Bragg reflections of the high temperature lattice, whose parameters are given in table I ;

- ii) an elastic deformation of the main (high temperature) Bravais lattice ;
- iii) a huge change of intensity of some main Bragg reflections.

More quantitatively figure 2a gives the temperature dependence of a superlattice reflection. It shows a rapid increase of intensity from 136.8 K ($\equiv T_c$) to 134 K, then a smoother rate of increase for lower temperatures. No saturation in its rate of increase is observed down to 25 K the lowest temperature reached. The average intensity of the superlattice reflections is about one tenth of that of the main reflections. Isotropic pretransitional fluctuations can be observed up to about 200 K.

Figure 2b gives the temperature dependence of a main Bragg reflection strongly affected by the phase transition. It shows a strong decrease of intensity in the first five degrees below T_c , then a more gentle decrease of intensity down to 80 K, where about 85 % of the intensity is lost. The dip of intensity shown at T_c in figure 2b is probably an artifact produced by a slight misalignment of the crystal undergoing strong elastic deformations at T_c .

All the structural data are consistent with a continuous (2nd order) phase transition at T_c . Moreover the transition involves considerable structural modifications as emphasized by the strong intensity of the superlattice reflections, the important change of intensity of some main Bragg reflections and the elastic deformation of the Bravais lattice. A structural refinement of the low temperature structure is necessary in order to describe these modifications more precisely.

b) We have performed a low temperature investigation of the PF₆ salt with the fixed film-fixed crystal method down to 30 K (in order to detect a possible structural transition around

50 K), temperature at which anomalies are observed by ESR measurements (see next part). Our investigation does not reveal any superstructure formation at low temperatures but we have observed below 50 K an increase of the intensity of some Bragg reflections of the high temperature lattice. This last feature could be associated with a structural phase transition at constant unit cell volume breaking some symmetry elements of the high temperature $P_{21/n}$ space group.

ESR measurements.

For all the samples, Lorentzian lines are observed. The eigendirections of the g tensor were obtained after measuring the ESR signal for six different directions of the magnetic field. The eigenvalues are respectively :

$$g_{\min} = 2.0022(5) \quad g_{\text{int}} = 2.0070(5) \quad g_{\max} = 2.0100(5).$$

These eigendirections of the g tensor are related to the molecular axes : respectively the perpendicular to the molecular plane, the short molecular and the long molecular directions [9]. They do not correspond to simple crystallographic directions. For this reason we have not tried to compare in details the ESR data between the different $(\text{tTTF})_2\text{X}$ salts.

The ESR data for $(\text{tTTF})_2\text{ClO}_4$ are given in figure 3. The g factor being almost independent of temperature is not shown. These data correspond to a direction of the magnetic field close to $g_{\max}$. The magnetic susceptibility always decreases when cooling (note the semi-log scale in Fig. 3a). As shown in the inset, there is clearly a change of slope around 140 K (a semi-log plot of χT versus $1/T$ reveals a magnetic gap assuming $\chi = \frac{C}{T} e^{-\Delta/kT}$).

Fig. 3. — ESR data for the ClO_4 salt : (a) normalised susceptibility (a log-log plot is given in the inset), (b) linewidth.

From these data we get the following magnetic activation energy : $\Delta_H \approx 700$ K for $T \geq 140$ K, $\Delta_L \approx 1000$ K for $T \leq 140$ K. These two regimes are also visible from the temperature dependence of the linewidth which first decreases upon cooling and then increases below 140 K. These magnetic anomalies support the occurrence of a structural phase transition at 137 K. Finally, these data are very similar to those already published in reference [6] for $(\text{tTTF})_2\text{BF}_4$ since the results are very close above 100 K (below this temperature the susceptibility is very small and extrinsic effects are most likely to be observed). This is a strong argument to suggest that the tetrahedral geometry of the anion is relevant and that one may expect to observe related properties for the ReO_4 salt.

Fig. 4. — ESR data for the ReO_4 salt : (a) normalised susceptibility, (b) linewidth. The low T variation of the g factor is given in the inset.

The ESR data for this compound shown in figure 4 are clearly different. These magnetic features are typical of weakly dimerized salts such as those of the $(\text{TMTTF})_2\text{X}$ series [1]. At low temperatures the vanishing susceptibility and the divergence of the linewidth at $T_N \approx 20$ K are characteristic of the condensation of an antiferromagnetic ground state [10].

The ESR data for the SbF_6 salt are given in figure 5. The results for AsF_6 are very similar. The AsF_6 results resemble that shown in figure 4 for the ReO_4 salt. Most of the crystals are twinned [11] and the ESR spectrum is composed of several lines. Special care should be taken to separate these signals for a proper study of one of them. For this reason the data shown in figure 5 are not taken along a simple magnetic direction. This difficulty also explains the poor accuracy of the results given in reference [6] for the AsF_6 salt (the decrease of susceptibility at 60 K is an artifact due to the deformation of the composite ESR signal). The linewidth first decreases with T while the g factor is almost independent of temperature. At the same time the magnetic susceptibility decreases smoothly. Below 35 K antiferromagnetic fluctuations

Fig. 5. — ESR data for the SbF_6 salt : (a) g factor and linewidth, (b) normalised susceptibility.

Fig. 6. — ESR data for the PF_6 salt: (a) normalised susceptibility, (b) g factor and linewidth. The deduced orientation of the g tensors of the two lines observed below 50 K is given in the inset of figure 6a. In figure 6b, the results for both lines are given below 50 K.

are observed. The Néel temperature is respectively $T_N \approx 25$ K and 19 K for the AsF_6 and SbF_6 salts. In the next section we show antiferromagnetic data that confirm the occurrence of a magnetic ordering.

The results for the PF_6 salt are given in figure 6. Above 50 K a single line is observed with a smooth T dependence of the susceptibility and linewidth. At the same time, the g value is T independent (for this experiment the magnetic field was applied close to $g_{\min}$). Around 50 K we observe a splitting of the ESR signal into two lines. The new characteristics of the g tensor were obtained from a study of the rotation figures at low temperatures. The deduced eigendirections are given in the inset of figure 6. Within the accuracy of the experiment the eigenvalues are the same and the g_{int} direction is common to the two lines. Thus the low T

Fig. 7. — ESR data for the Br salt: (a) linewidth. The log-log plot which shows the critical behavior close to the magnetic ordering is given in the inset (the slope of the continuous line is 1.5). Also shown is the g factor temperature dependence close to the Néel temperature. (b) Normalised susceptibility.

eigendirections are simply deduced from the room temperature tensor by a rotation of about $\pm 10^\circ$ around g_{int} . Since these rotations are related to the molecular axes directions [9] the results suggest that below 50 K the molecules rotate by about 10° around their short molecular axis. The occurrence of two lines then indicates two different molecular orientations in the structure. Since no superstructure has been observed below 50 K by X-ray studies, it is possible to interpret the ESR data by a staggered rotation of the two dimers composing the unit cell. A low temperature refinement of the structure is necessary to clarify this point. In addition to the ESR line splitting, a sudden drop of the linewidth ΔH and of the spin susceptibility χ_n is observed (Fig. 6). However our data suggest that the susceptibility remains finite and gapless below this anomaly.

Results for the Br salt are given in figure 7. This behavior is also typical of salts of type I. The condensation of the AF order is observed with the highest Néel temperature ever reported: $T_N \approx 33$ K. As expected the linewidth diverges when approaching T_N . The particularly clear divergence of the linewidth in temperature allows a rather accurate determination of the corresponding critical exponent. This determination is performed by the log-log plot in the inset of figure 7a. The deduced value of the exponent agrees quite well with the mean field theoretical prediction ($\mu = 1.5$) of reference [12].

Antiferromagnetic resonance.

The ESR data suggest that the ReO_4 , Br, AsF_6 and SbF_6 salts have a low temperature antiferromagnetic ground state. Because of the sample quality, antiferromagnetic resonance (AFMR) has only been detected for the last two salts below the Néel temperature T_N . The experimental temperature (4.5 K) was low enough compared with T_N to consider that the zero temperature limit is reached.

The results are given in figure 8. Simple crystal directions (shown in inset) were chosen as rotation axes. In both cases the experiment was limited by the morphology of the crystals: good quality crystals were usually too small for a quantitative study of AFMR. Moreover, most of the samples are twinned as shown by the occurrence of two ESR signals.

In the case of the SbF_6 salt, a rather big crystal was found giving only one ESR line. The X-ray characterisation has shown that it was a collection of several crystals oriented in very close directions. Since no other crystal of reasonable size was available, we have used this sample for the AFMR study. Its AFMR spectrum consists of two lines following very similar rotation patterns. Figure 8 (a, b) shows the patterns for the narrowest line. The continuous lines in this figure give the fit using the Nagamiya theory [13]. This allows the determination of the

Table II. — AFMR parameters deduced from the fit using the Nagamiya theory. For the SbF_6 salt, (a) and (b) refer to the two observed signals. $r = 1 - \chi_{\parallel}/\chi_{\perp}$ is taken equal to 1 (zero temperature limit). Ω_- and Ω_+ are the zero-field frequencies. θ and φ are the polar angles of the rotation axes (see inset of Fig. 8) in the magnetic frame.

	r	Ω_+ (kG)	Ω_- (kG)	θ°	φ (°)
SbF_6	1	12.8	7.4	0	—
a)	(1)	(12.3)	(7.1)	(0)	—
b)	1	12.8	7.4	85	85
	(1)	(12.3)	(7.1)	(85)	(85)
AsF_6	1	13.3	7.6	10	25

Fig. 8. — (a) and (b) AFMR rotation patterns for $(tTTF)_2SbF_6$. The orientation of the crystal and the rotation axes are given in the inset. The continuous lines give the fit using the Nagamiya theory. The theoretical parameters are given in table II. (c) Deduced orientation of the magnetic axes relative to the crystal. Note that the easy axis is either at $\approx 80^\circ$ or $\approx 100^\circ$ from a . (d) Corresponding data for the AsF_6 salt. The theoretical parameters are also given in table II.

eigenvalues and eigendirections of the magnetic anisotropy which are reported in figure 8c. The fit of the broadest signal gives the same position of the magnetic axes within the experimental accuracy. The zero field frequencies are about 4 % smaller than those of the narrow line. We have presently no clear explanation for this result which may be simply the consequence of the imperfection of the sample used. The corresponding parameters are given in table II. The zero field frequencies $\Omega_{\pm}$ are similar to those observed for the other organic compounds [10]. For both lines, $r = 1$ is a reasonable value since the experimental temperature is small with respect to T_N .

For the AsF_6 salt, only small crystals were available and probably because of polarisation effects, only the bubble-like pattern has been detected (Fig. 8d). Moreover, only one line was found. The parameters deduced from the fit are also given in table II. As in the previous case,

$r = 1$ is obtained and a very similar position of the easy axis is suggested although the determination of the magnetic anisotropy is incomplete. Compared with the narrow line of SbF₆, the zero field frequencies are approximately 4 % larger, in agreement with the slightly larger T_N found for the AsF₆ salt.

Discussion.

A striking feature of the (TTF)₂X series is the wide variety of behaviors found when the anion is changed. With X, at least three different crystallographic structures are found at room temperature in this series (Tab. I). Each structural type has a different temperature behavior of the electrical conductivity (Fig. 1) and stabilizes a ground state of different nature. ESR results suggest a magnetic phase transition for the AsF₆, SbF₆, ReO₄ and Br salts. The antiferromagnetic ground state has been firmly confirmed in the former two salts by AFMR measurements. A structural phase transition with a superstructure formation is observed in the ClO₄ salt at 137 K. This phase transition changes the activation energy of the spin degrees of freedom (deduced from spin susceptibility measurements, Fig. 3) but not the charge degrees of freedom (deduced from conductivity measurements, Fig. 1). ESR measurements suggest that the PF₆ salt could undergo a structural phase transition at about 50 K. At this temperature a drop of spin susceptibility (Fig. 6) and an increase of the activation energy of the electrical conductivity (Fig. 1) are observed. Let us now discuss these different behaviors more precisely.

1. (TTF)₂ClO₄. — The room temperature lattice parameters of the ClO₄ salt are given in table I. They are very close to those of the BF₄ salt for which a structure refinement shows at room temperature [6] :

- an alternate ordering of the tetrahedral anion and a tetramerisation of the organic stack along the *a* direction
- a uniform ordering of the anions in the other two directions.

With respect to the $a \times b \times c$ prototype unit cell of the Bechgaard salts (or that of the AsF₆ salt), the room temperature structure of the BF₄ and ClO₄ salts can be described by a $2a \times b \times c$ supercell corresponding to the ordering of the tetrahedral anions with the wave vector $(1/2, 0, 0)$. Although the $a^*/2$ component amounts to the $2k_F$ wave vector of the 1D electron gas in the 2 : 1 series of organic conductors, the tetramerisation of the organic stack may not be at the origin of the electronic localization since a similar activation energy is observed in the non-tetramerized AsF₆ salt. One alternative is that the activated behavior is due, as in many other salts of type I, to the $4k_F$ charge localization effects of one charge per dimer of molecules. Moreover the $2k_F$ tetramerisation of the organic stacks could be responsible for the activated behavior of the spin susceptibility (Fig. 3) as the formation of tetramers leads to a pairing of two spins in a singlet state. This pairing creates a gap in the magnetic excitation spectrum (i.e. singlet-triplet splitting in the extreme case of well decoupled tetramers). This last limit is certainly not encountered in the ClO₄ salt above T_c since the observed magnetic gap is of the order of a few $k_B T$. Moreover, in agreement with this interpretation, an activated spin susceptibility is not observed in the AsF₆ salt containing only dimerized stacks.

The ClO₄ salt undergoes a structural phase transition at $T_c = 137$ K (a similar transition at a slightly lower temperature is expected for the BF₄ salt whose ESR behavior above 100 K is nearly identical to that of the ClO₄ salt [6]). This phase transition exhibits quasi-isotropic pretransitional fluctuations, which seems to indicate that it is driven by the interstack coupling (an intrastack driving force leads to quasi 1D pretransitional fluctuations as in a pure Peierls or spin-Peierls instability). At this transition a doubling of the lattice parameters in the *b* and *c*

directions, transverse to the stacking axis, is observed. This new periodicity can be explained by a sequence of intradimer or interdimer distortions out of phase in all directions. As a tetramer is made of two dimers the periodicity in the stacking direction **a** is kept. This and the considerable structural modifications observed at T_c on the main lattice could be easily understood if the instability relaxes Coulomb repulsions between charges localized on neighboring tetramers and between tetramers and anions. Usually the minimization of Coulomb interactions leads to an out-of-phase ordering of charge extrema consistently with the information given above.

The main effect of the distortion on magnetic properties is an increase of the magnetic gap. We believe that such a feature is more likely the consequence of the distortion than its driving force. When it is the case, as for the spin-Peierls instability of related compounds like $(\text{TMTTF})_2\text{PF}_6$ or $(\text{BCPTTF})_2\text{PF}_6$, the phase transition occurs at a much lower temperature (15-30 K) [7, 14] than in $(\text{tTTF})_2\text{ClO}_4$.

2. $(\text{tTTF})_2\text{PF}_6$. — At first it is surprising, with respect to the $\text{TMTT}(\text{Se})\text{F}$ prototype series, that salts with octahedral anions could adopt different structures. Table I shows that this is the case in the $(\text{tTTF})_2\text{X}$ series for the $(\text{PF}_6, \text{AsF}_6, \text{SbF}_6)$ anions. The PF_6 salt is monoclinic with $Z = 2$ while the AsF_6 and SbF_6 salts are triclinic with $Z = 1$. In addition the PF_6 salt probably incorporates two solvent molecules per unit cell. This certainly implies a different packing of the tTTF molecules. A more detailed comparison between these salts requires a full structure determination. Nevertheless it is clear that the difference in packing arrangement has a considerable influence on their physical properties, especially on the electrical conductivity and low temperature ground state. Figure 1 shows that the charges are much less localized in the PF_6 salt than in the AsF_6 and SbF_6 ones. A progressive localization occurs in the former case at low temperatures (i.e. below about 200 K) a behavior which resemble that of $(\text{TMTTF})_2\text{PF}_6$ with however a much smaller activation energy ($\Delta \sim 100$ K compared to 600 K [7]). This last feature could explain why $(\text{tTTF})_2\text{PF}_6$ shows an unusual phase transition at about 50 K where the charge activation energy Δ exhibits a further increase by a factor of 2 (Fig. 1) and where the spin susceptibility decreases by a factor of 4 (Fig. 6a). This means that both the charge and spin degrees of freedom are involved in the transition. These features are partially reminiscent of those observed in Peierls transitions with, however, an important difference since the spin susceptibility remains flat (i.e. gapless) below the transition. Such a situation could be achieved by a partial pairing below 50 K of two dimers per unit cell. The pairing could arise from a staggered rotation of the dimers previously invoked to explain the splitting of the eigendirections of the g tensor. Moreover the sample could remain paramagnetic if the pairing does not occur on every organic chain. This situation implies the occurrence of non-equivalent chains in the low temperature structure. This can be obtained by breaking at least one symmetry element of the $\text{P}_{21/n}$ high temperature space group. As the structural arrangement of the tTTF molecules is not known the mechanism of this transition cannot be further discussed.

Last but not least, it is striking that by the drop of the spin susceptibility and of the ESR linewidth the transition found in $(\text{tTTF})_2\text{PF}_6$ recalls that previously reported at 269 K and 273 K in the $(\text{BEDTTTF})_2\text{X}$ salts of AsF_6 and SbF_6 respectively [15]. The results are slightly different in these materials since a doubling of the unit cell is observed along the **b** direction of best conductivity at the transition. However it should be noted that two non-equivalent stacks are found in the low temperature structure of these BEDTTTF salts [16].

3. $(\text{tTTF})_2\text{AsF}_6$ and SbF_6 . — The AsF_6 and SbF_6 salts show a substantial $4 k_F$ localization of their charge degrees of freedom at room temperature and below. Moreover an antiferromagnetic ordering is found in both cases at low temperature.

Up to now, only the room temperature structure of the AsF₆ salt is known [6]. However the AsF₆ and SbF₆ salts have very similar lattice parameters (see Tab. I) which indicates that both compounds certainly adopt the same structure. (tTTF)₂AsF₆ is isomorphous to the Bechgaard salts (TMTTF or TMTSeF salts) with at least two noticeable differences :

- the molecules are not perpendicular to the stacking axis. This can be checked by the determination of the g tensor eigendirections. In particular the one corresponding to $g_{\min}$ makes an angle with the needle direction $\mathbf{a}$. This seems to be a general characteristic of the (tTTF)₂X series ;
- the angle γ ($\approx 86^\circ$ see Tab. I) is larger than that found in the TMTTF or TMTSeF series ($\approx 70^\circ$).

These structure differences have some consequences on the magnetic anisotropy that we shall discuss in the following.

From the structure of Bechgaard salts, the characteristics of the magnetic anisotropy have been calculated as a function of the magnetic superstructure. For sulfur compounds, dipolar interactions were shown to be dominant and the results are essentially a function of the $\mathbf{b}$ component q_b of the magnetic ordering [17]. This wave vector can be related to a parameter ϕ as follows [18] :

$$q_b = \frac{b^*}{2} \left(1 + \frac{2\phi}{\pi} \right) . \quad (1)$$

The anisotropy energy and the position of the magnetic axes are therefore function of ϕ which is a function of the transfer integrals in the $(\mathbf{a}, \mathbf{b})$ plane. In particular ϕ is drastically dependent of the balance between the different components of the transverse interactions which are T dependent. Thus low temperature crystallographic data are necessary to estimate this parameter. On the other hand, when ϕ is determined, the other details of the structure are less relevant to estimate the magnetic anisotropy and a prototype structure has been used to discuss the role of ϕ within the TMTTF and TMTSeF series [18].

To illustrate this argument, we have calculated the magnetic anisotropy for a very simplified model of the structure of salts of type I. Since the correction due to the coupling in the c direction is small [18], we have used a 2D model. Each molecule is reduced to a point site and the lattice mimics the organization of the organic molecules. Diads are introduced in the $\mathbf{a}$ direction (by the introduction of d_1), $\gamma \neq 90^\circ$ and $a \approx b$. This lattice is shown in the inset of figure 9a. The results for $d_1 = a/2$, $b = a$, and $\gamma = 70^\circ$ are given in figures 9a and 9b.

As shown in figure 9, two domains labelled I and II are found whose limits are identified by a divergence of $R = W_{\text{IH}}/W_{\text{EI}}$ where W_{IH} and W_{EI} are the differences between the eigenvalues of the anisotropy energy in the intermediate-hard and easy-intermediate planes respectively. The divergence of R comes from the cancellation of W_{EI} at the borderline between the domains. Figure 9a also shows the sum $S = W_{\text{IH}} + W_{\text{EI}}$ in arbitrary units (an absolute determination would require a choice of the amplitude of the spin density wave condensed on the chains).

The calculated information on eigendirections is given in figure 9b. Due to the 2D nature of the calculation, one of the eigendirections of the magnetic anisotropy is $\mathbf{c}^* = \mathbf{a} \times \mathbf{b}$ and the other two are in the $(\mathbf{a}, \mathbf{b})$ plane. Following the notation given in the inset, this means that the polar angle φ of any eigendirection is either 0 or 90° . In the latter case the corresponding polar angle θ is 90° (the corresponding direction is $\mathbf{c}^*$). Thus only the knowledge of θ for two eigendirections is necessary to characterize the magnetic frame in this simple model. These results are given in figure 9b for the easy and intermediate axes. Continuous functions are obtained in each domain (considering that 0 and 180° are equivalent values of the angle θ). In particular, in domain II where θ_1 is 90° (i.e. the intermediate axis is along $\mathbf{c}^*$) there is an

Fig. 9. — (a) and (b) theoretical determination of the anisotropy using the simple model described in the text (the notation for the lattice and polar angles is given in the inset). (a) R is the ratio between W_{IH} and W_{EI} difference between the anisotropy energies in the intermediate-hard and easy-intermediate planes respectively (continuous line). S (dotted line) is the sum $W_{IH} + W_{EI}$ in arbitrary units. Domains I and II are defined in the text. (b) Polar angle θ_E (continuous line) and θ_I (dotted line) for the easy and intermediate axes as a function of ϕ . For these two figures we follow the presentation of reference [17]. (c) Effect on θ_E of a change of the triclinic angle γ .

almost linear correspondence between θ_E and ϕ . As already mentioned the crossover observed around 0° and 60° is the consequence of the interchange between the two lowest eigenvalues.

Similar results are found after a reasonable change of the different parameters. For example, a change of d_1 simply induces a small change of the slope $\theta_E(\phi)$ in domain II without modification of the crossover $I \leftrightarrow II$. The same conclusion applies when the ratio b/a is slightly modified. The influence of γ is illustrated in figure 9c. The main effect is a shift of the position of domains I and II. The slope $\theta_E(\phi)$ remains almost the same.

It is striking that we can reproduce so nicely the figures obtained with the complete calculation of reference [17]. The only difference is that c^* is not exactly an eigendirection because of the triclinic symmetry. Thus we use the conclusions of our model to discuss the tTTF salts. Since low T structural data are not available we use our results to deduce ϕ . In particular we take profit of the linear relation $\theta_E(\phi)$ to estimate ϕ from the AFMR determination of θ_E . In our case γ is close to 86° at 300 K (see Tab. I) and we also expect γ to be close to 90° at low temperatures. Thus we can use the continuous line in figure 9c. Within the experimental accuracy, θ_E is close to either 80° or 100° (the rotation axis in Fig. 8a can be either $+\mathbf{a}$ or $-\mathbf{a}$). In both cases figure 9c gives an estimate of ϕ close to 90° .

This result is important to discuss the nature of the low temperature ground state. Many results in the TMTTF series have been discussed using a purely 1D theory [4b]. In this description one should observe an antiferromagnetic ordering when the electronic localization is weak, a spin-Peierls ground state being favored in more strongly localized systems. This localization is experimentally revealed by the exponential increase of the electrical resistivity below the characteristic temperature T_p . This theory explains why in the TMTTF series the weakly localized Br salt presents an AF low T ground state while the more localized PF₆ and AsF₆ salts present a spin-Peierls distortion [3]. However, even in the TMTTF series, some results seem to contradict this analysis. The SCN salt presents a strong electronic localization below 160 K where a $4 k_F$ structural transition occurs [19] but has an AF ground state. In the same manner, although the localization gap is similar in the PF₆, AsF₆ and SbF₆ TMTTF salts only the last compound presents an AF ground state below 6 K [10]. Similar problems occur in other series of salts, the conclusion being that an AF ground state is also observed when a large electronic localization is present [20]. The present work supports this analysis. (tTTF)₂SbF₆ or AsF₆ exhibit an AF ordering although they are more localized than (TMTTF)₂PF₆ which presents a spin-Peierls transition.

It has been recently suggested that a quasi-1D theory considering the interchain interaction in the $\mathbf{b}$ direction is necessary to discuss the problem of the competition between low T ground states in more details [21]. In the case of the spin-Peierls instability the dominant interchain coupling which is kinetic favors the transverse wave vector q_b already given by (1) for the AF ordering. It would generally lead to an incommensurate superstructure. However the condensation of the spin-Peierls (SP) ground state implies a strong coupling with the underlying lattice and therefore a commensurate superstructure (this is an alternative way of thinking to the influence of the electronic localization). When this lock-in term is dominant only commensurate values of q_b are allowed for the SP distortion (i.e. $\phi = 0$ or 90°). Finally, Coulomb interchain couplings which favor distortions out of phase on neighboring chains can discriminate between these two values. Thus the spin-Peierls ground state will be only stabilised when $\phi \approx 0$ in (1). The observation of an AF ground state in tTTF salts with SbF₆ or AsF₆ where ϕ is close to 90° supports this analysis.

Conclusion.

We have described the structural and electronic properties of the (tTTF)₂X salts. In this series the charge carriers have a localized character. In the salts with AsF₆, SbF₆, ReO₄ or Br the spin degrees of freedom couple antiferromagnetically at low temperatures. In particular the Br salt orders at 33 K, the highest Néel temperature ever reported in the 2 : 1 series of organic salts. The analysis of the AF ground state of the AsF₆ and SbF₆ salts supports the argument that the competition between AF and spin-Peierls low T ground states is in part governed by the interchain coupling. New kinds of structural phase transitions have been found in the ClO₄ and PF₆ salts. Such transitions could be the result of a delicate balance between Coulomb interactions between localized charges in these 2 : 1 salts.

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