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X-ray investigation of the tetramethyldithiadiselenafulvalene (TMDTDSF)₂X series of organic conductors. II. Influence of the orientational disorder on the structural instabilities

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Résumé. — Nous présentons une étude par diffusion diffuse des rayons X des instabilités structurales d'une nouvelle série de conducteurs organiques, de stœchiométrie 2 : 1, construite sur la molécule TMDTDSF qui est un hybride des molécules TMTTF et TMTSF. Les résultats sont discutés en relation avec le désordre orientationnel de la molécule TMDTDSF caractérisé dans la partie I (TMDTDSF)₂PF₆ présente une instabilité structurale au vecteur d'onde $2k_F$ possédant un caractère mixte spin-Peierls (SP) — onde de densité de charge (ODC) avec une évolution en température intermédiaire entre celles des instabilités SP de (TMTTF)₂PF₆ et ODC de (TMTSF)₂PF₆. A basse température cette instabilité ne donne pas naissance à un ordre tridimensionnel à grande distance de type SP. Probablement à cause du désordre, des distortions locales unidimensionnelles de type SP coexistent avec un ordre magnétique. L'influence du désordre orientationnel de la molécule TMDTDSF sur les transitions de mise en ordre des anions (OA) est discutée en terme d'interactions et de champs aléatoires. Le désordre a un faible effet dans (TMDTDSF)₂ReO₄ qui subit une transition de phase stabilisant le vecteur d'onde $q_1 = (1/2, 1/2, 1/2)$ à une température critique intermédiaire entre celles de (TMTSF)₂ReO₄ et (TMTTF)₂ReO₄. Les effets de champs aléatoires sont importants dans (TMDTDSF)₂BF₄ qui présente une quasi-transition de phase au vecteur d'onde q_1 à une température « critique » plus basse que celle de (TMTTF)₂BF₄ et (TMTSF)₂BF₄. L'absence de transition de phase au vecteur d'onde q_1 dans (TMDTDSF)₂ClO₄ est attribuée aux effets conjugués des champs et interactions aléatoires.

Abstract. — We present an X-ray diffuse scattering investigation of the structural instabilities exhibited by a new series of 2 : 1 organic conductors based on the TMDTDSF molecule which is a hybrid between the TMTTF and TMTSF molecules. The results are discussed in relationship with the orientational disorder of the TMDTDSF molecule characterized in part I. (TMDTDSF)₂PF₆

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shows a $2 k_F$ structural instability having a mixed spin-Peierls (SP)-charge density wave (CDW) character which exhibits a thermal behavior intermediate between that exhibited by the $(\text{TMTTF})_2\text{PF}_6$ SP instability and the $(\text{TMTSF})_2\text{PF}_6$ CDW one. At low temperatures this instability does not condense into a tri-dimensional long range order SP ground state. Probably because of the disorder, one-dimensional local SP distortions coexist with a magnetic order. The influence of the orientational disorder of the TMDTDSF molecule on the anion ordering (AO) transitions is discussed in terms of random interactions and random fields. Disorder is found to have a weak effect in $(\text{TMDTDSF})_2\text{ReO}_4$ which undergoes a long range $q_1 = (1/2, 1/2, 1/2)$ AO phase transition at a critical temperature intermediate between those of $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTTF})_2\text{ReO}_4$. Random field effects are found to be important in $(\text{TMDTDSF})_2\text{BF}_4$ which exhibits a q_1 quasi AO phase transition at a « critical » temperature sizeably depressed with respect to those of $(\text{TMTTF})_2\text{BF}_4$ and $(\text{TMTSF})_2\text{BF}_4$. Random fields as well as random interactions are believed to be responsible for the absence of a q_1 AO phase transition in $(\text{TMDTDSF})_2\text{ClO}_4$.

1. Introduction.

Over the past ten years the tetramethyltetraselenafulvalenium salts, $(\text{TMTSF})_2\text{X}$, and tetramethyltetrathiafulvalenium salts, $(\text{TMTTF})_2\text{X}$, where X is a monovalent anion, have attracted a lot of attention because their phase diagram exhibits an impressive number of competing instabilities. Table I summarizes some of the ground states observed at ambient pressure in various salts.

The $(\text{TMTSF})_2\text{X}$ series based on octahedral anions ($\text{X} = \text{PF}_6, \text{AsF}_6, \text{SbF}_6$) shows a competition between a low pressure spin density wave (SDW) ground state [1, 2] and a high pressure superconducting state [3, 4], while at ambient pressure the $(\text{TMTTF})_2\text{X}$ series exhibits either a Spin-Peierls (SP) ground state ($\text{X} = \text{PF}_6, \text{AsF}_6$) [5-7] or an antiferromagnetic (AF) one ($\text{X} = \text{SbF}_6$) [8]. The SP ground state of $(\text{TMTTF})_2\text{PF}_6$ evolves towards an AF ground state under pressure [9].

These salts crystallize in the $\text{P}\bar{1}$ triclinic system [10, 11] where the zigzag stacking of organic molecules (along **a**) delimits cavities, each containing one anion X. Due to the 2 : 1 commensurate stoichiometry and to the inversion symmetry rendering all the molecular sites equivalent, the one-dimensional (1D) electron gas experiences a $4 k_F$ ($\equiv \mathbf{a}^*$) bond potential from the anion sublattice. This potential, together with the dimerization of the organic stack (partly associated with the $4 k_F$ response of the chain to the anionic potential [12]), contributes to a $4 k_F$ charge gap Δ_p ($\approx \pi T_p$). This gap has a pertinent effect at ambient pressure in the $(\text{TMTTF})_2\text{X}$ series [13], as evidenced by the observation of a progressive charge localization below $T_p \sim 230$ K [5, 14]. Well below T_p , the coupling between the spin degrees of freedom gives rise either to an AF or to non magnetic SP ground state. In the SP ground state, the spin pairing is achieved by an $\mathbf{a}^*/2$ ($\equiv \ll 2 k_F \gg$) lattice tetramerization. $4 k_F$ charge localization effects are not observed in the $(\text{TMTSF})_2\text{X}$ series [15]. Only an incipient quasi-1D $2 k_F$ CDW instability can be detected, below about 150 K-200 K, in the PF_6 [6] and AsF_6 [4] salts. This instability vanishes below about 30 K when the $2 k_F$ SDW fluctuations begin to diverge [16].

Additional instabilities occur in salts containing non-centrosymmetrical anions, such as the tetrahedra $\text{X} = \text{BF}_4, \text{ClO}_4, \text{ReO}_4$, which are disordered in the organic stack cavities at ambient temperature. They consist in a superstructure formation due to the ordering of anions for entropy reasons when the temperature is lowered [6, 17]. The superlattice periodicity stabilized by the anion ordering (AO) seems to depend upon a subtle balance between « direct » interactions [18], which favor a uniform ordering of tetrahedra in stack direction,

Table I. — Critical temperatures and critical wave vectors of various ground states observed at ambient pressure in (TMTSF)₂X, (TMDTDSF)₂X and (TMTTF)₂X salts.

X	TMTSF	TMDTDSF	TMTTF
PF ₆	$T_{SDW} = 12$ K $q_{SDW} = (0.5, 0.22, 0.06)$	$T_{SDW} = 7$ K and 1D SP short range order ($\xi_a \sim 25$ Å)	$T_{SP} \approx 15$ K $q_{SP} = (1/2, 1/2, 1/2)$
AsF ₆	$T_{SDW} = 12$ K	SDW ? 1D SP short range order	$T_{SP} = 11$ K
SbF ₆	$T_{SDW} = 12$ K	?	$T_{AF} = 6$ K $q_{AF} \sim (0.5, 0.05, ?)$
ClO ₄	$T_{AO} = 24$ K, $q_{AO} = q_2$ relaxed state : $T_s = 1.2$ K quenched state : $T_{SDW} \sim 6$ K $q_{SDW} \sim (0.5, 0.12, ?)$	q_1 AO short range order	$T_{AO} = 70$ K $q_{AO} = q_1$
BF ₄	$T_{AO} = 36$ K $q_{AO} = q_1$	q_1 quasi AO transition at $T'_{AO} \sim 22$ K	$T_{AO} = 40$ K $q_{AO} = q_1$
ReO ₄	$T_{AO} = 177$ K $q_{AO} = q_1$	$T_{AO} = 165$ K $q_{AO} = q_1$	$T_{AO} = 154$ K $q_{AO} = q_1$
NO ₃	$T_{AO} = 41$ K $q_{AO} = q_3$ $T_{SDW} = 8$ K	q_3 AO short range order	$T_{AO} = 50$ K $q_{AO} = q_3$

and mediated interactions through the $2 k_F$ response of the organic stack (i.e. « $2 k_F$ » SP response in the case of TMTTF stack or $2 k_F$ CDW response in the case of TMTSF stack), which favor an alternate ordering in chain direction [19]. At ambient pressure, the mediated interaction dominates in the salts with anions, such as ReO₄, in strong contact with the organic stack and in the TMTTF series where the $2 k_F$ SP response shows a low temperature divergence. In this case, the $q_1 = (1/2, 1/2, 1/2)$ AO transition involves also a $2 k_F$ CDW or SP distortion of the stacks [20-22] which respectively opens a gap in the charge and spin degrees of freedom (case of TMTSF salts) [23] or only in the spin degrees of freedom when the charges are already localized (case of TMTTF salts) [5, 24]. « Direct » interactions are dominant in TMTSF salts when the anions are in weak contact with the organic stacks. In this case no gap is opened at the AO and the same electronic ground states as those encountered in TMTSF salts with octahedral anions are found. This is well illustrated in the case of (TMTSF)₂ClO₄ where, depending upon the cooling rate at the $q_2 = (0, 1/2, 0)$ AO transition [25], either a superconducting ($T_s = 1.2$ K) or a SDW ($T_{SDW} = 6$ K) ground state are stabilized. This is also the case of (TMTSF)₂NO₃ [26] which stabilizes a SDW ground state [27] well below the $q_3 = (1/2, 0, 0)$ AO transition. The delicate balance between mediated and « direct »

interactions can also be reversed under pressure, probably because of the vanishing of the $2 k_F$ CDW response under pressure. This effect is particularly well documented in the case of $(\text{TMTSF})_2\text{ReO}_4$ where the AO wave vector changes from $\mathbf{q}_1$ to $\mathbf{q}_4 = (0, 1/2, 1/2)$ under pressure [28]. With the $\mathbf{q}_4$ uniform ordering in stack direction, $(\text{TMTSF})_2\text{ReO}_4$ presents either a SDW or a superconducting ground state [29].

The first motivation of the study of 2 : 1 salts based on the tetramethyldithiadiselenafulvalene (TMDTDSF) molecule, a hybrid between the TMTTF and TMTSF molecules, was the possibility, with the salts presenting physical properties intermediate between those of the $(\text{TMTSF})_2\text{X}$ and $(\text{TMTTF})_2\text{X}$ series [30, 31], of understanding how the instabilities evolve from one series to the other. The second motivation was, after the observation of orientational disorder of the TMDTDSF molecule [32], to study the influence of a well defined disorder (the characterization of which is the object of paper I) on the various instabilities exhibited by the Bechgaard salts.

The format of paper II is as follows. Experimental conditions are given in part 2. Structural instabilities shown by the $(\text{TMDTDSF})_2\text{X}$ salts are described in part 3, then a general discussion of the influence of disorder on these instabilities is the object of part 4.

2. Experimental.

The structural instabilities exhibited by the $(\text{TMDTDSF})_2\text{X}$ salts with $\text{X} = \text{BF}_4$, ClO_4 , ReO_4 , PF_6 , AsF_6 and SbF_6 , the disorder of which has been characterized in paper I, were studied in this paper. These salts were prepared at Orsay or Copenhagen according to the procedure described in reference [30]. For each kind of anion, several crystals, with a needle shape and a few mm long were used. They were from the same preparations as those used in magnetic and transport measurements [30-33].

The structural investigation was performed with the $\text{CuK}\alpha$ (1.542 Å) radiation obtained after (002) reflection of the X-ray beam on a doubly bent graphite monochromator. In the case of the SbF_6 material the Sb fluorescence background was partly suppressed with a thin aluminium foil placed before the detection (X-ray film).

The study of structural instabilities was performed using the fixed-film fixed-crystal photographic method between 300 K and 9 K, with the sample placed in a thermalised container. A semi-quantitative analysis of the weak diffuse scattering was performed from readings of the photographic films using a Joyce Loebble microdensitometer. In the case of the ReO_4 material exhibiting a well defined structural transition, the temperature dependence of a superlattice reflection intensity was measured with a home made linear detector.

3. Experimental results.

3.1 SALTS WITH OCTAHEDRAL ANIONS. — Figure 1 shows for the PF_6 salt, in addition to the Laue diffuse scattering considered in paper I, diffuse lines (white arrows) of weak intensity which are perpendicular to the $\mathbf{a}$ direction and located midway between two successive $h = \text{integer}$ Bragg layers. They provide evidence of $2 k_F$ 1D structural fluctuations. These lines are detected below about 150 K. Their intensity increases when the temperature decreases until about 20 K. Then below this temperature their intensity suddenly decreases. The same behavior was observed in another sample. The unusual thermal dependence of the $2 k_F$ peak intensity is more quantitatively shown in figure 3. Note in this figure that the peak intensity drops by about 40 % between 20 K and 16 K and saturates below the last temperature. No sizeable interchain correlations develop until 10 K, the lowest temperature reached. The half width at half maximum (H.W.H.M.) ⁽¹⁾ along a , Δq_a , also shown in figure 2, slightly

⁽¹⁾ In paper II we use the convention $\Delta q = 2 \pi \Delta s$, with s defined in paper I.

Fig. 1. — X-ray pattern from $(\text{TMDTDSF})_2\text{PF}_6$ at 20 K showing in addition to the broad and intense Laue scattering considered in paper I, very weak $2k_F$ diffuse lines (arrows). The a direction is horizontal.

Fig. 2. — Temperature dependence of the peak intensity and of the HWHM along $a(\Delta q_a)$ of the $2k_F$ diffuse lines of $(\text{TMDTDSF})_2\text{PF}_6$, obtained from microdensitometer reading of X-ray patterns similar to the one shown figure 1.

Fig. 3. — X-ray pattern from $(\text{TMDTDSF})_2\text{ReO}_4$ at 18 K showing (arrows) sharp q_1 superlattice reflections. The a direction is horizontal.

decreases for decreasing temperatures. After a Gaussian resolution correction, Δq_a leads to an intrachain correlation length ξ_a of 15 Å at 80 K which increases until about 25 Å (i.e. 7 intermolecular distances) at 10 K. It is interesting to remark that these lines are detected up to 150 K which is above the temperature ($T_p \sim 100$ K) at which $(\text{TMDTDSF})_2\text{PF}_6$ begins to exhibit charge localization effects according to the most recent conductivity measurements [33]. The onset temperature of the $2k_F$ fluctuations is comparable to that previously determined in $(\text{TMTSF})_2\text{PF}_6$, which does not exhibit charge localization effects. As far as the low temperature behavior is concerned, the $2k_F$ fluctuations of $(\text{TMDTDSF})_2\text{PF}_6$ are intermediate between those of $(\text{TMTSF})_2\text{PF}_6$, which vanish below 30 K, and those of $(\text{TMTTF})_2\text{PF}_6$, which diverge at the 15 K SP transition [6, 19]. The drop of $2k_F$ diffuse intensity below about 20 K in $(\text{TMDTDSF})_2\text{PF}_6$ could be correlated with the divergence of 3D SDW fluctuations observed by NMR [33]. $2k_F$ diffuse lines are also observed below about 135 K in $(\text{TMDTDSF})_2\text{AsF}_6$. However they are of weaker intensity than those of $(\text{TMDTDSF})_2\text{PF}_6$ and their intensity does not drop until 9 K, the lowest temperature reached. Finally no $2k_F$ diffuse lines could be detected in $(\text{TMDTDSF})_2\text{SbF}_6$.

3.2 SALTS WITH TETRAHEDRAL ANIONS. — It is found that all the ReO_4 , BF_4 and ClO_4 salts exhibit a q_1 AO structural instability. However, these salts differ by the spatial extent of the q_1 order : the ReO_4 salt undergoes a well defined phase transition, the BF_4 salt has a quasi-phase transition and the ClO_4 salt does not show any sign of phase transition down to 10 K.

Sharp q_1 superlattice reflections are observed below 165 K in $(\text{TMDTDSF})_2\text{ReO}_4$ (Fig. 3). This critical temperature (T_{AO}), is the average between those at which $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTTF})_2\text{ReO}_4$ undergo the q_1 AO transition (see Tab. I). At this temperature $(\text{TMDTDSF})_2\text{ReO}_4$ undergoes a metal to insulator phase transition involving both the charge and spin degrees of freedom as evidenced by conductivity [31] and magnetic [33] measurements respectively. Figure 4 gives the temperature dependence of a superlattice reflection. It shows a sharp increase of intensity below T_{AO} , nearly identical to that found in $(\text{TMTSF})_2\text{ReO}_4$ [34], but sharper than that previously reported in $(\text{TMTTF})_2\text{ReO}_4$ [35]. Pretransitional fluctuations consisting of broad quasi-isotropic diffuse scatterings are observed until about 200 K. Similar isotropic fluctuations are observed above T_{AO} in $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTTF})_2\text{ReO}_4$ [6, 17].

Fig. 4. — Temperature dependence of the peak intensity of a q_1 superlattice reflection of $(\text{TMDTDSF})_2\text{ReO}_4$ measured with a position sensitive linear detector.

Intense but broad q_1 superlattice spots are observed at low temperatures in $(\text{TMDTDSF})_2\text{BF}_4$ (Fig. 5a). These broad reflections have a symmetric profile for wave vectors nearly parallel to the chain direction and an asymmetric one along perpendicular wave vector directions. Figure 6 gives the temperature dependence of the q_1 peak intensity and of the HWHM of the diffuse scattering in chain direction (Δq_a) and in a perpendicular direction close

Fig. 5. — X-rays patterns from (TMDTDSF)₂BF₄ showing (arrows) intense and broad q_1 superlattice spots at 9.5 K in (a) and their broadening at 41 K in (b). The a direction is horizontal.

Fig. 6. — Temperature dependence of the peak intensity and of the HWHM along $a(\Delta q_a)$ and $b^*(\Delta q_b^*)$ of q_1 superlattice spots of (TMDTDSF)₂BF₄ obtained from microdensitometer reading of X-ray patterns similar to those shown figure 5.

to $b^*(\Delta q_b^*)$. This figure clearly shows by the saturation of the rate of decrease of Δq_a and Δq_b^* and by the rapid increase of the q_1 peak intensity, that (TMDTDSF)₂BF₄ undergoes a quasi-phase transition around $T'_{AO} \sim 21-23$ K. This behavior is analogous to that observed in the solid solution (TMTSF)₂(ClO₄)_{0.93}(ReO₄)_{0.07} (compare Fig. 6 with Fig. 1 of Ref. [36]). Below about 22 K only a q_1 AO short range order is established in (TMDTDSF)₂BF₄. The inverse of the HWHM shown in figure 6 gives, after a Gaussian resolution correction, the following « correlation lengths » : $\xi_a \sim 30$ Å and $\xi_{b^*} \sim 23$ Å below T'_{AO} . However the physical meaning of these lengths requires a detailed determination of the spacial dependence of the correlation function of the order parameter. This can be achieved only through an accurate analysis of the superlattice spot profile, which can be well fitted by a Lorentzian square function in the symmetric case. By these structural features (TMDTDSF)₂BF₄ contrasts with (TMTSF)₂BF₄ and (TMTTF)₂BF₄ which exhibit a well defined 3D long range q_1 AO at higher critical temperatures (36 K and 40 K respectively — see Tab. I). The charge degrees of freedom being frozen below $T_\rho \sim 110$ K [44], the 22 K quasi-transition of (TMDTDSF)₂BF₄ has been detected, in the spin degrees of freedom, by a faster rate of decrease of the magnetic susceptibility [45]. q_1 pretransitional fluctuations are observed until about 70 K in (TMDTDSF)₂BF₄. As shown in figure 5b, the broad diffuse spots broaden sizeably above T'_{AO} . At 40 K their inverse HWHM gives $\xi_a \sim 18$ Å and $\xi_{b^*} \sim 11$ Å, leading to

the same anisotropy ratio as below T'_{AO} . An anisotropic broadening of the pretransitional fluctuations is also observed above the 3D AO transition of $(TMTSF)_2BF_4$ and $(TMTTF)_2BF_4$. It means that the mediated interactions between anions (i.e. through the $2k_F$ response of the organic stack) play an important role in the q_1 AO mechanism of the BF_4 salts.

Figure 7 shows an X-ray pattern from $(TMDTDSF)_2ClO_4$ at 12 K. There is no evidence of the q_2 AO previously observed in $(TMTSF)_2ClO_4$ and its solid solutions $[(TMTSF)_{1-x}(TMTTF)_x]_2ClO_4$ [37] and $(TMTSF)_2(ClO_4)_{1-x}(ReO_4)_x$ [36] for x small. Only a weak and broad q_1 diffuse scattering can be detected below 150 K. Figure 8 shows that the q_1 peak intensity gradually increases upon cooling. There is, however, until 10 K no rapid change in its rate of increase, which could recall the one observed around 22 K in $(TMDTDSF)_2BF_4$, and which is taken as the signature of a quasi-phase transition. The HWHM of the broad diffuse scattering slightly sharpens upon cooling (Fig. 8). At low

Fig. 7. — X-ray pattern from $(TMDTDSF)_2ClO_4$ at 12 K showing (arrows) the weak q_1 short range order. The a direction is horizontal.

Fig. 8. — Temperature dependence of the peak intensity and of the HWHM along $a(\Delta q_a)$ and $b^*(\Delta q_{b^*})$ of the q_1 short range order of $(TMDTDSF)_2ClO_4$ obtained from microdensitometer reading of X-ray patterns similar to the one shown figure 7.

temperatures the correlation length of the q_1 short range order, estimated from the inverse HWHM is of about 10 Å in the **a** and **b*** directions. These correlation lengths are shorter than those measured in (TMDTDSF)₂BF₄. They are however comparable to those of the weak q_1 scattering observed in the [(TMTSF)_{0.995}(TMTTF)_{0.005}]₂ClO₄ [37] and (TMTSF)₂(ClO₄)_{0.93}(ReO₄)_{0.07} [36] solid solutions.

4. Discussion.

The structural instabilities shown by the (TMDTDSF)₂X salts (Tab. I) must be discussed in relationship with the analysis of the disorder performed in paper I. Let us here recall the main results of this study :

— in all the salts investigated the two orientations of the TMDTDSF molecule have equal probability and there is a statistical absence of orientation correlations ;

— associated to the orientational disorder and depending upon the relative molecular orientation, there is also a displacement of the molecules from their average position. The magnitude of the size effect is respectively of 0.1 Å and 0.03 Å for the 1st and 2nd neighbors in chain direction in the case of the PF₆ salt. The 1st neighbor size effects amounts to the dimerization amplitude of the organic stacks in the (TMTTF)₂X series [11]. It is larger than the weak dimerization found in the (TMTSF)₂X series [10]. 1st and 2nd neighbor size effect displacements are also comparable to the amplitude of distortion of the organic stacks occurring during the q_1 AO transition [20-22].

In the following we shall discuss the influence of the disorder, first on the intrastack structural instabilities then on the AO transitions.

4.1 MIXED SP-CDW INSTABILITY. — Quasi-1D structural fluctuations at the π/a ($\equiv 2 k_F$) critical wave vector are observed in the PF₆ and AsF₆ salts. They are weaker in the AsF₆ salt than in the PF₆ one. These fluctuations are not observed in the SbF₆ salts. The (TMTTF)₂X series exhibits the same behavior with the same anions [14]. However in (TMDTDSF)₂PF₆ and AsF₆ the fluctuations occur on a temperature range comparable to that of the incipient $2 k_F$ CDW instability of the TMTSF analogues [4, 6]. In (TMDTDSF)₂PF₆ and AsF₆ these fluctuations are detected above $T_p \sim 100$ K [33] and 80 K [44] respectively, temperatures at which the localization of charge degrees of freedom manifests itself in conductivity measurements. In (TMDTDSF)₂PF₆, they appreciably grow below T_p (Fig. 2) as in (TMTTF)₂PF₆ [6]. They have thus a mixed CDW and SP character. In this respect it can be shown [38] that the $2 k_F$ (bond) instability remains, whatever the strength of Coulomb repulsions between electrons. For small Coulomb interactions (with respect to the band width) the $2 k_F$ CDW affects both the charge and spin degrees of freedom. When the Coulomb interactions increase, a new $4 k_F$ CDW instability develops. This instability localizes the charge degrees of freedom (below T_p). In parallel the $2 k_F$ instability becomes more and more associated with the spin degrees of freedom and thus gradually evolves towards a SP instability. As the $2 k_F$ instability is detected on a temperature range exceeding T_p in (TMDTDSF)₂PF₆ and AsF₆, we are neither in a pure CDW nor in a pure SP regime. Thus (TMDTDSF)₂X has a behavior intermediate between those of the (TMTSF)₂X and (TMTTF)₂X series. In addition the $2 k_F$ SP-CDW structural fluctuations of (TMDTDSF)₂PF₆ show an interesting competition with the $2 k_F$ SDW (or AF) instability. Below, we shall only discuss the PF₆ salt because the magnetic properties of the AsF₆ and SbF₆ salts are not known.

Compared to (TMTSF)₂PF₆, the $2 k_F$ structural fluctuations are enhanced in (TMDTDSF)₂PF₆. the peak intensity increases more strongly upon cooling and the intrachain correlation length increases by a factor of 2 from (TMTSF)₂PF₆ ($\xi_a \sim 10$ Å) to (TMDTDSF)₂PF₆ ($\xi_a \sim 20$ Å). The vanishing of the $2 k_F$ CDW fluctuations of (TMTSF)₂PF₆

below 30 K takes place when the $2k_F$ SDW fluctuations begin to diverge [19]. In $(\text{TMDTDSF})_2\text{PF}_6$ the rapid drop of the intensity of the SP fluctuations below 20 K also occurs when 3D SDW fluctuations become critical [33]. However contrary to $(\text{TMTSF})_2\text{PF}_6$, the intensity of the $2k_F$ diffuse lines does not vanish at low temperatures, but saturates to a constant value (Fig. 2). This means that although a 3D magnetic order is established below 7 K in $(\text{TMDTDSF})_2\text{PF}_6$ [30], a significant proportion of chains either undergo a SP distortion or is still subject to SP fluctuations (we use here the SP designation because in the low temperature range at ambient pressure the charge degrees of freedom are frozen). The in-chain SP correlation length slightly decreases upon cooling. However at 10 K the average correlation length of the SP distortion is $\sim 25 \text{ \AA}$ in chain direction and there is no sizeable interchain correlations. With such a local SP order, the continuous decrease of spin susceptibility [33], especially in the temperature range where the $2k_F$ SP intensity drops and where 3D critical SDW fluctuations are observed, is difficult to rationalize. Our measurements mean that (at least above 10 K) $(\text{TMDTDSF})_2\text{PF}_6$ does not undergo a SP phase transition. The absence of a SP ordering either can result from the competition between low temperature SP and SDW fluctuations or (and) can be due to structural disorder. The first hypothesis has already been discussed above. Let us now examine the case of the disorder. It was previously shown [6] that in $(\text{TMTTF})_2\text{PF}_6$, where irradiation defects suppress the interchain coupling very rapidly, the 3D SP ordering is very sensitive to disorder. Here, the absence of a SP transverse short-range order could be ascribed either to the sizeable orientational and displacive disorder of the organic molecules or to the large average separation between the small number of chains which effectively experience the SP instability. In the latter case the SP instability could concern only a limited number of molecules whose positions are not too much disturbed by the size effects and whose intermolecular spacing is close to that of $(\text{TMTTF})_2\text{PF}_6$.

In conclusion the net increase of $2k_F$ intensity on cooling down to 20 K shows that the structural disorder does not inhibit the development of the SP instability. This could be explained by the fact that in a true spin-Peierls mechanism the magnetic interactions which are little affected by the disorder drive the lattice instability. But in TMDTDSF salts the spin pairing in an $S = 0$ state is probably badly transmitted to the lattice degrees of freedom because of the structural disorder. The structural disorder has apparently a very marginal effect on the magnetic coupling as proved by the observation of a 3D magnetic order in the PF_6 salt [30]. It has probably an important influence on the superconductivity because the PF_6 salt does not undergo a superconducting transition (down to 0.56 K) when the metallic state is restored under high pressure [30].

4.2 AO INSTABILITY. — Let us first consider $(\text{TMTTF})_2\text{X}$ [$(\text{TMTSF})_2\text{X}$] salts where X is a non-centrosymmetrical anion. In each cavity the anion can point towards the S[Se] of one of the two inversion symmetry related near neighboring molecules. The orientation of the anion is thus specified by an Ising variable η whose value is $+1$ or -1 if the anion points towards the right or left molecule. The AO transition can thus be described by a phenomenological Ising Hamiltonian [19, 39] :

$$H_0 = \frac{1}{2} \sum_{i,j} J_{ij} \eta_i \eta_j, \quad (1)$$

where J_{ij} is the interaction between anions located at sites i and j . Let us now consider $(\text{TMDTDSF})_2\text{X}$ salts with disordered organic molecules. The anions will thus experience three kinds of environment corresponding to the S-S, Se-S and Se-Se pairs of atoms towards which they can point (Fig. 9). Among them the Se-S environment breaks locally the inversion symmetry of the cavity. On site i this effect can be accounted for by the presence of an

Fig. 9. — Schematic illustration of the lattice potential experienced by an anion in Se-Se (a), S-S (b) and S-Se (c) environments.

additional field h_i coupled to the order parameter η_i . The Hamiltonian (1) will thus become :

$$H = H_0 + \sum_i h_i \eta_i . \quad (2)$$

The field h_i has a random distribution because the TMDTDSF disorder has no spatial correlations. In addition because of the TMDTDSF disorder and of the S or Se nature of the species in close contact with the anion, the mediated contribution to J_{ij} will also present some distribution. Randomness of both natures are also present in the $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{X}$ solid solution. However only a distribution of J_{ij} interactions is expected in the $(\text{TMTSF})_2\text{X}_{1-x}\text{Y}_x$ or $(\text{TMTTF})_2\text{X}_{1-x}\text{Y}_x$ solid solutions.

Both random fields and random interactions are invoked to explain the absence of a long range order in orientational glasses [40, 41]. Following these earlier works we shall discuss in the following their respective influence on the AO of the Bechgaard salts by comparing three relevant quantities obtained at a crude level of approximation (formula (A3)', (A7) and (A9) of the annex) :

— the mean interaction between anions

$$\bar{J}(x) = (1-x)J_0 + xJ_1 \quad (3)$$

— the variance of the J distribution

$$\text{Var}(J) = \sqrt{x(1-x)} |J_0 - J_1| \quad (4)$$

— the variance of the h distribution

$$\text{Var}(h) = \sqrt{x(1-x)} \sqrt{2} h . \quad (5)$$

In the case of solid solutions, J_0 and J_1 are interactions appropriate for pure salts ($x = 0$ and $x = 1$ respectively ; $J > 0$ or < 0 for staggered or uniform coupling). In principle $\bar{J}(x)$ and $\text{Var}(J)$ must be defined on all the directions of interaction between the anions. If pure

salts adopt the same wave vector of ordering (q_1 in most of the cases), the $\text{Var}(J)/\bar{J}$ ratio can be estimated by replacing $|J_0|$ and $|J_1|$ in (3) and (4) by the corresponding AO critical temperatures. This ratio is more inaccurately estimated if pure salts adopt different wave vectors of ordering such as q_1 and q_2 for example. If it is assumed in this example that the interaction along a (staggered for q_1 , uniform for q_2) dominates the AO and mainly determines T_{AO} , this ratio can be estimated by replacing J in (3) and (4) by the corresponding values of T_{AO} with opposite signs. It is interesting to remark that this crude assumption predicts (Eq. (3)) for $(\text{TMTSF})_2(\text{ClO}_4)_{0.35}(\text{ReO}_4)_{0.65}$, a q_1 AO, at a temperature, $T_{AO} = 107$ K, very close to that experimentally observed: 109 K [34, 36]. In the following we shall also assume that equations (3) and (4) with $x \sim 0.5$ can be applied to the $(\text{TMDTDSF})_2X$ series of hybrid molecules.

Equation (5) gives $\text{Var}(h)$ for the solid solution $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2X$. The same expression is obtained in the case of $(\text{TMDTDSF})_2X$ with c^+ (defined in paper I) instead of x . $2h$ is the asymmetry of the anion site energy for an Se-S environment (Fig. 9c). If h is in first approximation independent of the anion, $\text{Var}(h)$ is proportional to the square root of the intensity of the Laue scattering. With this hypothesis $\text{Var}(h)$ has about the same value in the ReO_4 , BF_4 and ClO_4 salts.

An orientational glassy behavior is obtained when the interactions are strongly disordered, i.e. when $\text{Var}(J) > \bar{J}$ [40, 41]. This is the case of random or frustrated interactions, a situation encountered in spin glasses. In the opposite limit, $\text{Var}(J) < \bar{J}$, the disorder is not large enough to suppress the divergence of critical fluctuations and thus the phase transition.

Random fields also compete with order [42]. When $\text{Var}(h) > \bar{J}$, the system has no long range order. However it has been shown [43] that, for 3D interactions, a low temperature long range order is established in the case of small random fields.

As the critical temperatures of the q_1 AO are very close in $(\text{TMTTF})_2X$ and $(\text{TMTSF})_2X$ for $X = \text{ReO}_4$ and BF_4 (Tab. I) a weak disorder of interaction is expected in the corresponding TMDTDSF salts. By replacing J by the corresponding T_{AO} the following ratios of equation (4) over equation (3) are obtained :

$$\frac{\text{Var}(J)}{\bar{J}} = 0.07 \quad \text{for } X = \text{ReO}_4,$$

$$\frac{\text{Var}(J)}{\bar{J}} = 0.05 \quad \text{for } X = \text{BF}_4.$$

As these ratios are comparably small, the observation of a well defined AO phase transition in the ReO_4 salts and of only a quasi-phase transition in the BF_4 salt points out the key role of the random fields in the latter case. As similar values of $\text{Var}(h)$ are expected for both salts, the differences observed could be ascribed to large variations of the $\text{Var}(h)/\bar{J}$ ratio when $\bar{J}$ decreases by a factor 4 from BF_4 to ReO_4 . The observation of a well defined q_1 AO transition in $(\text{TMDTDSF})_2\text{ReO}_4$ at a critical temperature which is the average between those of $(\text{TMTTF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{ReO}_4$ means that $\text{Var}(h) < \bar{J}$. In contrast, the observation in $(\text{TMDTDSF})_2\text{BF}_4$ of a q_1 quasi AO transition at 22 K, a value much lower than 38 K, the average critical temperature of $(\text{TMTTF})_2\text{BF}_4$ and $(\text{TMTSF})_2\text{BF}_4$, means that $\text{Var}(h) > \bar{J}$.

In $(\text{TMDTDSF})_2\text{ClO}_4$ by replacing the « J » by the corresponding $\pm T_{AO}$, the ratio of equation (4) over equation (3) gives :

$$\frac{\text{Var}(J)}{\bar{J}} \sim 2.$$

The large disorder of interactions and also the increase of $\text{Var}(h)/\bar{J}$ from the BF_4 to the ClO_4 salt (due to the decrease of $\bar{J}$), can be taken as responsible for the absence of any sign of AO transition in $(\text{TMDTDSF})_2\text{ClO}_4$. When the disorder of interaction dominates, the suppression of the AO transition is due to the formation of domains of competing $\mathbf{q}_1$ and $\mathbf{q}_2$ fluctuations, as observed for example in the $(\text{TMTSF})_2(\text{ClO}_4)_{1-x}(\text{ReO}_4)_x$ solid solution [34]. However in $(\text{TMDTDSF})_2\text{ClO}_4$ we have only succeeded to detect short range $\mathbf{q}_1$ structural fluctuations. This again points out the key role of random fields to which the random interactions add their effects for a complete suppression of the AO transition.

A glass state is characterized by the Edwards-Anderson order parameter q_{EA} , which for an orientational (Ising) glass is defined by [46, 47]:

$$q_{\text{EA}} = \frac{1}{N} \sum_i \langle \eta_i \rangle^2 = \sum_q |\langle \eta_q \rangle|^2 \quad (6)$$

X-ray scattering experiments measure the instantaneous correlation function of η_q , the Fourier transform of η_i .

$$\begin{aligned} S(q, t=0) &= \langle |\eta_q|^2 \rangle \\ &= |\langle \eta_q \rangle|^2 + \langle |\delta \eta_q|^2 \rangle. \end{aligned} \quad (7)$$

If η_q is separated into a frozen part ($\langle \eta_q \rangle$) and a fluctuating part ($\delta \eta_q$), q_{EA} is thus obtained by the q integration of the frozen contribution to $S(q, t=0)$. This separation is generally difficult to perform. However, in the case of the BF_4 salt, the saturation of the HWHM of the $\mathbf{q}_1$ superlattice peak (Fig. 6) means that the AO is frozen below T'_{AO} . The rapid growth of the $\mathbf{q}_1$ peak intensity observed below this temperature thus indicates a net increase of the Edwards-Anderson order parameter q_{EA} . The elastic peak observed in neutron scattering experiments, whose intensity is proportional to q_{EA} , behaves similarly at the freezing temperature of collective variables in certain orientational glasses [48].

Further studies are necessary in order to describe the nature of the $\mathbf{q}_1$ AO short range order in $(\text{TMDTDSF})_2\text{BF}_4$. Here let us remark that the observed Lorentzian square profile of the symmetric part of the broad superlattice reflections is that expected [42, 49] when the order is destroyed by random fields. Alternatively the same profile can also be explained by a random distribution of domain sizes [50]. Superlattice spots with a Lorentzian square profile are also observed in the case of $\mathbf{q}_1$ and $\mathbf{q}_2$ AO short range orders in the $(\text{TMTSF})_2(\text{ReO}_4)_{1-x}(\text{ClO}_4)_x$ and $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{ClO}_4$ solid solutions. The asymmetric profile observed for certain wave vector directions is more subtle to understand. By analogy with similar findings in orientational glasses [46, 51] this asymmetry could be caused by a linear coupling between the anion orientational order parameter and a deformation field induced by the disorder.

Let us now discuss the relationship between the $\mathbf{q}_1$ AO and the nature of the electronic ground state. In $(\text{TMDTDSF})_2\text{ReO}_4$ at ambient pressure the long range $\mathbf{q}_1$ AO opens a well defined gap both in the charge [31] and spin [33] degrees of freedom at T_{AO} . This is due to the fact that, because T_{AO} and $T_p \sim 210$ K [44] are very close, the electrons are not completely localized at T_{AO} . The electrons are localized below $T_p \sim 110$ K and 135 K in the BF_4 and ClO_4 salts respectively [44]. Thus only the coupling between the spin degrees of freedom is important near T'_{AO} in the BF_4 salt. The faster rate of decrease of spin susceptibility observed below T'_{AO} [45] can be viewed as due to the opening of a pseudo gap in the spin excitations, such a gap corresponding to a local SP distortion of the organic stack associated with the $\mathbf{q}_1$ AO. No low temperature magnetic measurements have been performed in $(\text{TMDTDSF})_2\text{ClO}_4$. However as the correlation length ξ of the $\mathbf{q}_1$ AO remains comparable to the interdimer separation, the SP distortion of the organic stack will not be important enough to

produce anomalies in the thermal dependence of the spin susceptibility. Above 10 kbars, when T_p is suppressed, a clear metal-insulator transition is observed in the BF_4 and ClO_4 salts [31]. This electronic transition is probably not driven by a well defined $\mathbf{q}_1$ AO transition because it seems unlikely that pressure could improve the short range nature of the $\mathbf{q}_1$ AO due to the frozen nature of the TMDTDSF disorder. From the small value of the electrical gap measured in pressurized samples, such a transition could be of magnetic origin [31]. But in this high pressure range, it is not known if a SDW ground state can coexist with a local $\mathbf{q}_1$ AO or if the stabilization of a magnetic ground state requires a change of the AO wave vector, as is the case in non-disordered salts such as $(\text{TMTSF})_2\text{ReO}_4$ [28, 29]. However the ambient pressure study of the $(\text{TMDTDSF})_2\text{PF}_6$ salt shows that a SDW order can coexist with a local SP distortion. This means that the SDW order could be stabilized inhomogeneously in $(\text{TMDTDSF})_2\text{BF}_4$ and ClO_4 salts under pressure, for example in domains where there is no $2 k_F$ structural distortion of the organic stack associated with a local $\mathbf{q}_1$ AO.

5. Conclusion.

Two main results have been obtained from the study of structural instabilities exhibited by the $(\text{TMDTDSF})_2\text{X}$ series of organic conductors. First, from the observation of a quasi 1D « $2 k_F$ » structural instability in the PF_6 and AsF_6 salts, we have shown that there is a continuity between the SP and CDW instabilities observed in the TMTTF and TMTSF analogues respectively. This study also shows that the 1D SP instability, which is driven by 1D magnetic interactions, is moderately sensitive to structural disorder. However, disorder seems to prevent the 3D coupling required to achieve a complete SP phase transition. Second, we have shown that both random fields and random interactions due to the structural disorder could have a pertinent effect on the AO phase transitions. The study of the ReO_4 , BF_4 and ClO_4 salts has shown the key influence of random fields on the AO transition of the $(\text{TMDTDSF})_2\text{X}$ salts. In the light of these new results, an investigation of the relationships between disorder effects and structural instabilities exhibited by the $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{X}$, $(\text{TMTTF})_2\text{X}_{1-x}\text{Y}_x$ and $(\text{TMTTF})_2\text{X}_{1-x}\text{Y}_x$ solid solutions is underway [34].

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Annex.

Let us consider a random solid solution where a given site can be occupied by the species X(Y) with the probabilities x and $1 - x$. Each site has an Ising variable which interacts with its neighbors according to the Hamiltonian (1). The average interaction $\bar{J}_{ij}$ between a couple (i, j) of Ising variables is :

$$\bar{J}_{ij} = x^2 J_{ij}^{XX} + (1 - x)^2 J_{ij}^{YY} + 2x(1 - x) J_{ij}^{XY} \quad (\text{A1})$$

where x^2 , $(1 - x)^2$ and $2x(1 - x)$ are the probability to have XX, YY and XY pairs of atoms connected by the interactions J^{XX} and J^{YY} and J^{XY} respectively. If it is assumed that :

$$J^{XY} = \frac{J^{XX} + J^{YY}}{2}, \quad (\text{A2})$$

(A1) becomes :

$$\bar{J}_{ij} = xJ_{ij}^{XX} + (1-x)J_{ij}^{YY} \quad (\text{A3})$$

$$[\text{Var}(J_{ij})]^2 = x^2(J_{ij}^{XX} - \bar{J}_{ij})^2 + (1-x)^2(J_{ij}^{YY} - \bar{J}_{ij})^2 + 2x(1-x)(J_{ij}^{XY} - \bar{J}_{ij})^2 \quad (\text{A4})$$

becomes with approximation (A2) :

$$\text{Var}(J_{ij}) = \sqrt{\frac{x(1-x)}{2}} |J_{ij}^{XX} - J_{ij}^{YY}|. \quad (\text{A5})$$

This derivation is valid for a solid solution of anions. In the case of a solid solution of organic molecules [(TMTTF)_x(TMTSF)_{1-x}]₂X the calculation is not so obvious. In an effective medium description of the organic sublattice where there is a probability x (the concentration of TMTTF molecules) to have the same interaction as in pure (TMTTF)₂X (J_{ij}^S) and a probability $(1-x)$ to have the same interaction as in pure (TMTSF)₂X (J_{ij}^{Se}), $\bar{J}_{ij}$ has the same dependence upon x as that given by (A3) :

$$\bar{J}_{ij} = xJ_{ij}^S + (1-x)J_{ij}^{\text{Se}}. \quad (\text{A3})$$

However with :

$$[\text{Var}(J_{ij})]^2 = x(J_{ij}^S - \bar{J}_{ij})^2 + (1-x)(J_{ij}^{\text{Se}} - \bar{J}_{ij})^2 \quad (\text{A6})$$

one gets :

$$[\text{Var}(J_{ij})]^2 = \sqrt{x(1-x)} |J_{ij}^S - J_{ij}^{\text{Se}}| \quad (\text{A7})$$

where (A7) is $\sqrt{2}$ times larger than (A5).

In the [(TMTSF)_{1-x}(TMTTF)_x]₂X solid solution the anion X on the site i experiences no random field when it has an S-S (with a probability x^2) or an Se-Se (with a probability $(1-x)^2$) symmetrical environment. It feels a local field, let say, $+h$ for the Se-S environment, occurring with a probability $x(1-x)$, and $-h$ for the S-Se environment occurring with the same probability. This leads to :

$$\bar{h}_i = 0, \quad (\text{A8})$$

and to

$$[\text{Var}(h_i)]^2 = 2x(1-x)h^2$$

or

$$\text{Var}(h_i) = \sqrt{2x(1-x)} h. \quad (\text{A9})$$

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