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R. Moret, J.P. Pouget, R. Comès, K. Bechgaard. X-ray study of the anion ordering transition in di (tetramethyltetraselenafulvalen)-ium perchlorate (TMTSF) $_2$ ClO $_4$: quenching and irradiation effects. Journal de Physique, 1985, 46 (9), pp.1521-1532. 10.1051/jphys:019850046090152100 . jpa-00210098

HAL Id: jpa-00210098

<https://hal.science/jpa-00210098>

Submitted on 4 Feb 2008

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Classification

Physics Abstracts

61.50K — 61.80C — 64.70

X-ray study of the anion ordering transition in di(tetramethyltetraselenafulvalen)-ium perchlorate (TMTSF)₂ClO₄ : quenching and irradiation effects

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(Reçu le 20 février 1985, accepté le 6 mai 1985)

Résumé. — Nous présentons les résultats d'une étude par diffraction des rayons X de la transition de phase de (TMTSF)₂ClO₄ à 24 K. L'influence de la vitesse de refroidissement est caractérisée par son effet sur l'intensité et la largeur des réflexions de surstructure qui apparaissent à la transition. Nous avons mis en évidence d'importants effets d'irradiation sur cette transition de mise en ordre des anions, non observés précédemment pour les autres composés de la série (TMTSF)₂X. L'irradiation réduit rapidement l'intensité des réflexions de surstructure et abaisse la température de transition. Un phénomène de recuit partiel du désordre induit par l'irradiation est observé. Les intensités de 220 réflexions de surstructure ont été mesurées, et une analyse partielle montre que la mise en ordre des anions en représente la contribution essentielle. On en conclut que les distorsions des chaînes TMTSF associées à la transition sont faibles (ce qui diffère des observations déjà effectuées dans (TMTSF)₂ReO₄).

Abstract. — We report the results of an X-ray diffraction study of the phase transition of (TMTSF)₂ClO₄ at 24 K. The influence of the cooling rate is evaluated by its effect on the intensity and width of the superstructure reflections appearing at the transition. We also report important irradiation effects on this anion ordering transition, previously unobserved in other compounds of the (TMTSF)₂X family. The superstructure reflection intensities are strongly reduced and the transition temperature is lowered upon X-ray irradiation. Partial annealing of the irradiation induced disorder is observed. The intensities of 220 superstructure reflections were measured and a preliminary analysis shows that anion ordering accounts for most of the intensity. We conclude that distortions of the TMTSF backbone at the transition are minor (in contrast to the features previously reported for (TMTSF)₂ReO₄).

1. Introduction.

The competition between superconductivity and an insulating antiferromagnetic state in (TMTSF)₂ClO₄ has attracted attention in the last two years.

Realization of these different ground states can be controlled by thermal treatment in the low-temperature region, i.e. below about 40 K.

NMR [1, 2], EPR and resistivity measurements [3] have shown that rapid cooling (> 30 K/min) (quenched state) generates a magnetic state (spin density wave, SDW). In contrast slow cooling (0.1 K/min) (relaxed state) gives rise to a superconducting state below 1.2 K [4, 5] changing in high magnetic fields to a

magnetic state with intriguing Hall effect and magnetoresistance [6-8]. These two different behaviours are coupled to a structural phase transition which occurs at 24 K, and which is considered to involve orientational ordering of the ClO₄⁻ anions [9, 10] as follows : at high temperature the non centrosymmetric anions are disordered in the triclinic P $\bar{1}$ space group of the structure with two equivalent orientations related by an inversion centre. In the relaxed state obtained by slow cooling, the anions order and alternate along the *b* axis only, forming a superstructure characterized by a wave vector $q = (0, 1/2, 0)$. Rapid cooling below 40 K freezes the anion disorder while intermediate states can be obtained by intermediate cooling rates or when a quenched sample is annealed below 24 K [3, 10, 11].

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Other physical properties directly related to the anion ordering transition like the specific heat anomaly [12] or the thermal contraction of the chain axis, a , below 24 K [13] are of course very sensitive to the cooling rate.

The special role of the $(0, 1/2, 0)$ wave vector in relation to superconductivity has been considered in various papers [14-17], but the understanding of the effective interactions is still lacking. It is accepted that the anion potential plays a key role in these interactions and to learn more we have performed an X-ray study of the 24 K structural phase transition of $(\text{TMTSF})_2\text{ClO}_4$ at atmospheric pressure. We have studied the influence of the cooling rate and have found remarkable irradiation effects. We confirm the anion ordering hypothesis and find that the transition is associated with much smaller distortions of the organic stacks than in the case of the $(1/2, 1/2, 1/2)$ ordering transition of $(\text{TMTSF})_2\text{ReO}_4$ [18, 19] at 180 K.

After a brief description of the experimental conditions (Sect. 2), cooling rate effects are presented and discussed in section 3, X-ray irradiations effects in section 4 and the structural features of the anion ordering transition in section 5. Concluding remarks are given in section 6.

2. Experimental.

The $(\text{TMTSF})_2\text{ClO}_4$ untwinned single crystal ($0.3 \times 0.5 \times 3 \text{ mm}^3$) studied here was chosen from a batch of crystals grown by electrocrystallization similar to those used in references [1, 3, 4, 5, 8, 9]. The experiment was performed using an X-ray diffractometer equipped with a Displex cryocooler. We used the normal beam geometry with a lifting scintillation detector and the $\text{CuK}\alpha$ radiation from a 1.5 kW (50 kV, 30 mA) X-ray tube was selected by the (002) reflection of a doubly-bent graphite monochromator. This point focussing geometry provides a high photon flux at the expense of a relatively low resolution. The crystal was mounted with the needle axis, a , in the vertical direction of the diffractometer. In order to perform measurements with only small irradiation damages (see Sect. 4), the crystal was translated along this direction, with respect to the X-ray beam, several times during the experiment. The sample was also exposed to the X-ray beam only during the strict time necessary for the measurements. The cell parameters were found to be : $a = 7.29 \text{ \AA}$, $b = 7.68 \text{ \AA}$, $c = 13.28 \text{ \AA}$, $\alpha = 84.49^\circ$, $\beta = 86.69^\circ$, $\gamma = 70.36^\circ$ at room temperature and $a = 7.08 \text{ \AA}$, $b = 7.63 \text{ \AA}$, $c = 13.13 \text{ \AA}$, $\alpha = 84.09^\circ$, $\beta = 87.50^\circ$, $\gamma = 69.06^\circ$ at $T = 11 \text{ K}$, in reasonable agreement with previous measurements [45, 39].

3. Cooling rate effects.

3.1 RESULTS. — The crystal was first cooled to 11 K at the maximum cooling rate of the set up (about 2 hours from room temperature and a cooling rate

of 3 K/min or more below 40 K). Superstructure reflections with a reduced wave vector $(0, 1/2, 0)$ were easily detected, thus confirming previous photographic [9] and diffractometer [10] studies. One of the strongest observable reflections $(\bar{1}, \bar{2.5}, \bar{3})$ was selected for the present study.

At 11 K, its profiles were recorded along the a^* , b^* , c^* reciprocal directions. The scan along c^* is shown in figure 3a. To a very good approximation, the profile can be fitted with a Gaussian. Its half width at half maximum (H.W.H.M.) is $\Delta Q_{a^*} = 0.025 \text{ \AA}^{-1}$, $\Delta Q_{b^*} = 0.019 \text{ \AA}^{-1}$ and $\Delta Q_{c^*} = 0.011 \text{ \AA}^{-1}$, along the a^* , b^* and c^* directions respectively. These values are larger than the experimental resolution $\Delta^R Q_{a^*} = 0.021 \text{ \AA}^{-1}$, $\Delta^R Q_{b^*} = 0.013 \text{ \AA}^{-1}$ and $\Delta^R Q_{c^*} = 0.007 \text{ \AA}^{-1}$ measured (see below) at the same position (here we shall use the convention $\mathbf{a}^* \cdot \mathbf{a} = 2\pi$) to express the reciprocal vector.

Then, the crystal was slowly heated (about 0.5 K/min) from 11 K. Figure 1 shows the temperature dependence of the peak intensity of the $(\bar{1}, \bar{2.5}, \bar{3})$ superstructure reflection. The intensity is almost constant up to 21 K where a small increase is observed, then it drops at about 23 K as the phase transition occurs. Above 24.5 K, critical scattering can be seen up to 30 K or higher, as first reported in the photographic study [9]. It will be described at the end of this part. After 30 min at 40 K, the crystal was slowly cooled at a speed of 0.25 K/min with stages of 5 min at each point of intensity measurement. The heating and cooling curves coincide above 23 K but in the slow cooling case one obtains a much larger low-temperature intensity, which saturates at a value around 10 600 counts/s, below about 18 K.

Then, at 11 K, the peak profiles of the $(\bar{1}, \bar{2.5}, \bar{3})$ reflection were recorded along the a^* , b^* , c^* reciprocal directions. The scan along c^* is shown in figure 3b.

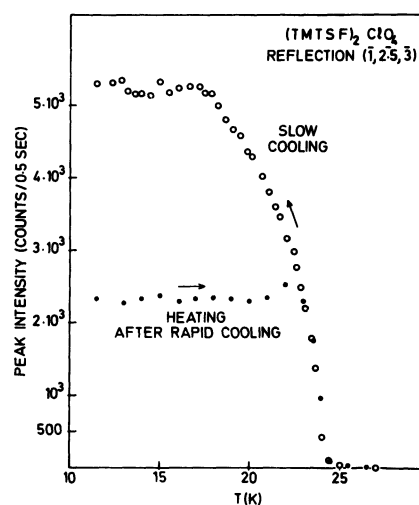


Fig. 1. — Temperature dependence of the $(\bar{1}, \bar{2.5}, \bar{3})$ superstructure reflection intensity in $(\text{TMTSF})_2\text{ClO}_4$. Different behaviours are displayed for slow heating (0.5 K/min) after rapid cooling (3 K/min) and slow cooling (0.25 K/min).

It shows, with respect to scan 3a, a sharpening of the superstructure reflection. Similar narrowing effects are also observed along the *a** and *b** directions. The width obtained in the slow cooling case is the same as for the (1̄, 2̄, 3̄) main Bragg reflection and it is limited by the instrumental resolution.

The slow cooling curve compares well with the temperature dependence previously observed [9, 10]. By extrapolation, one obtains a transition temperature $T_0 = 24.2 \pm 0.2$ K which agrees fairly well with the value obtained by various techniques [3, 11, 20].

Above T_0 , one observes weak precursor scattering at the superstructure points. This scattering broadens as the temperature is increased as was observed in the photographic study [9]. Figure 2 shows scans of the corresponding diffuse peaks along the reciprocal axes at 25.2 K. The profile can be relatively well fitted by a Lorentzian. Its H.W.H.M. is approximately isotropic and increases strongly as the temperature increases in the vicinity of T_0 ; from 25.2 K to 26.5 K, ΔQ_{a^*} increases from 0.040 Å⁻¹ to 0.093 Å⁻¹, ΔQ_{b^*} from 0.027 Å⁻¹ to 0.046 Å⁻¹ and ΔQ_{c^*} from 0.025 Å⁻¹ to 0.054 Å⁻¹.

A crude analysis of the widths (subtraction of the HWHM of the resolution) yields correlation lengths, ξ , of the order of 50 to 80 Å at 25.2 K ($T_0 + 1$ K) and in the range 15-30 Å at 26.5 K ($T_0 + 2.3$ K).

3.2 ANALYSIS OF THE DATA. — Owing to irradiation effects which will be described in section 4, let us mention that the cooling rate effects have been measured on a previously non-irradiated part of the crystal and that 3 hours were necessary to collect the data of figure 1. Figure 4 shows that irradiation effects during this time (reduced by annealing above 14 K) lead to small corrections, which do not alter the present analysis.

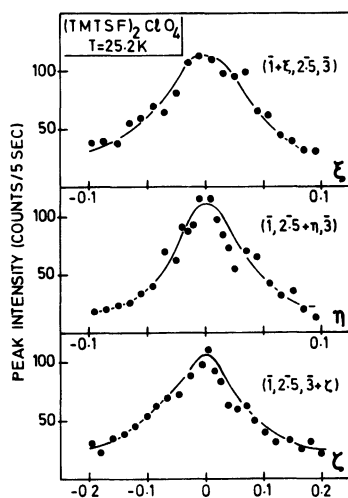


Fig. 2. — Scans of the (1̄, 2̄, 3̄) diffuse scattering peak in the precursor regime at $T : 25.2$ K ($T_0 + 1$ K). No 1-D character is observed and one obtains approximate correlation lengths of 50 Å along *a*, 80 Å along *b* and 60 Å along *c*.

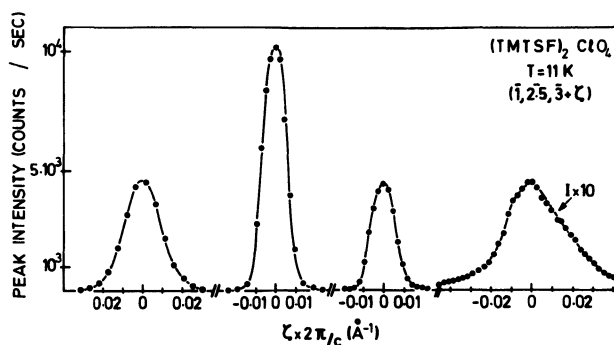


Fig. 3. — Comparison of quenching and irradiation effects on the widths of the (1̄, 2̄, 5̄, 3̄) superstructure reflection : a) partly quenched state, b) slowly cooled, « relaxed » state, c) slowly cooled state after 19 hours irradiation (~ 0.02 mol % of defects), d) slowly cooled state after 78 hours of irradiation (~ 0.08 mol % of defects). Note that quenching is more efficient in broadening the reflection than irradiation effects.

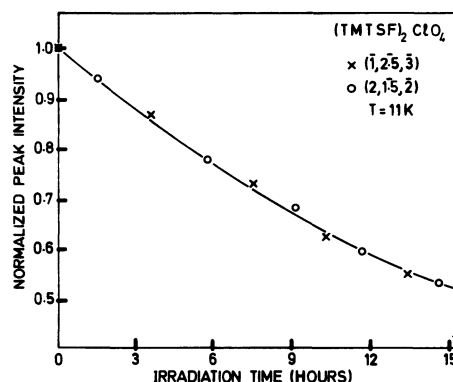


Fig. 4. — Irradiation dependence of the peak intensity of 2 superstructure reflections (1̄, 2̄, 5̄, 3̄) and (2, 1̄, 5̄, 2̄) of (TMTSF)₂ClO₄ at 11 K.

We have performed two thermal treatments of (TMTSF)₂ClO₄ at cooling rates of 0.25 K/min and 3 K/min. With our slowest cooling conditions (0.25 K/min), the « relaxed » (TMTSF)₂ClO₄ stays metallic [21] and becomes superconducting at 1.2 K [5]. With our maximum cooling rate (3 K/min) (TMTSF)₂ClO₄ displays a semi conducting (SDW) behaviour below 4 K [21] before becoming superconducting at about the same temperature as in the relaxed state [22]. In our experimental set up the maximum cooling rate is not fast enough to obtain a complete suppression of the superconductivity [22] and the sample is in a partly quenched or intermediate state.

However, figures 1 and 3a and b show that rapid cooling of (TMTSF)₂ClO₄ leads to a decrease of the peak intensity and to a broadening of the superlattice reflections.

The low temperature peak intensity ratio of our slow and rapid cooling cases (about 2.3 — see Fig. 1) compares qualitatively well with the results of Kagoshima *et al.* where similar cooling speeds were used (15 K/40 min and 15 K/5 min, see Fig. 1 of Ref. [10]).

In addition, peak broadening along the three reciprocal axes shows that in partly quenched samples

the order is spatially limited. In the simplest approximation we shall consider that the sample is composed of ordered domains of the same size. If the ordered domain contains N_a , N_b , and N_c unit cells along the a , b and c directions, respectively, the \mathbf{q} dependence of the scattered intensity, with respect to the wave vector \mathbf{Q} , of a superstructure reflection is given by the formula [23] :

$$I(\mathbf{Q} + \mathbf{q}) = I(\mathbf{Q}) \times \left[\frac{\sin^2 \frac{(N_a \mathbf{q} \cdot \mathbf{a})}{2}}{\sin^2 \frac{(\mathbf{q} \cdot \mathbf{a})}{2}} \right] \times \left[\frac{\sin^2 \frac{(N_b \mathbf{q} \cdot \mathbf{b})}{2}}{\sin^2 \frac{(\mathbf{q} \cdot \mathbf{b})}{2}} \right] \times \left[\frac{\sin^2 \frac{(N_c \mathbf{q} \cdot \mathbf{c})}{2}}{\frac{(\mathbf{q} \cdot \mathbf{c})}{2}} \right] \quad (1)$$

This gives a peak profile very close to a Gaussian. The H.W.H.M. of the profile along the a direction ΔQ_a , is thus related to the size of the domain, $L_a = N_a a$, along this direction by the Scherrer formula [23] :

$$L_a = 0.888 \pi \Delta Q_a^{-1}.$$

Similar formulae relate the sizes of domains $L_b = N_b b$ and $L_c = N_c c$ along the b and c directions, to the H.W.H.M. ΔQ_b and ΔQ_c respectively. The H.W.H.M. ΔQ which enters in the Scherrer formula, and which represents the intrinsic broadening due to finite size effects of scattering domains, is obtained from the measured H.W.H.M. $\Delta^e Q$ corrected by the experimental resolution $\Delta^R Q$. With a Gaussian correction [23], consistent with the observation of a Gaussian profile and the description of the intrinsic broadening by equation (1), one gets :

$$\Delta Q = [(\Delta^e Q)^2 - (\Delta^R Q)^2]^{1/2}.$$

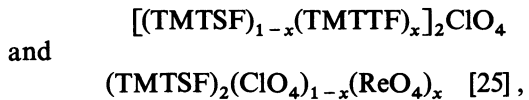
Using the data of part 1, we deduce, for the 3 K/min cooling rate case, domain sizes of about $L_a \sim 200 \text{ \AA}$, $L_b \sim 200 \text{ \AA}$ and $L_c \sim 350 \text{ \AA}$ along the a , b and c directions respectively. This gives relatively isotropic domains of quite large volume ($\sim 10^7 \text{ \AA}^3$ or 10^4 high temperature unit cells).

These domain sizes, and especially those obtained along the a direction, must be considered as giving only an order of magnitude, because, due to the weak broadening of the superlattice reflections (20-50 % of the experimental resolution), resolution corrections are very important. They are surprisingly of the same order of magnitude as those obtained by Kagoshima *et al.* [10] for a much faster cooling rate of 100 K/min of the sample (the correlation length ξ of reference [10] must be converted into our domain length L by the formula $L = 0.888 \pi \xi$).

The number of ClO_4 anions which belong to ordered domains in the rapidly cooled sample can be estimated from the integrated intensity of superstructure reflections like $(1, \bar{2}, \bar{3})$, assuming that in these ordered domains, the order parameter keeps

the same value as in slowly cooled samples. In that case, we find that about 70 % of the anions belong to ordered domains in our 3 K/min cooled sample. Thus in this crude picture 30 % of the anions are disordered. In a more realistic picture, a sizeable fraction of this quantity may belong to domain walls or less ordered regions.

3.3 DISCUSSION. — Let us first discuss the relation of these results to other physical properties observed for $(\text{TMTSF})_2\text{ClO}_4$ having undergone a similar thermal treatment and for the solid solutions



where for $x \geq 0.5$ % and $x \geq 1$ % respectively, the superconductivity is suppressed at the expense of the SDW ground state. A structural study of the anion ordering has been performed only in the former alloys [9, 26]. It shows that already 0.5 % of TMTTF in $(\text{TMTSF})_2\text{ClO}_4$ reduces considerably the correlation length of the ordered domains to values $\xi \sim 20\text{-}30 \text{ \AA}$ ($L \sim 60\text{-}90 \text{ \AA}$), comparable to those observed in pure $(\text{TMTSF})_2\text{ClO}_4$ at $T_0 + 2 \text{ K}$. In this sample the ordering temperature is also found to be depressed by about 4 K. However, the « 20 K transition temperature » of the alloy



can be viewed more reasonably as the transition below which there is either a large increase in the number of « ordered » domains or (and) a large increase of the order parameter in these domains; each domain remaining small in size and embedded in disordered regions.

It is generally assumed that superconductivity develops in the domains where the ClO_4 anions are ordered. Good evidence is provided by the combination of earlier specific heat measurements [5] showing, that in a 10 K/min quenched sample

(50 ± 10) % of the electronic specific heat is involved in the superconducting pairing, and by the present X-ray study indicating that about 70 % of the anions are ordered in the 3 K/min quenched sample. The X-ray studies also show that upon quenching or upon alloying, the size of the ordered regions is reduced. Thus one can rationalize that in the presence of too small and too separated ordered domains, as those formed in the alloy



or in rapidly quenched samples, superconductivity cannot develop. In the opposite situation, the presence of larger ordered domains in relatively close contact does not affect significantly the superconductivity, as observed in the 3 K/min cooled sample [21].

In addition, a SDW ground state which also competes with the superconducting ground state can develop upon quenching or upon alloying [3, 22]. The two ground states may coexist either microscopically or belong to different regions of the sample. Various studies [5, 11] of partly quenched (TMTSF)₂ClO₄ have suggested that the intermediate state is an inhomogeneous mixture of superconducting and SDW regions. The magnetic islands are thus believed to coincide with the disordered regions, where either a change of intercolumnar transfer energy [27] or the suppression of the (0, 1/2, 0) superlattice periodicity [28] favours the SDW instability.

In order to discuss annealing effects in partly quenched (TMTSF)₂ClO₄, let us come back to figure 1, showing for the 3 K/min cooled sample a small increase of the peak intensity upon heating around 22 K. This small bump can be attributed to an annealing effect resulting in a slight improvement of the ordering as the temperature approaches the transition temperature T_0 . Such annealing effects have been observed before by X-ray [10], electrical and magnetic measurements [3, 11]. The magnitude of the intensity increase due to annealing is time dependent so that a slower heating rate would have given rise to a higher bump also extending towards lower temperatures (i.e. beginning earlier on heating). On a timescale of about half an hour, a sizeable increase of the superstructure intensity of a quenched sample can be observed at annealing temperatures larger than 19 K [10, 29]. At a temperature of 18 K, the increase begins to be detected only after about 15 hours of annealing [29]. Thus, several days are necessary to recover a sizeable part of the superstructure intensity lost by quenching. These results show clearly that the kinetics of the annealing depends critically on the temperature. Such slow kinetics are probably controlled by the speed at which domain boundaries move. A preliminary analysis of the intensity vs. time annealing curves indicates that a $I = K(T) \log(t)$ variation is obeyed reasonably well. More details on the kinetics of the annealing process will be reported elsewhere [29].

The increase of the ordered domain size with time has been directly observed by the narrowing of the superlattice reflections or quenched samples upon thermal annealing above 18 K [29].

In figure 1 the slow cooling curve also shows a saturation of the superstructure intensity below about 18 K (where annealing effects begin to occur in quenched samples). We assume that as the ordering proceeds kinetics slows down and that a cooling rate of 0.25 K/min is too fast around 18 K. To achieve full ordering a lower cooling rate is needed. We believe that slower cooling would restore a normal and continuous temperature dependence of the intensity and order parameter. Actually, as it was pointed out to us by C. Gaonach and C. Noguera, the temperature dependence of the superlattice peak intensity, which is proportional to the square of the order parameter, may be analysed within the 3D Ising model. Thus, a good fit of the slow cooling curve of figure 1 is obtained using the calculated temperature dependence of the order parameter for the Ising model on a simple cubic lattice [56]. In particular we find that the order parameter saturates at 0.9 below 17.5 K. While the use of an Ising order parameter is natural since the tetrahedra present two orientations, the appropriateness of a simple cubic lattice model is less obvious. Therefore the good agreement mentioned above suggests that the effective interaction between the 6 near neighbour tetrahedra is relatively isotropic, in agreement with the quasi-isotropy of the structural fluctuations above T_0 (Fig. 2).

4. X-ray irradiation effects.

4.1 RESULTS. — During the diffractometer study we observed important effects of the X-ray irradiation on the superstructure intensity and on the phase transition. The purpose of this section is to quantify these effects as a function of the irradiation time on our experimental set up. The irradiation dose will be estimated in part 2 of this section.

First, we have measured at 11 K, figure 4, the irradiation dependence of the peak intensities of two strong superstructure reflections ($\bar{1}, \bar{2}, \bar{5}, \bar{3}$) and ($\bar{2}, \bar{1}, \bar{5}, \bar{2}$). Prior to this measurement, the diffraction data of section 3 had been collected so that the crystal had been exposed already to about 4 hours of irradiation. Time 0 corresponds to the situation obtained by slow-cooling at the end of the thermal treatment of figure 1. ($\bar{1}, \bar{2}, \bar{5}, \bar{3}$) and ($\bar{2}, \bar{1}, \bar{5}, \bar{2}$) were used as standard reflections while intensity measurement of a number of superstructure reflections was performed for refinement of the superstructure at 11 K. The intensity of the standard reflections shows the same irradiation dependence and it is reduced by a factor of 2 after 16 hours of irradiation. In the same time, the intensity of 6 standard reflections from the basic structure showed no overall decrease although small variations were noticed.

Thus, after a total time of about 19 hours of irradiation, the profile of the $(\bar{1}, \bar{2}, \bar{5}, \bar{3})$ reflection was recorded along the a^* , b^* and c^* directions. The scan along c^* is shown in figure 3c. This figure shows that the peak width is identical to that of scan (b) (non-irradiated sample), although the peak intensity has been divided by about 2. The same width was observed for scans made along a^* and b^* . In these 3 directions, the observed width corresponds to the experimental resolution.

Then the sample was heated from 11 K to 40 K. The data are shown in curve 2 of figure 5 (curve 1 corresponds to the slow cooling data of Fig. 1). Surprisingly, for a slowly cooled sample, we observe a marked increase of the intensity beginning at 14 K with a maximum at about 18.5 K resulting in a broad hump. Then, the intensity decreases as the transition takes place, but the slope is smaller than for the initial thermal treatment with more rounding in the 23-25 K region. After a 1 hour stage at 40 K, we obtained curve 3 on slow cooling. The intensity rises even more slowly, but reaches higher values than in the low temperature part of curve 2. The cooling process was stopped accidentally for 65 hours at 16.5 K causing the observed jump. Then, the intensity remains fairly level down to 11 K. The low temperature values is close to the maximum obtained upon heating at the top of the hump (curve 2). At the end of scan 3, profiles of the $(\bar{1}, \bar{2}, \bar{5}, \bar{3})$ reflection were taken along the a^* , b^* and c^* directions. No increase of the peak width from the experimental resolution could be detected. During the recording of data shown in curves 2 and 3, the sample has been exposed to about 4 hours of irradiation. This gives a total amount of 23 hours of irradiation.

After about 18 more hours of irradiation (giving a total number of 41 hours of irradiation, twice the amount before the 2-3 thermal treatment), the same heating-cooling cycle was repeated (curves 4 and 5) corresponding to an irradiation time comparable to that of the previous cycle. The heating curve also shows a bump though smaller and the slope reduction and rounding is more pronounced. Upon cooling, the behaviour is now different from the previous thermal cycle since the intensity does not recover the low-temperature value of curve 4, but only reaches about 50%. Thus, with the increase by a factor 2 of the number of irradiation induced defects, the shape of the heating-cooling cycle has qualitatively changed. Further heating-cooling cycles, performed after even more irradiation show that the annealing effects observed in curves 2, 3, 4 no longer exist. Actually, from the «fresh sample» value of 10 600 counts/s the peak intensity at 11 K of the $(\bar{1}, \bar{2}, \bar{5}, \bar{3})$ reflection dropped to about 1 400 counts/s after 44 hours of irradiation, and to about 450 counts/s after 78 hours of irradiation. At this stage of irradiation peak profiles along the a^* , b^* and c^* direction were taken. The scan along c^* is shown in figure 3d. Now a sizeable broadening can be observed. More quantitatively an H.W.H.M. of

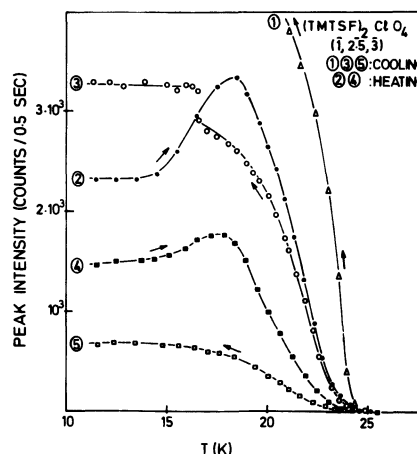


Fig. 5. — Temperature dependence of the peak intensity of the $(\bar{1}, \bar{2}, \bar{5}, \bar{3})$ superstructure reflection for different stages in the irradiation process. The X-ray irradiation time increases from curve 1 to 5, as described in the text.

$\Delta Q_a^* = 0.063 \text{ \AA}^{-1}$, $\Delta Q_b^* = 0.049 \text{ \AA}^{-1}$ and $\Delta Q_c^* = 0.073 \text{ \AA}^{-1}$ can be measured along the a^* , b^* and c^* directions respectively.

During this study, we also found that the intensity of the main reflections which did not change very much until stage 2-3, then decreased strongly and after stage 5, the loss varied from 10% to 50% depending on the specific reflection, which is still much less than the variation of $(\bar{1}, \bar{2}, \bar{5}, \bar{3})$. No systematic study of the intensity decay of the main reflections under irradiation was done, however.

4.2 DETERMINATION OF THE DEFECT CONCENTRATION.

— Previous studies have dealt with the effects of irradiation in molecular crystals and especially 1-D organic conductors [30]. In our case, the defects probably consist of alterations of the TMTSF molecules such as broken bonds or chemical rearrangement of the molecule although no information on the chemical species eventually produced is available. Damaged molecules may also induce cross linking between stacks.

Let us now estimate the irradiation dose received by the samples on our experimental set up. In a previous study of irradiation effects on TMTSF-DMTCNQ [31] we found that one day of exposure to the X-ray beam produces about 0.02 mol% defects. Knowing that 1 300 Mrad creates 1 mol% of defects in this compound [32], one can estimate the irradiation dose of our experimental set up at 26 Mrad per day. In $(\text{TMTSF})_2\text{ClO}_4$, it has been recently determined [33] that 1 000 Mrad creates 1% of localized spins per mole of TMTSF. Thus one day of exposure creates 0.026% of localized spins per mole of TMTSF in this sample. A direct check of this value has been performed by measuring the low temperature ESR susceptibility of a fresh sample irradiated during 180 hours at 25 K on our experimental set up. This measurement, performed at the SESI of CEN Fontenay aux Roses following

the procedure described in reference [33], gives 0.2 % of spins per mole of TMTSF. This means that one day of irradiation on our experimental set up creates 0.027 % of spins per mole of TMTSF, a value in perfect agreement with the previous less direct estimation. In the following instead of % of spins per mole of TMTSF, we shall write shortly mol % of defects.

4.3 DISCUSSION. — From the data of figure 4, one deduces that 0.018 mol % of defects created at 11 K, are enough to reduce by a factor 2 the intensity of superstructure reflections. With such a low concentration it is normal to find little effect on the main reflections. However, one should note that one generally estimates a volume change of about 1 molecular volume per defect [30]. The remarkably strong sensitivity of the superstructure reflections to a low concentration of defects implies that each defect created on a TMTSF molecule has a long range influence and perturbs the anion ordering inside a large volume. This volume must contain about 1 500 unit cells (3 000 organic molecules), in order to explain that 0.018 mol % of defects disorder half of the anions. This number is much larger than that found to perturb the 1-D electrical conductivity (~ 700 molecules [32]) and to pin the CDW's (~ 30 molecules [31]) in TMTSF-DMTCNQ. One interesting point is that the rate of decrease of the peak intensity is reduced as time goes on (within experimental errors, the normalized peak intensity decreases exponentially with increasing irradiation time in Fig. 4). This indicates that, as the number of disordered anions increases, the efficiency of irradiation diminishes because more and more defects are created in already disordered regions.

The behaviour upon heating and slow cooling of the (1, 2.5, 3) peak intensity at the lowest stages of irradiation (curves 2 and 3 of Fig. 5) namely :

- the increase of the peak intensity forming a broad hump upon heating (curve 2),
- the gain of intensity at 11 K after having performed a thermal cycle above T_0 (curve 3),

recalls some of the features found in the cooling rate study (see Fig. 1).

However, they cannot be due to the previously observed annealing effects in a quenched sample because the crystal had been slowly cooled before irradiation. They have to be related to a partial annealing of the disorder created by irradiation. Such disorder might be due to the quenching of anions in the disordered state after an overheating above T_0 of the vicinity of an organic molecule damaged during the radiolytic process. This process might explain why a large perturbed volume is formed around each defect.

Curves 2 and 3 in figure 5 show that either upon heating between 14 K and 18.5 K or by cycling above T_0 only a small fraction of the volume perturbed (estimated at about 35 % of that disordered by 19 hours of irradiation at 11 K) has been recovered. This means that probably only the outer parts of the

perturbed volumes, which experiences less disorder are annealed. With a higher amount of damaged molecules and an enhanced level of disorder coming from the strong overlap between the perturbed volumes surrounding the defects, the annealing effects are no longer observed (curves 4 and 5 of Fig. 5). In addition, comparison of heating curves with the same heating rate as in figures 1 and 5 shows that the threshold temperature for annealing is lower in irradiated samples (14 K) than in quenched samples (19 K) and that the effect is stronger.

Let us now discuss the peak profiles of figure 3b, c, d which correspond to successive stages in the irradiation history of the crystal. Scan (c) was taken after irradiation and corresponds to stage 2 in figure 5. The peak width is identical to that of scan (b) although the peak intensity has been divided by about 2. A comparison of scans (a) and (c) is worthwhile because the peak intensities are the same. It shows that a partial quenching of the anion disorder is much more efficient in reducing the size of ordered domains than the production of irradiation defects in a fully ordered (slowly cooled) sample. This result tells us that the ordered domains have a smaller spatial extent in the partly quenched state than in the « irradiated » one, although the estimated amount of ordered molecules is similar in both cases (in fact the integrated intensity of peak (a) is somewhat larger due to its broader width, a fact which strengthens the argument). This can be rationalized as follows. As a result of quenching, the crystal consists of « small » ordered domains in an overall disordered crystal, while upon irradiation « small » disordered regions are observed in an overall ordered crystal. This means that at low concentration, the defects, randomly created by radiolysis, can be considered as « localized defects » perturbing locally an ordered matrix. Each defect induces a local disorder of the anion whose size can be estimated (see above) at about 1 500 high temperature unit cells (a volume of $\sim 10^6 \text{ \AA}^3$). Therefore, up to a certain level of disorder these defects do not perturb significantly the spatial extent of the order of the anions, because the superstructure reflections do not broaden appreciably, as shown in the scan (c) of figure 3 for a sample having about 0.02 mol % of defects. This result is not changed after having performed a thermal cycling above T_0 with this sample (curves 2 and 3 of Fig. 5).

We have not done a systematic study to determine at which defect concentration a broadening of the superlattice begins to be detected. Scan (d) of figure 3 shows that a large broadening can be observed for about 0.08 mol % of defects in (TMTSF)₂ClO₄. With this sample, the broadening is approximately isotropic, giving coherence lengths in the range 40-60 Å. Also the integrated intensity of the peak is about 1/10 that of scan (b), showing that about 90 % of the anions are then disordered. Clearly for 0.08 mol % of defects only small ordered regions in an overall disordered crystal remain, a situation opposite to that encountered for

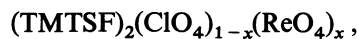
0.02 mol % of defects. Thus, we can estimate that the remaining ordered regions will no longer exist for more than 0.1-0.2 mol % of defects. This result is in perfect agreement with a recent ESR study of irradiated $(\text{TMTSF})_2\text{ClO}_4$ showing that there is no difference between rapid and slow cooling treatment of samples having more than 0.2 mol % of defects [33].

The superlattice reflection of $(\text{TMTSF})_2\text{ClO}_4$ with 0.08 mol % of defects resembles that of the alloy $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{ClO}_4$ with a concentration x of a few percent of TMTTF [26]. This indicates that irradiation defects are much more effective than substituting TMTTF molecules to suppress the anion ordering transitions.

It is interesting to notice that irradiation defects as well as thermal fluctuations above T_0 limit the structural order in a quasi-isotropic way in the anion ordering transition of $(\text{TMTSF})_2\text{ClO}_4$, while in compounds exhibiting CDW Peierls transitions like TMTSF-DMTCNQ [31] or TMTTF-TCNQ [34], they transform satellite reflections into diffuse sheets. A very anisotropic broadening of the $q = (1/2, 1/2, 1/2)$ satellites reflections occurring below the 15 K « spin Peierls » transition of $(\text{TMTTF})_2\text{PF}_6$ is also observed after about 15 hours of irradiation on our experimental set up. These different behaviours demonstrate that the fluctuations and the related forces at work in the anion ordering transition have a nature different from that acting in the CDW Peierls and spin Peierls transitions.

The transition temperature is also influenced by irradiation as can be extracted from figure 5. Extrapolation of the intensity curves leads to temperatures of $24.2 \text{ K} \pm 0.2$ for curve 1 (< 0.002 mol % defects), $23.5 \pm 0.2 \text{ K}$ for curves 2 and 3 (~ 0.02 mol % defects) and $23 \text{ K} \pm 0.4 \text{ K}$ for curves 4 and 5 (~ 0.045 mol % defects). Our data indicate a decrease of 0.7 K for $c \simeq 0.020$ % defects, giving a rate $\frac{dT_0}{dc} \simeq -35 \text{ K/mol \%}$.

A decrease of the transition temperature when the concentration of defects increases is a well-documented phenomenon for 1-D conductors [30]. In our present case, alternative results on the influence of defects on the anion ordering transition temperature are provided by studies of alloys. For



ERP and conductivity studies [25] have shown that the transition temperature is decreased by about 4 K for $x = 0.01$ ($\frac{dT_0}{dx} = -4 \text{ K/\%}$). In the case of $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{ClO}_4$ which should have a closer relationship with irradiation defects since the impurities are introduced in the organic chains, X-ray measurements have found a decrease of T_0 by 4 K for $x = 0.005$ ($\frac{dT_0}{dx} = -8 \text{ K/mol \%}$) [31, 26].

These values show that the sensitivity to irradiation defects is therefore much higher than for substitution of ReO_4 anions or TMTTF molecules. This is consistent with the large effect on the superstructure reflection intensities and the « disordering influence » of the irradiation defects. It goes along with the picture that irradiation probably modifies the TMTSF molecule and may even break it into smaller molecules which represents a more dramatic perturbation of the local structure than the substitution done by alloying.

The ratio found, $\frac{dT_0}{dc} \simeq -35 \text{ K/mol \%}$, is comparable to that found for the metal-SDW insulator transition ($-60 \pm 30 \text{ K/mol \%}$) of irradiated $(\text{TMTSF})_2\text{PF}_6$ [35]. It is not very much lower than that found for the decrease of the CDW Peierls transition temperature of TMTSF-DMTCNQ (-110 K/mol \%) (36), and that estimated for the decrease of the superconducting transition of irradiated $(\text{TMTSF})_2\text{PF}_6$ [37] and $(\text{TMTSF})_2\text{ClO}_4$ ($\gtrsim -100 \text{ K/mol \%}$) [38].

5. Structural features of the anion ordering transition.

5.1 STRUCTURAL ANALYSIS. — Apart from the above study of the 24 K structural phase transition, we also collected X-ray superstructure reflection intensity data in order to verify the anion ordering hypothesis and to determine eventual structural distortions. We measured the peak intensities of 220 superstructure reflections belonging to the $(2kl)$, $(\bar{1}kl)$, $(0kl)$ and $(1kl)$ reciprocal planes. Irradiation effects were taken into account by normalization of the intensities using intensity *versus* time curves such as those in figure 4. Polarization corrections were applied, but absorption was neglected. We performed a preliminary analysis of the superstructure by comparison of the observed and calculated intensities. These were calculated from the atomic positions and temperature factors determined by Gallois *et al.* from neutron diffraction for the average structure of $(\text{TMTSF})_2\text{ClO}_4$ at 7 K [39]. We first tested the anion ordering effect on the superstructure reflection intensities. Using a $(a \times 2b \times c)$ unit cell with alternation of the two ClO_4^- orientations (related by the inversion centre present in the average structure) along b , the reliability index (so called R index, $R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum F_{\text{obs}}$, F_{obs} and F_{calc} being the observed and calculated structure factors) is on the order of 0.34. This value should be compared to that obtained for $(\text{TMTSF})_2\text{ReO}_4$ where introduction of anion ordering only gave a value larger than 0.8. In the perhenate case, structural distortions are quite important and necessary in order to obtain a better fit and to decrease R to about 0.2 [18]. This was confirmed later by a full structure refinement [19]. From this comparison with $(\text{TMTSF})_2\text{ReO}_4$ we infer that structural distortions are weaker in $(\text{TMTSF})_2\text{ClO}_4$.

In order to estimate the distortions we refined the position of the chlorine atom in ClO_4 and of the TMTSF molecules, considered as rigid, using a simple trial-and-error and least-squares program already used in reference [18].

A displacement of the TMTSF molecules brings no significant improvement of the fit and we estimate that their displacement is less than 0.01 Å. The chlorine atoms displacement has a stronger influence and refinement decreases R to about 0.26 for a shift of approximate components 0.04 Å, 0.05 Å and 0.035 Å along the a , b , and c directions respectively. The magnitude of this displacement is close to that of the Re atom in the low-temperature phase of $(\text{TMTSF})_2\text{ReO}_4$. However it happens to be different when considering the interactions with the TMTSF stacks. In $(\text{TMFSF})_2\text{ReO}_4$, the Re atom from an anion presenting a short Se-O distance (~ 3.0 Å) with a neighbouring TMTSF molecule moves towards this molecule (see the hatched anion of Fig. 3 in Ref. [18]). On the contrary, for $(\text{TMTSF})_2\text{ClO}_4$ where the corresponding Se-O distance is much larger (3.34 Å) (though still shorter than the sum of the Van der Waals radii), the Cl atom from the same anion moves away from the TMTSF molecule as shown in figure 6.

A more detailed and accurate analysis of these displacements has been done recently by Gallois *et al.* using both neutron data of the average structure and our X-ray superstructure reflection data [40]. This analysis gives a better description of the Cl atom displacement and of the geometry of the anion. It is in fair agreement with the present work, revealing only a weak distortion of the TMTSF stacks.

5.2 DISCUSSION. — In addition to the discussion concerning the displacement of the Cl atom, it is of interest to compare the relative role of the stack distortion and the anion ordering in the structural phase transitions of $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{ClO}_4$ at ambient pressure; both transitions involving the ordering of tetrahedral anions. In $(\text{TMTSF})_2\text{ReO}_4$, below 180 K, the anions order with a $(1/2, 1/2, 1/2)$ wave vector, which means that their orientation alternates in the chain direction. This order, which does not minimize the electrostatic repulsion between the tetrahedra [41, 42] is probably stabilized by the divergence at $2k_F$ ($\equiv 1/2 a^*$) of the response function of the 1D electronic gas *via* the anion-electron coupling. Consequently, there is a distortion of the organic stack at the phase transition [18, 19]. Depending on the interpretation, the electrical gap observed below 180 K is either the consequence of the $2k_F$ instability of the Fermi surface [42] or due to electron localization effects induced by the strong anion potential [15]. In $(\text{TMTSF})_2\text{ClO}_4$, below 24 K, the anions order with the $(0, 1/2, 0)$ wave vector. Now, the lattice periodicity is kept in the chain direction ($q_a = 0$). This uniform order minimizes the electrostatic repulsion between anions. Along the b direction, because of the strong

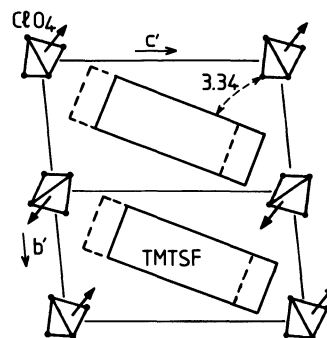


Fig. 6. — Schematic projection along a of two unit cells of $(\text{TMTSF})_2\text{ClO}_4$ in the low-temperature phase. The ClO_4 tetrahedra belong to a given b - c plane. Only the oxygen atoms are represented. The TMTSF molecules located underneath are symbolized by rectangles. The direction of the Cl atom displacements is shown by arrows. This figure can be compared to figure 3a from reference [18] or figure 1 from reference [19], showing the different displacement pattern found in $(\text{TMTSF})_2\text{ReO}_4$.

deviation of the γ angle ($\sim 70^\circ$) from 90° , it is not obvious without an accurate calculation whether the $q_b = 0$ or the $q_b = 1/2$ ordering wave vector minimizes the electrostatic repulsion between the tetrahedra.

The observation of no significant distortion of the organic stack seems to indicate that the electron anion coupling plays a minor role at the structural phase transition of $(\text{TMTSF})_2\text{ClO}_4$.

In this respect it is interesting to notice that a recent measurement [12] of the specific heat anomaly at the phase transition gives a configuration entropy $\Delta S = R \log 2$: a value expected from an order-disorder transition with 2 possible configurations of tetrahedron in the disordered state. Also, the electrical properties of the salt do not change dramatically at the structural phase transition: $(\text{TMTSF})_2\text{ClO}_4$ is metallic below 24 K (for relaxed samples) with a better rate of increase of the electrical conductivity [20, 3]. This may arise from a decrease of the electronic scattering rate due to the decrease of the anion disorder potential.

At this stage, it is tempting to suggest that the $(0, 1/2, 0)$ order might be stabilized only by the direct anion-anion interaction. However this simplest picture presents two difficulties:

— along the c direction, the electrostatic interaction between anions passes through (a, b) sheets of organic molecules,

— a substitution, as small as 0.5% TMTSF molecules by the sulfur analogue TMTTF, breaks the $(0, 1/2, 0)$ long range order.

The role of the organic stacks in the anion ordering process is qualitatively illustrated from pressure effect on T_0 (hydrostatic pressure modifies electronic parameters like the intrastack and interstack overlap integrals). In $(\text{TMTSF})_2\text{ReO}_4$, where there is a sizeable contribution of the organic stacks at the 180 K transition, the $(1/2, 1/2, 1/2)$ anion ordering transition is

destabilized under pressure [43], whereas in $(\text{TMTSF})_2\text{ClO}_4$, where it seems that the organic stacks have a marginal influence at the 24 K transition, the $(0, 1/2, 0)$ ordering transition temperature is nearly pressure independent [44].

X-ray diffuse scattering experiments on the solid solutions $[(\text{TMTSF})_{1-x}(\text{TMTTF})_x]_2\text{ClO}_4$ have shown that $(\text{TMTSF})_2\text{ClO}_4$ is at the borderline between the $(0, 1/2, 0)$ and $(1/2, 1/2, 1/2)$ instabilities [26]. Until now only a phenomenological model [15] has considered the competition between these various instabilities. However, in addition to the direct anion-anion coupling, two physical parameters may control the balance between the two ordering wave vectors :

— the electron-anion coupling, whose strength depends on the size, the electronegativity of the anion and on the TMTSF-anion distances. With a shorter Se-O contact distance [45], and a charge more localized on the O atoms, the Coulomb coupling of the anion with the electron gas of the TMTSF stacks is probably stronger in $(\text{TMTSF})_2\text{ReO}_4$ than in $(\text{TMTSF})_2\text{ClO}_4$.

— the dimensionality of the electron gas. In particular, the divergence of the $2 k_F$ electron-hole response function is strongly reduced by increase of the two dimensional character of the electronic structure, [46]. The increase of dimensionality can be achieved either by cooling or by applying pressure.

Strong electron-anion coupling and divergence of the $2 k_F$ electron-hole response function are certainly necessary to stabilize the $(1/2, 1/2, 1/2)$ ordering wave vector. In $(\text{TMTSF})_2\text{ClO}_4$ the weaker electron anion coupling and the « two dimensional » character of the Fermi surface at low temperature make certainly not favourable the stabilization of the $(1/2, 1/2, 1/2)$ superstructure. Under pressure, the increase of the two dimensional character of the Fermi surface of $(\text{TMTSF})_2\text{ReO}_4$ is probably also at the origin of the instability of the $(1/2, 1/2, 1/2)$ superstructure.

6. Conclusion.

In the family of $(\text{TMTSF})_2\text{X}$ and $(\text{TMTTF})_2\text{X}$ salts containing non-centrosymmetric anions which all exhibit anion ordering transitions at ambient pressure, $(\text{TMTSF})_2\text{ClO}_4$ is unique by the slow kinetics of its 24 K transition.

This may be due to the relatively low transition temperature of $(\text{TMTSF})_2\text{ClO}_4$ (the lowest of the family).

Another explanation may arise from the presence of competing $(1/2, 1/2, 1/2)$ and $(0, 1/2, 0)$ ordering wave vectors leading to a nearly frustrated ground state for $(\text{TMTSF})_2\text{ClO}_4$, as suggested in reference [15]. In this respect, cooling rate effects have been recently observed in $(\text{TMTSF})_2\text{ReO}_4$ near the critical pressure at which the metallic state is restored [47]. This is interpreted to be also a zone of competing orderings. However, if the $(1/2, 1/2, 1/2)$ and $(0, 1/2, 0)$ competing

orderings have been clearly observed in $(\text{TMTSF})_2\text{ClO}_4$ and its alloys [26], there is up to now, no direct evidence that the quenched state would favor the other $(1/2, 1/2, 1/2)$ periodicity, as also suggested in reference [15].

It would be interesting to look for kinetic effects in other salts which exhibit ordering transitions at relatively low temperature like $(\text{TMTSF})_2\text{NO}_3$ or $(\text{TMTSF})_2\text{BF}_4$. If the anion disorder could be quenched in some cases then the low temperature properties of the solid would be modified and different electronic ground states might be obtained.

In the present case, our results demonstrate that to achieve full ordering of the anions the slow cooling treatment should not be limited to a range of a few degrees around 24 K, but it should be extended down to 15 K or even lower. In addition, it is worth noticing that cooling rates of 0.25 K/min are too fast for the final steps of the ordering. Recently, the anomalous high field Hall effect observed in $(\text{TMTSF})_2\text{ClO}_4$ [7, 8] was found to be very sensitive to cooling rate [48] even in the limit of the slowest cooling rates [7].

An important and unexpected result of this study is the very high sensitivity of the transition to X-ray irradiation. Once again $(\text{TMTSF})_2\text{ClO}_4$ is unique because we have found no significant effects on the superstructure reflection intensities for other salts. Thus when similar irradiation conditions were used in previous X-ray diffractometer studies of $(\text{TMTSF})_2\text{ReO}_4$ [18, 19] and $(\text{TMTTF})_2\text{SCN}$ [49] as well as during the fixed-film fixed-crystal monochromatic Laue method which was used to characterize all the ordering transitions known to date and which needed much longer exposure times, such drastic effects would have been also detected. Therefore, similar or higher irradiation doses were applied in these studies, and there is no reason to believe that the defect concentrations depend on the salt if one assumes that the defects concern mainly the organic molecules. The reason why these defects created at 10 K affect a larger volume and destroy the ordering in very large regions of the crystal in the case of $(\text{TMTSF})_2\text{ClO}_4$ is not known, but it probably indicates that the energy gained by ordering of the ClO_4^- anions is small, in accordance with the low transition temperature. A possible explanation is that, because of the low transition temperature of $(\text{TMTSF})_2\text{ClO}_4$, a local overheating of the sample above T_0 occurring in the vicinity of a defect, during its formation, followed by the rapid quenching of this region can increase considerably the size of the perturbed volumes. In other salts having a higher ordering transition and faster kinetics, these effects are probably of much less importance.

Influence of irradiation and quenching on the anion ordering can also be discussed in relation to superconductivity. It is well known that superconductivity is rapidly destroyed in $(\text{TMTSF})_2\text{ClO}_4$ by the introduction of irradiation defects : only less than 0.01 mol % defects kill superconductivity [38]. Introduction of disorder in the anion sublattice also destroys super-

conductivity as shown by quenching which creates orientation disorder, and by alloying [23, 24] which creates substitution disorder. Thus, one may speculate whether disorder of the anions is responsible for the suppression of the superconductivity in both cases. The answer needs a careful comparison of the anion disorder. Upon quenching the superconductivity is probably suppressed due to reduction of the size and of the number of the ordered domains and the onset of magnetism. However, $(\text{TMTSF})_2\text{ClO}_4$ remains superconducting below about the same critical temperature, with about 30 % of the volume of the crystal where the anions are « disordered » (3 K/min cooled sample). At irradiation doses of about 0.01 mol % defects, above which superconductivity is suppressed, there is about the same volume ($\sim 30\%$) of the crystal where the anions are disordered. In addition the long-range order of the anions is preserved for these irradiation doses. Therefore irradiation appears to be more effective in suppressing superconductivity than anion disorder induced by quenching. A qualitative explanation may be that irradiation has a double effect on the long range coherence of the electronic system namely a « direct » one due to the potential of the damaged TMTSF molecules and an « indirect » effect through the extra potential created by the disordered anions.

A possible test of the sensitivity of the irradiation induced anion disorder on the superconducting transition might be to compare accurately the drop of the superconducting transition temperature as a function of the amount of irradiation defect in $(\text{TMTSF})_2\text{ClO}_4$ and in $(\text{TMTSF})_2\text{PF}_6$; the latter compound does not present an ordering transition of the PF_6^- anion.

An important result of the present work has been that the organic stack of $(\text{TMTSF})_2\text{ClO}_4$ does not suffer important distortion, in contrast to what is found for $(\text{TMTSF})_2\text{ReO}_4$. Thus, if the ordering wave vectors result from competition between direct anion-anion interactions and electron-anion interactions, the organic stack will play a minor role in the phase transition when the former interaction is the strongest. This might also be the case in the 41 K transition of $(\text{TMTSF})_2\text{NO}_3$ characterized by the wave vector $(1/2, 0, 0)$ [41]. In this compound the very weak electron-anion coupling is demonstrated by structural refi-

nements [50] giving a very large Se-O contact distance. With triangular anions located nearly in the (a, b) plane [50], it is easy to find a configuration with uniform order (> >) of NO_3 molecules along the b direction and alternate order ($\text{Y } \text{A}$) along the a direction, which minimizes the electrostatic repulsion between anions. In addition, we may speculate that there is not a subsequent distortion of the organic stack from the observation that :

a) the stabilization of a $q_a = 2 k_F = 1/2$ wave vector in chain direction does not open an electrical gap [51] in the band structure (except under pressure where electron gas-anion interactions probably increase) [52];

b) the transition temperature does not depend appreciably on pressure [52].

In contrast, the 160 K structural transition of $(\text{TMTTF})_2\text{SCN}$, characterized by the $(0, 1/2, 1/2)$ wave vector [53], may be primarily of electronic origin (i.e. with a substantial distortion of the organic stack) because :

a) it is accompanied by a metal insulator phase transition, which is suggested to be the result of a $4 k_F$ localization of electrons on the organic stacks [53];

b) the structural transition is very sensitive to pressure effects [54];

c) the SCN^- ion is close to the (bc) plane [55], and the uniform order along a and alternate order along b and c of SCN^- dipoles do not minimize their electrostatic coupling.

Acknowledgments.

We thank S. Bouffard, P. Garoche, M. Heritier, D. Jérôme, K. Murata, C. Noguera, S. Ravy, M. Ribault, M. Sanquer and S. Tomiç for useful discussions. The authors are also extremely grateful to M. Sanquer for having performed the ESR determination of the irradiation dose received by one of our $(\text{TMTSF})_2\text{ClO}_4$ samples, and to B. Gallois for having provided his neutron results on the low temperature average structure of $(\text{TMTSF})_2\text{ClO}_4$.

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