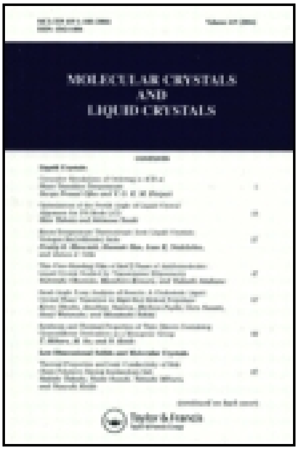

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QUENCHING AND IRRADIATION EFFECTS ON ANION ORDERING IN $(TMTSF)_2C\ell O_4$

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Abtract The anion ordering transition of $(TMTSF)_2C\ell O_4$ has been studied by X-ray diffraction down to 10 K. Influence of the cooling speed on the intensity and width of (0,1/2, 0) superstructure reflections is demonstrated. Partly quenched and relaxed states are characterized. X-ray irradiation has a very strong influence on the anion ordering. The transition temperature decreases and the reflection intensities are reduced upon irradiation. A preliminary analysis of 220 superstructure reflections shows that ordering of the anions accounts for most of their intensities so that associated lattice distortions are weak. This is in contrat with $(TMTSF)_2ReO_4$ where the latter were important, especially for the organic stack.

INTRODUCTION

$(TMTSF)_2C\ell O_4$ exhibits a variety of physical properties and ground states depending on the speed of cooling through the 24 K anion ordering transition. By slow cooling one obtains a superconducting state at ambient pressure[1,2] and very interesting Hall effects in high magnetic field,[3,4,5] while a spin density wave state is stabilized by fast cooling[6,7,8] . Extensive studies of these properties are under way as reported in these proceedings. The structural behavior of this compound is also very peculiar though less well documented[9,10,11]. The 24 K transition involves the ordering of the $C\ell O_4$ ions with the wave vector q = (0, 1/2, 0)[9,10]. The high temperature disorder of the anions can be quenched by fast cooling while full ordering is obtained by sufficiently slow cooling[11].The present paper reports new X-ray diffuse scattering results on this transition. A more extended paper is to be published[12].

EXPERIMENTAL

The $(TMTSF)_2ClO_4$ crystal (0.3×0.5×3 mm^3) was mounted on a diffractometer with the normal beam, lifting counter geometry and cooled down to 10 K using a Displex cryocooler. Maximum cooling rate was 3 K/min below 40 K. The use of a doubly bent graphite monochromator provided a high beam power at the expense of a relatively low resolution : $\Delta Q \approx 0.02$ Å^{-1} in the vertical ($\vec{a}$) direction and 0.01 Å in the (b^*- c^*) horizontal plane.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of one of the strongest superstructure reflections ($\bar{1}$, $\overline{2.5}$, $\bar{3}$) (reduced wave vector 0, 1/2, 0). In the slow cooling case (0.25 K/min) one obtains a continuous transition while a cooling speed of 3 K/min reduces the peak intensity by more than 50%. The loss of intensity is attributed to an incomplete ordering of the anions due to partial quenching. This is in agreement with the results of Kagoshima et al. In the slow cooling case the intensity saturates below about 17 K which indicates that the cooling speed of 0.25 K/min is too high in the final stages of the ordering and that a slower speed should allow a more complete ordering. Also worth noting is the small bump around 23 K on the heating curve, which comes from annealing effects occuring just below the transition temperature. The annealing process becomes faster as the temperature approaches T_c in agreement with previous results[11]. Actually we have found that below 18 K the annealing effect becomes extremely slow.

There is a weak precursor scattering above T_c and up to 30-40 K. Figure 2 shows scans of the ($\bar{1}$, $\overline{2.5}$, $\bar{3}$) reflection along the reciprocal axes at 25.2 K. The peak is broad and nearly isotropic which confirms previous photographic studies[9]. Correlation lengths are on the order of 50-80 A at this temperature and drop rapidly as T increases.

We have found that the X-rays used in our diffuse scattering experiment (CuKα radiation, 50 kV, 30 mA)have a very strong influence on the superstructure reflections. Figure 3 shows the peak intensity of 2 typical reflections as a function of irradiation time. After15 hours of irradiation the intensity is almost reduced by a factor of 2. From previous results on irradiation effects[13] we can estimate that about 0.016 mol% defects have been created during this time. The very high sensitivity of the anion ordering on irradiation is thus dramatic if one considers that the disordered region associated with each defect must contain roughly 1500 units cells. On the other hand there is little effect on the main reflections for this irradiation time which is not surprising given the very low concentration of damaged organic molecules. For higher irradiation doses obtained with

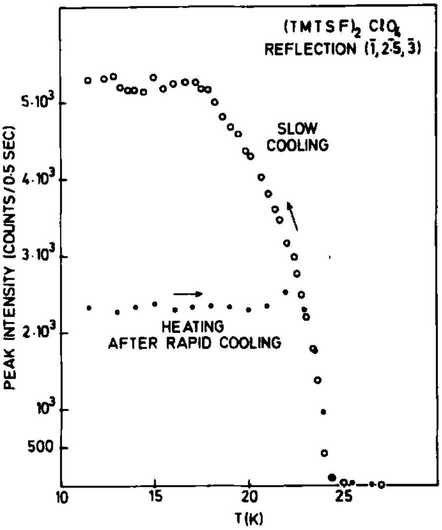

FIGURE 1 : Temperature dependence of the $(\bar{1}, \overline{2.5}, \bar{3})$ peak intensity. Slow cooling : 0.25 K/min., Heating : 0.5 K/min and rapid cooling : 3 K/min.

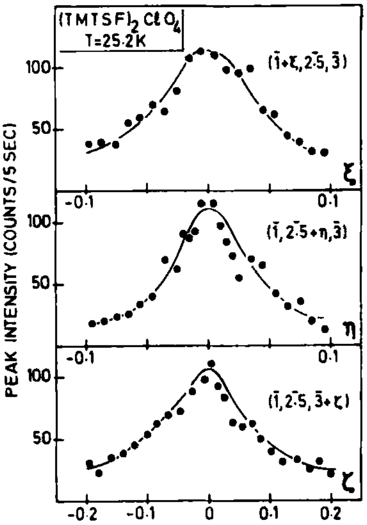

FIGURE 2 : Scans of the $(\bar{1}, \overline{2.5}, \bar{3})$ diffuse scattering peak in the precursor regime. The correlations are roughly isotropic.

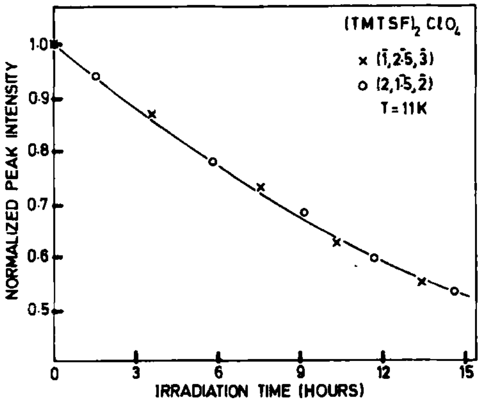

FIGURE 3 : Irradiation time dependence of 2 typical superstructure reflections at 11 K.

1 or 2 days of irradiation the main reflections are also affected but much less than the superstructure ones. This effect deserves a more detailed study.

Annealing effects are also observed for anion disorder induced by irradiation and they are even stronger than those found in the case of quenching. They start to be visible at a lower temperature, 15 K, perhaps below. We also point out a shift of the transition temperature upon irradiation with a rate $dT_c/dc \simeq -45$ K/%. This value is much higher than for disorder introduced by alloying, - 4K/% for $\mathrm{TMTSF\ C\ell O_{4\,x}}$[14] and -8 K/% for $\mathrm{TMTSF_{1-x}\ TMTTF_x\ C\ell O_4}$[9]. Interestingly enough it is closer to what is found for the superconducting transition in irradiated $\mathrm{(TMTSF)_2PF_6}$[15] and $\mathrm{(TMTSF)_2C\ell O_4}$[16].

Figure 4 shows a comparison of the peak scans made along c* for the $(\bar{1}, \overline{2.5}, \bar{3})$ superstructure reflection at low temperature for different conditions of thermal treatment or irradiation. Scans (a) and (b) correspond to the slowly and rapidly cooled cases in figure 1 (with little irradiation) while scan (c) was taken after 15 hours of irradiation. Comparing scans (a) and (c) which have the same peak intensity we note that there is no broadening of the peak in the case of irradiation, as compared to scan (b), while a significant one is produced by quenching (scan (a)). This is probably related to differences in the type of disorder present

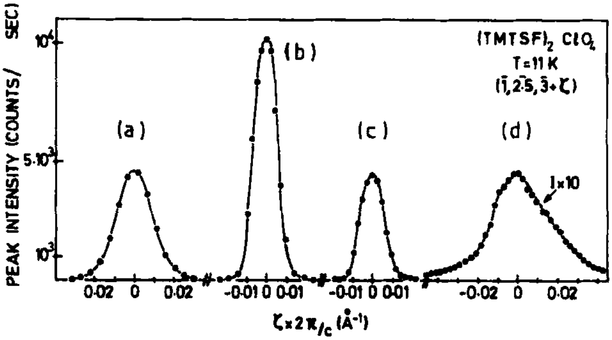

FIGURE 4 : Comparison of quenching and irradiation effects on the width of the $(\bar{1}, \overline{2.5}, \bar{3})$ reflection.

a) partly quenched state
b) slowly cooled relaxed state (R)
c) R state after 15 hours irradiation
d) R state after about 100 hours irradiation.

in the crystal. Through quenching the growth of ordered domains is stopped and the peak broadening reflects the limited domain size (scan (a)). In the case of irradiation defects introduced in a slowly cooled crystal these defects are created at random so that disordered regions are randomly distributed and do not modify the coherence length at least in the first stages (scan (c)). Thus a higher level of disorder is needed to broaden the peaks as is shown for scan (d) corresponding to about 100 hours of irradiation but where the intensity is now much lower.

We have also measured the intensities of 220 superstructure reflections in order to characterize the structural modifications brought about at the transition. Starting from the low-temperature average structure[17] we have performed a preliminary analysis of the intensity data. It shows that the ordering of the anions in a a×2b×c unit cell (ferro-like orientations in the a and c directions but antiferro-like along b) accounts for most of the intensity. Therefore the organic stacks is not distorted (or very little) and the only significant shift is that of the chlorine atom which is on the order of 0.1 Å , mainly along b. A more accurate refinement has just been made by Gallois et al[18] and it is in fair agreement with the above results.

This should be compared with the case of $(TMTSF)_2ReO_4$ where the 177 K metal-insulator transition is associated with an antiferro-like ordering of the ReO_4^- orientations along a, b and c. In contrast with $(TMTSF)_2C\ell O_4$ the transition presents an important displacive character with distortions of the organic stacks in particular. Simplifying the different behaviors of these two salts it appears that in (TMTSF) $C\ell O_4$ the electron-anion coupling is weak and the direct anion-anion interaction along a is minimized by the ordering while in $(TMTSF)_2ReO_4$, where the electron anion coupling is stronger, the response function of the 1D electron gas diverges at $2k_F$ ($a^*/2$) creating an insulating state.

We conclude with a short discussion of these results. The slow kinetics of the 24 K anion ordering transition of $(TMTSF)_2C\ell O_4$ is so far unique. This may be related to the relatively low temperature (lowest of the family) and also to competing (1/2,1/2,1/2) and (0, 1/2, 0) wave vectors for the transition[10]. It would be interesting to look for possible kinetics effects in salts which exhibit ordering transitions at relatively low temperature like $(TMTSF)_2NO_3$ or $(TMTSF)_2BF_4$. We also note that kinetic effects much slower than considered here have been shown to play a key role on the anomalous Hall effects observed in high magnetic fields[18].

Our results on the irradiation effects can be discussed in relation with superconductivity. It is known that 0.01% irradiation defects kill superconductivity[16] and we have found that a substantial part of the anions are disordered by such a low concentration of defects. Moreover quenching[7,2,19] and alloying[14,20] also suppress superconductivity. So the role of the irradiation-induced anion disorder is probably crucial in this respect and one might suggest that the high sensitivity of superconductivity to irradiation is actually due the high sensitivity of the anion order to irradiation, as we have shown here. However this argument does not readily apply to the behavior of $(TMTSF)_2PF_6$ for example where no evidence of an anion ordering transition has been found so far.

Returning to the contrasted effects of the anion ordering transitions in $(TMTSF)_2\ C\ell O_4$ and $(TMTSF)_2ReO_4$ and especially the involvement of the organic stacks as revealed by the distortions we note that it would be interesting to examine other salts like $(TMTSF)_2NO_3$ or $(TMTTF)_2SCN$. In the former, the 41 K (1/2, 0, 0) anion ordering transition does not open a Fermi surface gap and the anion-electron interaction should be weak[21]. The transition should have a weak displacive character for the molecular stack. The 160K (0, 1/2, 1/2) anion ordering transition of $(TMTTF)_2SCN$ is a metal-insulator one[22] and does note minimize the direct anion-anion interaction. Then the electronic origin of the transition is likely to involve a molecular stack distortion.

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