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X-ray evidence of a structural phase transition in di-tetramethyltetraselenafulvalenium perchlorate [(TMTSF)$_2$ClO$_4$], pristine and slightly doped

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Diffuse x-ray scattering studies of the quasi-one-dimensional conductor di-tetramethyltetraselenafulvalenium perchlorate [(TMTSF)$_2$ClO$_4$], both in its pristine form and when slightly doped with the sulfur analog tetramethyltetrathiafulvalene (TMTTF), reveal the formation of a low-temperature superstructure, which may involve an ordering of the ClO$_4$ anions. Superstructure reflections are characterized by the unexpected wave vector $\vec{q}=(0,\frac{1}{2},0)$, which might also be stabilized under pressure in the superconducting salts (TMTSF)$_2$ReO$_4$ and (TMTSF)$_2$FSO$_3$. The occurrence of a phase transition at 24 K in pristine (TMTSF)$_2$ClO$_4$ provides a clue for the understanding of the dependence on the cooling rate of the electronic ground state of (TMTSF)$_2$ClO$_4$.

In the field of quasi-one-dimensional (1D) conductors, the study of tetramethyltetraselenafulvalene and tetramethyltetrathiafulvalene salts, (TMTSF)$_2X$ and (TMTTF)$_2X$, respectively, where X is an anion such as PF$_6^-$, ClO$_4^-$, ReO$_4^-$, etc., has aroused considerable interest. The main reason is the discovery of a superconducting state below about 1 K in (TMTSF)$_2$PF$_6$ under high pressure[1] and at room pressure in (TMTSF)$_2$ClO$_4$.[2] However it appears now that, in addition to superconductivity, these salts can exhibit below about 10 K several kinds of ground states: either it can be a magnetic insulator such as (TMTSF)$_2$PF$_6$ at low pressure[3] or a nonmagnetic, Peierls-type, insulator as in the sulfur analog (TMTTF)$_2$PF$_6$.[4,5] This depends on the magnetic or structural nature of the $2k_F$ instability of the electronic gas (by stoichiometry $2k_F=0.5a^*$, where a^* is the reciprocal vector corresponding to the chain direction). The (TMTSF)$_2X$ and (TMTTF)$_2X$ salts all crystallize in the triclinic space group $P\bar{1}$. In an idealized structure (neglecting transverse hopping) the reciprocal-lattice vector of the anion lattice has a component along the stacking direction equal to $4k_F$ $(=a^*)$. It has been shown[6,7] that the various instabilities might be controlled by umklapp scattering produced by the $4k_F$ periodicity of the anion lattice. Finally, it has been observed that most of the salts which contain noncentrosymmetric anions and which are structurally disordered at room temperature may stabilize a $2k_F$ periodicity at low temperature by alternate ordering of the anions in the chain direction. This is particularly the case with (TMTSF)$_2$ReO$_4$ below 180 K,[4,8,9] (TMTSF)$_2$FSO$_3$ below 87 K,[10,11] and (TMTTF)$_2$ClO$_4$ below 70 K,[4,5] where, after a first-order phase transition, tetrahedral anions order with the wave vector $\vec{q}_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. It has been shown in the former salt[12] that the ReO$_4^-$ ordering is accompanied by a subsequent distortion of the organic sublattice which causes the large electronic gap observed below 180 K.[9] Under pressure, the insulating phase of (TMTSF)$_2$ReO$_4$ (Ref. 13) and (TMTSF)$_2$FSO$_3$ (Ref. 14) disappears and, with the reestablishment of the metallic state, superconductivity has been reported in these compounds. In this respect it is interesting to notice that a preliminary x-ray investigation of the superconducting salt at ambient pressure, (TMTSF)$_2$ClO$_4$, which also contains tetrahedral anions, failed to detect "$2k_F$" superlattice reflections down to 10 K.[4] A very different behavior is shown by (TMTSF)$_2$NO$_3$ which undergoes a $2k_F$ structural phase transition at 41 K, characterized by the wave vector $\vec{q}_2=(\frac{1}{2},0,0)$, and maintaining the metallic state.[8,15] This phase transition is kept under pressure, and superconductivity was not found in (TMTSF)$_2$NO$_3$ down to 50 mK.[16] From these studies it was (erroneously) suggested that anion disorder is essential to stabilization of a superconducting state.[2,13]

A recent study[17] of the solid solution [(TMTSF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ for $x<0.30$ has shown that the various instabilities are very close to each other. The superconducting state transforms very quickly with increasing x into a magnetic insulating state, which itself changes into a nonmagnetic ground state for $x > 0.04$. In pure $(TMTSF)_2ClO_4$, depending on the authors, a magnetic state (or magnetic fluctuations), is[18,19] or is not[2,20] established a few degrees above the superconducting transition. Further measurements show, in fact, that this state appears only in fast cooled samples.[21,22] Thus it was suggested that thermal treatment may influence the electronic instabilities via the kinetics of anion ordering. But until now no direct evidence of such a structural transition has been found.

The main purpose of this Communication is to show the formation of a superstructure, characterized by the unexpected wave vector $\vec{q}_3=(0,\frac{1}{2},0)$ in slowly cooled $(TMTSF)_2ClO_4$, and for low x values in the solid solution $[(TMTSF)_{1-x}(TMTTF)_x]_2ClO_4$. The new ordering periodicity of tetrahedral anions may also occur above 11 kbar in $(TMTSF)_2ReO_4$ (Ref. 13) and 6 kbar in $(TMTSF)_2FSO_3$,[14] when the metallic state is reestablished.

$(TMTSF)_2ClO_4$ crystals used in this study are similar to those studied in Refs. 2, 18, and 21–23. $[(TMTSF)_{1-x}(TMTSF)_x]_2ClO_4$ alloys come from the same batches as those used in Ref. 17, and were characterized by electronic microprobe spectroscopy and x-ray emission for S (K line) and Se (L line). Concentrations found were $x=0.005\pm0.001$, $x=0.02\pm0.003$, $x=0.04\pm0.007$, $x=0.065\pm0.005$, and $x=0.3\pm0.05$. Approximate dimensions of crystals were $3\times0.2\times0.1$ mm^3. The x-ray investigation was performed with the fixed-film, fixed-crystal method already used in previous studies of 1D conductors.[4] In order to obtain the wave vector of the superstructure, different projections of reciprocal space on the photographic film were used. Samples were put in a helium-filled container where the temperature could be precisely controlled and measured. They were slowly cooled at a rate of 1°/min around 25 K.

Figure 1 shows two low-temperature x-ray patterns taken at 1(a) 21 K and 1(b) 15 K for the alloy with $x=0.005$, which are also typical of pure $(TMTSF)_2ClO_4$. They reveal between 21 and 15 K very important changes in reciprocal planes perpendicular to the chain direction: (1) Between patterns A and B some Bragg reflections have disappeared or undergone a drastic change in intensity, and (2) several diffuse spots of pattern A have condensed into new Bragg reflections in pattern B. With the fixed-film, fixed-crystal method it is difficult to analyze the first feature, which might come from a slight elastic distortion of the lattice or (and) from a structure factor change related to a phase transition. Structural refinements are necessary to clarify this point. The second feature is characteristic of superlattice reflections appearing at a structural phase transition. This point is further illustrated by Fig. 2 which shows the temperature dependence of the intensity of a superlattice reflection of $(TMTSF)_2ClO_4$. It yields a transition temperature T_c of 24 K, where an anomaly on the slope of the electrical conductivity of $(TMTSF)_2ClO_4$ has been observed[20,22] and suggested as being related to a phase transition.[20] This phase transition seems to be continuous and leads to a better conducting state below 24 K in slowly cooled samples. This behavior recalls that of $(TMTSF)_2NO_3$ (Refs. 8 and 15) at 41 K. However, $(TMTSF)_2NO_3$ and $(TMTSF)_2ClO_4$ differ strongly by their low-temperature superstructure ($\vec{q}_2/\vec{q}_3$ wave vector) and by their electronic ground state (magnetic insulator[15,16] or superconductor[2]) at ambient pressure and lower temperature.

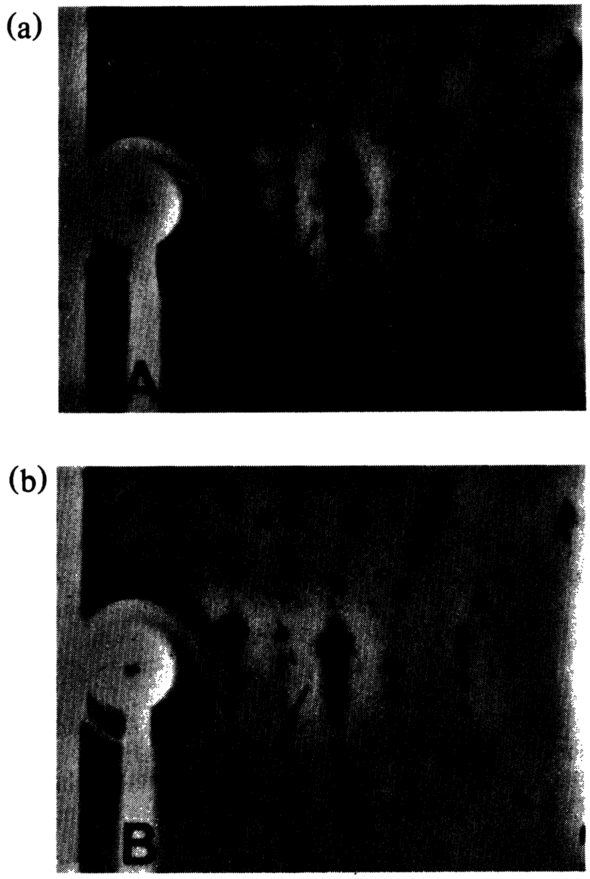

FIG. 1. Diffuse x-ray scattering from $[(TMTSF)_{0.995}(TMTTF)_{0.005}]_2ClO_4$ at (a) 21 and (b) 15 K. Arrows point to the low-temperature superstructure reflections in pattern B, and to the high-temperature isotropic precursor scattering in pattern A. The chain direction a is horizontal in both patterns.

Above T_c, the superlattice reflections broadened isotropically into diffuse spots which can be observed until about 40 K. With increasing x, the transition

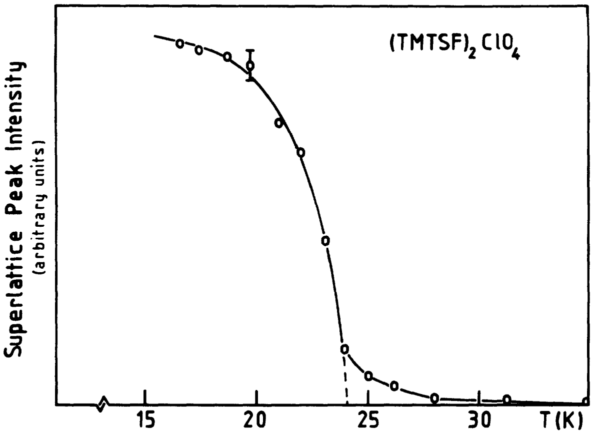

FIG. 2. Temperature dependence of the superlattice reflection intensity showing clearly the 24-K structural phase transition of (TMTSF)$_2$ClO$_4$. Note the critical scattering above 24 K.

temperature decreases rapidly: "T_c" $=20$ K for $x=0.005$ and "T_c" <16 K for $x=0.02$.[26] However, broad and isotropic spots remain observable below 40 K for samples with $x=0.02$, 0.04, and 0.065. The intensity and width are relatively independent of x. At 17 K, for $x=0.065$, the structural change is still correlated isotropically over a distance of 20 Å. No change in the intensity of the main Bragg reflections is observed in the short-range-order regime. Finally, in the sample with $x=0.3$, the short-range order is not observed above 15 K, the lowest temperature reached in this study.

With respect to the host crystal lattice, superstructure reflections occur at the wave vector $\vec{q}_3=(0,\frac{1}{2},0)$ which lead to a $a\times 2b\times c$ superstructure. The high intensity and the isotropic distribution of the diffuse intensity above T_c of these superstructure reflections are similar to that of the superlattice spots occurring, at a different wave vector $\vec{q}_1$, in (TMTSF)$_2$ReO$_4$, (TMTSF)$_2$FSO$_3$, and (TMTTF)$_2$ClO$_4$. These have been shown to be (partially) due to ordering of the anions.[12] However, in (TMTSF)$_2$ClO$_4$ the ordering of ClO$_4$ along the chain direction retains the lattice periodicity. This ordering minimizes electrostatic repulsion along a in the anion lattice, which is not the case for the alternate ordering of ReO$_4$ in (TMTSF)$_2$ReO$_4$.[8,9] By increasing direct electrostatic interaction between tetrahedra along a, pressure may stabilize in (TMTSF)$_2$ReO$_4$ and (TMTSF)$_2$FSO$_3$ the "metallic" $\vec{q}_3$ ordering with respect to the "insulating" $\vec{q}_1$ ordering. In this respect, one can notice in Fig. 3 of Ref. 13 an anomaly at about 33 K on the slope of the electrical resistivity of (TMTSF)$_2$ReO$_4$ at 12.5 kbar, which resembles that found at 24 K and the ambient pressure in (TMTSF)$_2$ClO$_4$.[20]

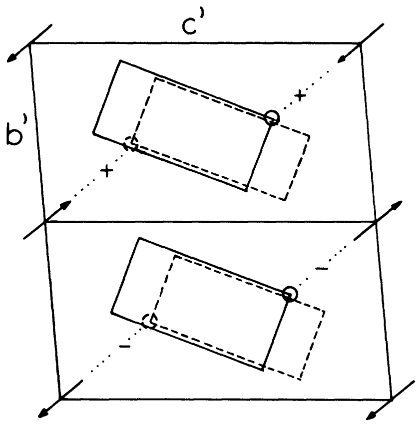

FIG. 3. Schematic projection of the structure of (TMTSF)$_2$ClO$_4$ on a plane perpendicular to the stacking direction. The main effect below 24 K is the loss of some inversion centers with the consequence that neighboring stacks are no longer identical. This is indicated by + or − relating to close Se-O contacts. (The orientation of ClO$_4^-$ is indicated by arrows, the TMTSF molecules by rectangles.)

Without knowing the full structural details of the superstructure below 24 K, we can model some of the consequences of the $\vec{a}\times 2\vec{b}\times\vec{c}$ periodicity. The new unit cell must contain four TMTSF molecules. The main effect of the superstructure is loss of some inversion centers and the fact that (TMTSF)$_2$ClO$_4$ below 24 K contains two different types of TMTSF stacks (either *with* or *without* close anion contacts) as schematically indicated in Fig. 3. There is no *a priori* reason to assume that the ordering is accompanied by distortions or changes in the dimerization (in contrast to what was found in a recent refined structural study of the $2\vec{a}\times 2\vec{b}\times 2\vec{c}$ superstructure of [(TMTSF)$_2$ReO$_4$ (Ref. 12)] because the molecules in the individual stacks still have the same environment. These structural changes with $4k_F$ periodicity are, however, possible (Fig. 3) and may influence the umklapp scattering emphasized as an important factor by recent theories.[6,7] The effect of the unexpected $4k_F$ superstructure formation in superconducting (TMTSF)$_2X$ salts has never been considered in theoretical treatments of these materials. However, several features of (TMTSF)$_2$ClO$_4$ at low temperature can be explained by the $4k_F$ anion ordering process. In particular, it has been observed by thermal measurements[23] that the superconducting transition of (TMTSF)$_2$ClO$_4$ is depressed by 22% by fast cooling of the sample across T_c. Because of the slow kinetics of anion ordering, fast cooling of (TMTSF)$_2$ClO$_4$ freezes in anion disorder, which creates disordered potentials on the conducting stacks. An earlier theory[24] has explicitly shown that disordered potentials rapidly kill superconductivity in 1D conductors. Experimentally, a very rapid vanishing of the superconducting state has been observed by alloying (TMTSF)$_2$ClO$_4$ with TMTTF (Ref. 17) and by x-ray irradiation of (TMTSF)$_2$PF$_6$.[25] As magnetic and superconducting fluctuations compete at low temperature in (TMTSF)$_2$ClO$_4$, the destabilization of the superconductivity favors the antiferromagnetism.[19,21,22]

Contrary to what was believed until now, anion ordering appears as a necessary condition to achieving higher superconducting transition temperature. However this ordering must stabilize a $4k_F$ periodicity, $2k_F$ ordering leading either to an insulating state or at least to a depression of the density of states at the Fermi level, which are not favorable conditions for getting superconductivity.

In conclusion, we have shown that anion ordering with wave vector $\vec{q}_3=(0,\frac{1}{2},0)$ develops in (TMTSF)$_2$ClO$_4$ below 24 K, in contrast to previous assumptions,[2,13] and have suggested that this is a general feature for (TMTSF)$_2X$ salts at low T and above characteristic pressures, when X is a tetrahedral anion.

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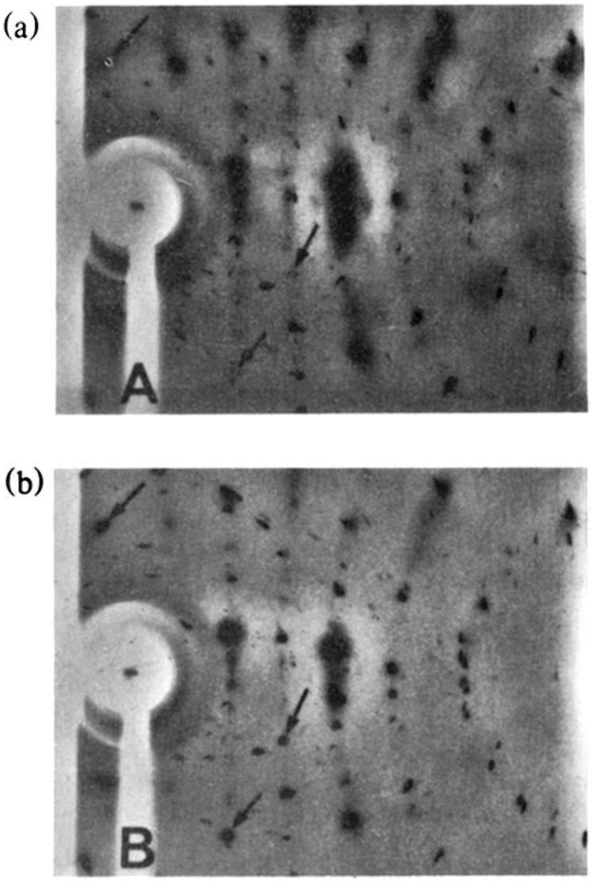
[26] In fact for $x=0.005$, the long-range order is lost, but there is still a rapid increase of the superlattice intensity at "T_c" = 20 K. See J. P. Pouget, R. Moret, R. Comes, G. Shirane, K. Bechgaard, and J. M. Fabre in Ref. 11.



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