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X-Ray Scattering Evidence for Anion Ordering and Structural Distortions in the Low-Temperature Phase of Di(Tetramethyltetraselanafulvalenium) Perrhenate [$(TMTSF)_2ReO_4$]

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This paper reports x-ray intensity analysis of the superlattice reflections associated with the order-disorder transition of di(tetramethyltetraselenafulvalenium) perrhenate [$(TMTSF)_2ReO_4$] at $T_c \simeq 180$ K. The results confirm the earlier proposed anion ordering and reveal large distortions of the anion array and of the TMTSF molecular stacks which are fairly well described by rigid displacements. Strong modulations of the overlap between TMTSF molecules along the stacks are clearly established and provide a key to the understanding of the metal-insulator transition observed at T_c.

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The ground state of the isomorphous quasi-one-dimensional organic conductors $(TMTSF)_2X$ (where TMTSF stands for tetramethyltetraselenafulvalenium), ranging from superconducting to magnetic or nonmagnetic insulating, changes with the nature of the anion X, but this dependence is far from being clearly understood. Apart from electronegativity or size, the various anions which can be accommodated into the structure can be classified according to symmetry: octahedral (PF_6^-, AsF_6^-, ...), tetrahedral (ClO_4^-, BF_4^-, ReO_4^-, ...) triangular (NO_3^-, ...) or linear (SCN^-, ...).[1] The available structural data show that these anions stand on inversion centers in the $P\bar{1}$ space group, at least at room temperature.[1,2] In the case of noncentrosymmetric anions the resulting conflict is generally considered to imply some sort of structural disorder with two (or more) orientations of the anions so that the inversion centers are present on average only. Low-temperature phase transitions have been associated with an ordering of these anions through the formation of superstructures,[3] although no detailed structural investigation has been made so far.

We present here the results of the first attempt to characterize the structural modifications involved in the low-temperature phase transition in a $(TMTSF)_2X$ material containing a noncentrosymmetric anion. X-ray intensity analysis confirms the anion ordering and shows very clearly that it is accompanied by distortions of both anion and organic-molecule sublattices. These findings provide evidence that interactions between the conducting organic stacks and the anions drive the metal-insulator transition of $(TMTSF)_2ReO_4$ and may be important in other $(TMTSF)_2X$ salts.

The metal-insulator transition of $(TMTSF)_2ReO_4$ occurs at $T_c \simeq 180$ K and atmospheric pressure[4] and is revealed in the transport, optical, and magnetic properties.[5] Recent x-ray diffuse scattering studies[3] have shown that it is accompanied by the formation of a superstructure characterized by a wave vector $\vec{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In addition, precursor scattering in the form of broad and fairly isotropic diffuse peaks is observed above T_c, up to about 250 K. It is very different from the charge-density-wave–driven diffuse sheets present in one-dimensional metals like tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) above their Peierls transition.[3]

To determine the structural changes associated with the metal-insulator transition we have measured and analyzed a number of the superlattice reflections which appear below T_c. These reflections had been first observed by the "monochromatic Laue" technique as well as counter detection on a diffractometer.[3] However, with use of monochromatized Cu $K\alpha$ radiation from a 12 kW generator their intensities become strong enough to allow recording by conventional photographic methods. Figure 1 shows an x-ray oscillating-crystal pattern taken at $T = 150$ K in these conditions. Besides layers of high-intensity reflections (often overexposed) corresponding to the high-temperature periodicity, one observes weaker intermediate layers coming from a doubling of the repeat distance along a. Weissenberg photographs of the intermediate layers have been made and the indexing of the reflections confirms the superlattice reflection wave vector $\vec{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. An additional complexity of indexing arose from twinning,[6] present in all the large crystals we have studied (typical dimensions $4 \times 0.2 \times 0.2$ mm^3).

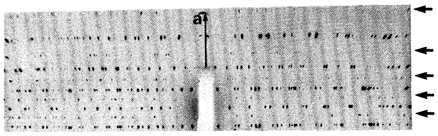


FIG. 1. X-ray oscillating-crystal photograph of $(TMTSF)_2ReO_4$ around $\vec{a}$, at $T \simeq 150$ K. Arrows point to the superlattice layers.

The reciprocal superlattice is body centered with respect to the main lattice and one can choose for the direct lattice either a primitive unit cell with axes $\vec{a}+\vec{b}$, $\vec{b}+\vec{c}$, $\vec{c}+\vec{a}$ (a, b, c, refer to the high-temperature unit cell) or a nonprimitive face-centered unit cell $2\vec{a}$, $2\vec{b}$, $2\vec{c}$, although nonconventional in the triclinic system. We have found it more convenient to use the latter description, keeping in mind that the unit-cell volume only doubles at the transition.

Intensity measurements of 160 superlattice reflections were used, belonging to the $(1 \pm 1\, l)$, $(5\,1\,l)$, $(5\,3\,l)$, $(1\,\overline{1}\overline{1}\,l)$, $(1\,\overline{1}\overline{5}\,l)$, $(1\,k \pm 1)$, and $(1\,k \pm 3)$ reciprocal-lattice rows in different layers. The data were extracted from the Weissenberg photographs by densitometry. Lorentz and polarization corrections were applied whereas absorption corrections were precluded by the twinning.

The intensity analysis was carried out by comparison of the observed intensities with calculated values obtained for several hypothetic models with use of a trial and error computer program. These calculations are based on the atomic coordinates and thermal parameters determined by Rindorf, Soling, and Thorup[2] (RST) at 120 K for the average structure.

We first consider the alternation of inverted ReO_4^- anions along the three unit-cell axes. This model leads to calculated intensities generally much weaker and of smoother wave-vector dependence than the data, as shown for example in Fig. 2(a) for the $11l$ reflections. Other structural modifications are obviously associated with the transition.

The next model we examine consists in allowing the ReO_4^- anions to be also displaced from their original positions as suggested by electron density maps obtained for $(TMTSF)_2BF_4$ (Ref. 7) and $(TMTTF)_2BF_4$ (TMTTF denotes tetramethyltetrathiafulvalenium).[8] Rigid translations of the anions, alternating in direction along a, b, and c and keeping the average structure unchanged, are varied simultaneously by steps whose size is reduced in an iterative process. This brings a marked improvement of the fit (see Fig. 2), and the conventional reliability index

$$R = \sum \left| F_{\mathrm{obs}} - |F_{\mathrm{calc}}| \right| / \sum F_{\mathrm{obs}}$$

(F_{obs} and F_{calc} are the observed and calculated structure factors) decreases from 0.83 to 0.55. However the agreement is not satisfactory enough, which clearly indicates that the model still overlooks some important structural features.

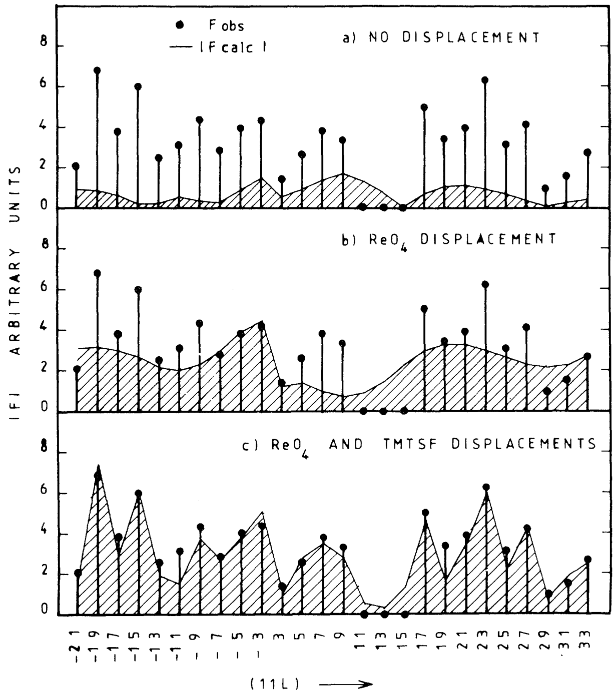


FIG. 2. Comparison of observed and calculated 11*l* reflection intensities for three different models: (a) ordering of the ReO_4^- anions only, (b) ordering and rigid displacements of the anions, and (c) same as in (b) plus rigid displacements of the TMTSF molecules.

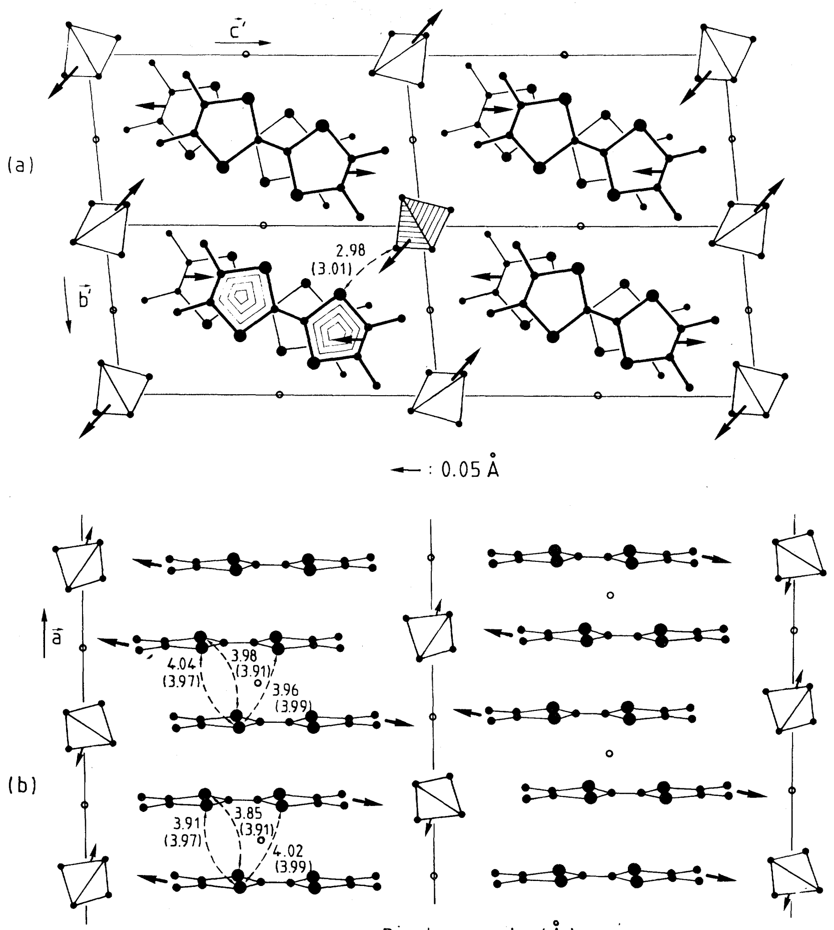
At this point the simplest way of modifying the model consists in introducing distortions of the organic stacks also. This can be done by allowing rigid translations of the TMTSF molecules while retaining the $P\bar{1}$ space group and preserving the average structure as determined by RST. Introducing these translation components proved to be crucial as visible in Fig. 2(c) where the fit is now satisfactory. The R value ranges from 0.18 to 0.27 depending on the reciprocal-lattice rows, yielding consistent values for the six translation components. These are listed in the table of Fig. 3 with their accuracies (estimated empircally from parameter step values bringing no significant alteration of the fit).

We point out that both types of distortions (ReO_4 and TMTSF) are necessary to obtain a reasonable fit since refinement of the TMTSF position alone (keeping the ReO_4^- anion ordering) does not reduce R below 0.50.

Before discussing these results a few comments should be made about their validity and limitations. Although the fit appears quite good on a plot such as Fig. 2(c) the R values are still high when compared with structure refinement standards. This may be caused by several reasons: (i) The superlattice intensities, though measurable, are roughly 10 times weaker than the main reflections, (ii) our densitometric measurements are estimated to involve a 5% error, (iii) the absorption effect may not be negligible, especially given the presence of twins, and (iv) the RST thermal parameters, used here, can be questioned considering the observed displacements. A more fundamental problem concerns the rigid-molecules, rigid-anions approximation since weak intramolecular (and intra-anion) distortions are very likely to occur. Also uncertain is the assumption we have made to keep the inversion centers thus retaining the $P\bar{1}$ space group. A complete refinement of all atomic positions (and thermal parameters) should be made but it would require many more observed reflections than available here (it should also include the main reflections). It is beyond the scope of the present study. However, we are confident about having identified the most prominent structural features associated with the order-disorder transition.

The anion ordering and displacement pattern are represented in Fig. 3 and some significant intermolecular distances are compared with those of the RST 120-K average-structure determination. Some remarkable features are noted below. The TMTSF molecular stacks are distorted by translations, mainly along $\vec{c}$ [Fig. 3(a)] which result in alternate increases and decreases of the intrastack overlap for successive unit cells. On the other hand, the shortest Se-Se contacts between neighboring stacks (along $\vec{b}$) either keep constant or change very little. The correlation between the TMTSF molecules and anion displacements can be analyzed as a cooperative phenomenon involving in particular the very short Se-O bond (previously reported to be much shorter than the Van der Waals distance[2,9]) which is maintained and even slightly shortened [see Fig. 3(a)] in the superstructure. Steric effects may be involved too as seen in Fig. 3(b) where the anions seem to be "pushed" in the *a* direction by the TMTSF molecules. Thus, the displacements of the TMTSF molecules act as links between *a*-*b* planes of displaced and ordered anions.

These results have important implications concerning the nature of the metal-insulator aspect of the $(TMTSF)_2ReO_4$ transition which has recently led to conflicting views.[3,5,9] The strong modu-



Displacements (Å)

	ReO_4	TMTSF
ΔX	0.03 (0.015)	-0.01 (0.015)
ΔY	0.06 (0.01)	0 (0.01)
ΔZ	-0.05 (0.01)	-0.055 (0.01)

FIG. 3. Translation components and corresponding displacement pattern for $(TMTSF)_2ReO_4$ at $T \simeq 150$ K. In the table the displacement values are given for the hatched ReO_4^- anion and TMTSF molecules shown in (a) (with estimated accuracies in parenthesis). (a) View along $\vec{a}$. $\vec{b}'$ and $\vec{c}'$ are the projections of $\vec{b}$ and $\vec{c}$. The Re atoms are omitted and the b-c plane of oxygen tetrahedra is located above the TMTSF molecules. (b) Side view of the stacks. Note the overlap variation between TMTSF molecules in the a direction and the synchronous anion displacements. The arrow lengths are proportional to the displacement values. Some intermolecular distances are given along with the RST average-structure values (in parenthesis).

lation of the overlap integrals due to sizable intrastack distortions with the $2k_F$ (i.e., $a^*/2$) wave vector can account for the large electrical gap (0.2 eV)[5] opened below T_c. This is certainly the most effective cause of the Fermi-surface alteration and, accordingly, it can stabilize the insulating state. However, such an effect appears to be the result of the coupling with the anion array whose disorder at high temperature may provide the extra degrees of freedom for stabilization of the $2k_F$ periodicity at low temperature.

Similar distortions of both organic and anion sublattices might occur in other salts with tetrahedral anions which exhibit metal-insulator transitions associated with anion ordering. On the other hand, with anions of different shapes, having different interactions with the organic sublattice, some of the distortions should vary in nature and magnitude or even be suppressed. This might be the case of $(TMTSF)_2NO_3$ which shows a different superstructure,[3] $2a \times b \times c$, and no metal-insulator transition at $T = 41$ K.[10]

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Observation of Ultrasonic Anomaly near a Smectic-*A* – Smectic-*C* Phase Transition

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The first observation is reported of an anomalous attenuation and velocity dispersion near a smectic-*A*–smectic-*C* phase transition in a liquid crystal. The anomaly is found to be strongly anisotropic and dominated by the Landau-Khalatnikov relaxation of the order parameter in contrast with other liquid-crystalline phase transitions.

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Possible second-order phase transitions in liquid crystals, nematic to smectic-*A* (*N*-*A*) and smectic-*A* to smectic-*C* (*A*-*C*), were proposed by de Gennes[1,2] in analogy with superfluid ^{4}He ($n = 2$, $d = 3$ universality class). Of the two the latter has received much less attention, though unlike the former[3] no controversy surrounds the second-order nature of the *A*-*C* transition. In this Letter we present the first experimental evidence of the existence of anomalies in both the attenuation and the velocity dispersion of longitudinal ultrasound near the *A*-*C* phase transition.[4,5]

The Ginzburg-Landau free energy for the *A*-*C* transition can be written as[6]

$$\delta F \equiv F - F_0 = A|\psi|^2 + B|\psi|^4 + D|\nabla\psi|^2 + \dots, \qquad (1)$$

where ψ is the complex order parameter, $\psi = \psi_0 e^{i\varphi}$ with ψ_0 the tilt angle of the molecular orientations from the layer normal and φ the azimuth. Above the transition temperature T_{AC}, $\langle\psi_0\rangle$ is identically zero, while below T_{AC} it grows continuously. The transition is driven by A (which is proportional to the elastic modulus keeping the molecules normal to the layer) going to zero. A recent x-ray scattering study[6] has shown that the growth of ψ_0 is essentially mean-field-like and an appropri-

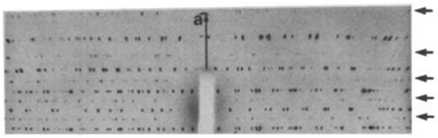

FIG. 1. X-ray oscillating-crystal photograph of $(TMTSF)_2ReO_4$ around $\vec{a}$, at $T \simeq 150$ K. Arrows point to the superlattice layers.