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Classification

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X-ray diffuse scattering study of superstructure formation in tetramethyltetraselenafulvalenium perrhenate $(\text{TMTSF})_2\text{ReO}_4$ and nitrate $(\text{TMTSF})_2\text{NO}_3$

J. P. Pouget, R. Moret, R. Comes

Laboratoire de Physique des Solides (*), Université Paris Sud, Bâtiment 510, 91405 Orsay, France

and K. Bechgaard

H. C. Oersted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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Résumé. — L'étude par diffusion diffuse des rayons X des conducteurs unidimensionnels $(\text{TMTSF})_2\text{ReO}_4$ et $(\text{TMTSF})_2\text{NO}_3$ a mis en évidence, à basse température, des réflexions de surstructure qui pourraient être dues à une mise en ordre des contre-ions ReO_4^- et NO_3^- . Ces réflexions sont caractérisées par les vecteurs d'onde $\mathbf{q} = (1/2, 1/2, 1/2)$ pour le perrhenate et $\mathbf{q} = (1/2, 0, 0)$ pour le nitrate, montrant un doublement de volume de la maille élémentaire. Dans $(\text{TMTSF})_2\text{ReO}_4$, cette transition de phase coïncide avec la transition métal-isolant observée à 180 K, tandis que dans $(\text{TMTSF})_2\text{NO}_3$ elle annonce un état de meilleure conductivité observé en-dessous de 41 K.

Abstract. — X-ray diffuse scattering studies of one dimensional conductors $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{NO}_3$ reveal the formation of low temperature superstructures which might involve an ordering of the counter ions ReO_4^- and NO_3^- . The superstructure reflections are characterized by wave vectors $\mathbf{q} = (1/2, 1/2, 1/2)$ for the perrhenate and $\mathbf{q} = (1/2, 0, 0)$ for the nitrate, which double the unit cell volume in both cases. In $(\text{TMTSF})_2\text{ReO}_4$ this phase transition coincides with the metal insulator transition observed at 180 K, whereas in $(\text{TMTSF})_2\text{NO}_3$ it corresponds to a better conducting state observed below 41 K.

Structural studies of the newly synthesized [1] superconducting compounds such as $(\text{TMTSF})_2\text{PF}_6$ [2], $(\text{TMTSF})_2\text{AsF}_6$ [3] and $(\text{TMTSF})_2\text{ClO}_4$ [4], failed to reveal the characteristic features of Peierls transitions as usually observed in one dimensional conductors [5]. This has been generally interpreted as reflecting the mutual exclusion of the instabilities leading respectively to the superconducting state and to the Peierls insulator [6, 7].

Among the $(\text{TMTSF})_2$ salts, $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{NO}_3$ display unique features compared to the other members of the family. $(\text{TMTSF})_2\text{ReO}_4$ becomes superconducting above 11.5 kbars [8] and nevertheless reveals at lower pressures a first order metal insulator transition ($T_c \simeq 180$ K at atmospheric pressure [9]). $(\text{TMTSF})_2\text{NO}_3$ does not become superconducting under pressure [10] albeit it is the best conductor of the family at room pressure, above its metal insulator transition which takes place at 12 K. This compound further reveals an intriguing anomaly

in its transport properties around 41 K, temperature below which one observes a faster rate of increase of its electrical conductivity [1].

The present paper reports an X-ray diffuse scattering investigation of $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{NO}_3$. Low temperature superstructures have been observed for the first time and we suggest that they are associated with an ordering of the counter ions ReO_4^- and NO_3^- . We briefly discuss the implications of this ordering in the light of the transport data.

$(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{NO}_3$ single crystals of approximate dimensions $5 \times 0.2 \times 0.2$ mm were from the same origin as those studied in references [1, 8, 9]. They are isostructural to $(\text{TMTSF})_2\text{PF}_6$, belonging to the triclinic P1 space group [9, 11]. The X-ray study presented here combines the photographic method for the survey of the diffuse scattering between 300 K and 10 K, and counter detection on an automatic diffractometer. Figure 1a presents a typical low temperature X-ray pattern from $(\text{TMTSF})_2\text{ReO}_4$ revealing very strong superstructure reflections half-way between layers of main Bragg reflections perpen-

(*) Laboratoire associé au C.N.R.S.

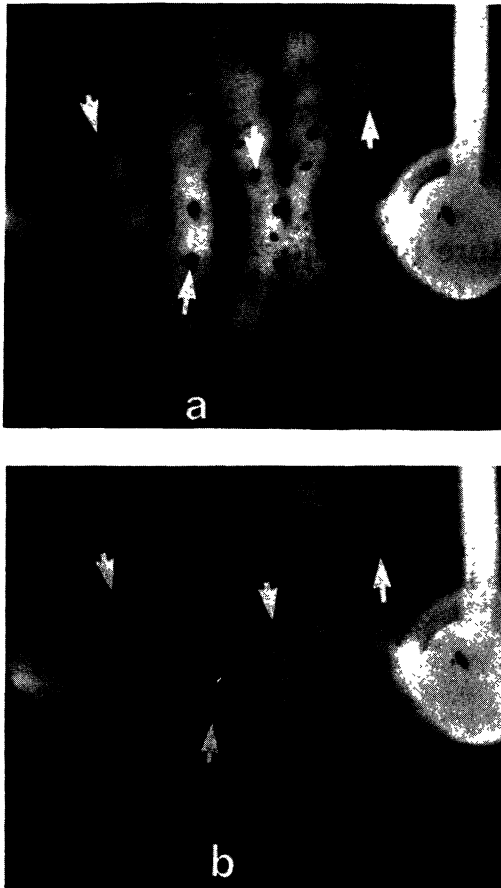


Fig. 1. — Diffuse X-ray scattering patterns from $(\text{TMTSF})_2\text{ReO}_4$ at (a) 150 K and (b) 177.5 K. Arrows point to the low temperature superstructure reflections in (a), and to the high temperature isotropic precursor scattering in (b).

dicular to the a stacking direction. These reflections are further characterized in figure 2a by typical scans from diffractometer measurements which give the precise wave vector of the superstructure reflection $\mathbf{q} = (1/2, 1/2, 1/2)$, corresponding to a triclinic superstructure $(\mathbf{a} + \mathbf{b}) \times (\mathbf{b} + \mathbf{c}) \times (\mathbf{c} + \mathbf{a})$. The temperature dependence of these superstructure reflections is given in figure 3, and yields a transition temperature of 176 K in fair agreement with the transport studies.

Figure 1b shows an X-ray pattern from the same $(\text{TMTSF})_2\text{ReO}_4$ taken just a few degrees above T_c . It reveals very clear precursor scattering in the form of broad and isotropic diffuse spots which are observed until about 250 K. Diffractometer scans in several directions confirm this isotropy of the precursor effects just above the transition temperature as illustrated in figure 2b.

X-ray patterns similar to those just described for $(\text{TMTSF})_2\text{ReO}_4$ have been obtained with $(\text{TMTSF})_2\text{NO}_3$. In this case the transition temperature is much lower ($T \approx 41$ K) and the wave vector of the superstructure reflections is different ($\mathbf{q} = 1/2, 0, 0$), leading to a $2a \times b \times c$ superstructure. However these reflections have comparable high intensities and

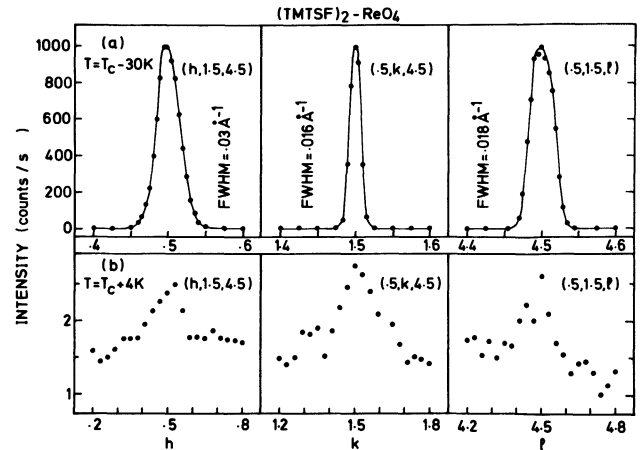


Fig. 2. — Typical diffractometer scans of $(\text{TMTSF})_2\text{ReO}_4$ showing : a) the intensity profiles of the (0.5, 1.5, 4.5) superlattice reflection in the low temperature phase. (The larger width along a^* is due to the experimental resolution in this direction); b) the corresponding precursor scattering above T_c . Note its broad and isotropic character.

temperature dependence for both compounds, and $(\text{TMTSF})_2\text{NO}_3$ exhibits also a precursor scattering consisting of broad diffuse spots which are detectable below about 75 K. One should note that the intensity of this precursor scattering decreases less abruptly for $(\text{TMTSF})_2\text{NO}_3$ than for $(\text{TMTSF})_2\text{ReO}_4$ which indicates a smoother transition (Fig. 3).

Considering alone the $0.5 a^*$ wave vector component in stacking direction of the superstructure reflections, one might think again of a Peierls transition. Indeed $0.5 a^*$ corresponds exactly to the value of $2 k_F$ deduced from a 1-D band scheme for the 1 : 2 stoichiometry of the $(\text{TMTSF})_2\text{X}$ salts.

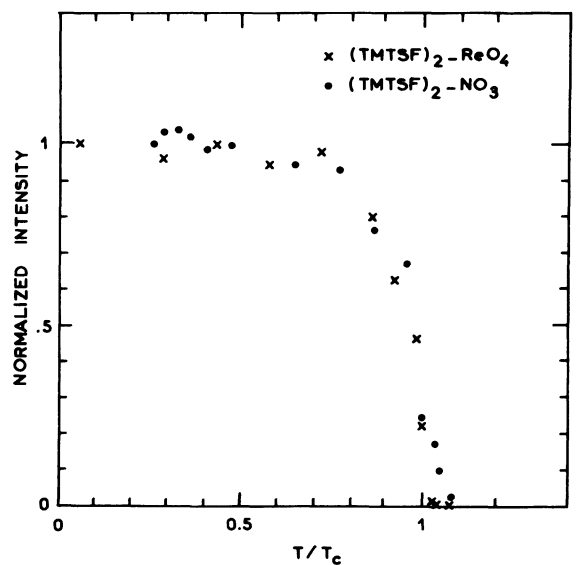


Fig. 3. — Temperature dependence of the superlattice reflection intensity as a function of reduced temperature (T/T_c) for both $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{NO}_3$.

A closer analysis of the structural data shows however that essential features are different from those expected from a Peierls transition. The precursor scattering is clearly three dimensional : the fairly isotropic distribution of intensity has nothing in common with the characteristic precursor scattering in diffuse sheets perpendicular to the conduction direction due to the 1-D Kohn anomaly [5]. The low temperature superstructure reflections are of high intensity : about 1/10 of the intensity of the parent main Bragg peaks, that is to say about 3 orders of magnitude stronger than the typical intensity of satellites due to a Peierls distortion [12].

Such features show that one has to consider a more important structural modification than a Peierls distortion. Structural disorder involving two possible orientations of the counter ions has already been explicitly considered in the conventional structure determination of salts containing non centrosymmetric ions like (TMTTF)₂BF₄ [13], (TMTSF)₂ClO₄ [9] and (TMTSF)₂ReO₄ [11]. In the case of (TMTSF)₂ReO₄ and (TMTSF)₂NO₃, the non centrosymmetric tetrahedral ReO₄⁻ and triangular NO₃⁻ ions are at room temperature located at the inversion centre of the triclinic P $\bar{1}$ unit cell. This implies again a structural disorder for ReO₄⁻ and NO₃⁻, with at least two possible orientations related by inversion. A low temperature ordering resulting from an alternation of these two orientations in the *a*, *b*, *c* directions could explain the observed superlattice in (TMTSF)₂ReO₄ below $T_c = 176$ K and account qualitatively for the order of magnitude of the superlattice intensities. Such an ordering could also account for the already reported superstructure reflections which exists below 70 K in (TMTTF)₂ClO₄ [7]. The situation is different in (TMTSF)₂NO₃ as indicated by the different $2a \times b \times c$ superstructure, and the triangular-shaped NO₃⁻ ions apparently alternate in chain direction only.

This kind of disorder involving mainly the oxygen atoms explains why superstructure reflections of comparable intensities are observed in the three compounds. However it is conceivable that the ordering of the counter ions induces also structural distortions, with the same wave vector, on the organic stacks. As the expected contribution of such distortions is weaker in intensity than that coming for the oxygen disorder, a detailed low temperature structural determination is necessary for a complete description of the phase transition. In this respect it is interesting to remark that the alternate ordering of ReO₄⁻ counter ions cannot be understood using direct electrostatic repulsion between tetrahedra. This is probably the signature of indirect interactions involving the organic molecules through short Se-O contacts for example.

Both the extra electrical potential due to the alternate ordering of the counter ions in the chain direction, and the modulation of intra-stack overlap integrals, coming from an eventual distortion of the organic lattice, with the same periodicity, will perturb the

Fermi surface of a half filled conduction band, by coupling $|k\rangle$ and $|k \pm q\rangle$ electronic states by an effective potential Vq . As a result the structural phase transition will be accompanied by a change in the transport properties.

In the case of a planar Fermi surface, and for any transverse component of the wave vector \mathbf{q} , this process, similarly to that invoked for the Peierls distortion, opens a gap and leads to a metal insulator transition. This might be the case at 176 K for (TMTSF)₂ReO₄. Other possibilities, such as the close nesting of a non planar (tight binding) Fermi surface along the wave vector of modulation $\mathbf{q} = (1/2, 1/2, 1/2)$ [14], or the effect of a strong potential Vq on an anisotropic Fermi surface of more arbitrary shape, must be also considered.

In (TMTSF)₂NO₃ on the contrary the 41 K transition is not a metal insulator transition, which might simply mean that, as a result of the structural transition, only partial gap are opened at the Fermi surface. Such a result is in consistence with the presence of a non planar Fermi surface which cannot be brought in close nesting along the observed modulation wave vector $\mathbf{q} = (1/2, 0, 0)$. This implies a very weak effective potential Vq (weaker than the largest transverse overlap integral). A non planar Fermi surface at low temperatures has indeed been inferred previously from the observation of Shubnikov-de Haas oscillations in (TMTSF)₂PF₆ under pressure [15], and optical measurements [16] revealed a cross over from a high temperature 1-D to a low temperature 3-D (or 2-D) Fermi surface in this compound.

(TMTSF)₂NO₃ further undergoes a metal insulator transition at 12 K. It is interesting to note that no significant change in the intensity of the superlattice reflections is observed at this temperature. This behaviour is consistent with a transition (probably of magnetic origin as in (TMTSF)₂PF₆ [17]) involving mainly the TMTSF stacks.

Besides the main features described above, a few other additional effects have been observed. Very faint 1-D scattering in the form of sheets perpendicular to the stacking direction *a*, with a wave vector $0.5 a^*$ corresponding to $2 k_F$, are observed below T_c in (TMTSF)₂ReO₄ and (TMTTF)₂ClO₄. In (TMTSF)₂ReO₄ this scattering vanishes at lower temperatures below about 50 K. In these salts, one observes below room temperature, another 1-D scattering in the form of sheets perpendicular to the stacking direction and running through the Bragg reflections of the main lattice, which correspond to the $4 k_F$ wave vector. This « $4 k_F$ » scattering sharpens with decreasing temperature until about 100 K, temperature below which it seems to merge into the main Bragg reflections. Both points need further investigation.

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