

Competition between organic superconductivity and a displacive structural modulation in bis(ethylenedithio) tetrathiafulvalene perrhenate, (BEDT-TTF)₂ReO₄

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The pressure-induced organic superconductor bis(ethylenedithio) tetrathiafulvalene perrhenate, (BEDT-TTF)₂ReO₄, is shown to undergo a first-order structural phase transition with an associated metal-to-insulator transition near $T_c = 77$ K at ambient pressure. Superstructure reflections with reduced wave vectors $\mathbf{q} = (\frac{1}{2}, 0, \frac{1}{2})$ are found using single-crystal x-ray diffraction. Evidence is presented that these are not associated with a change of the anion ordering, but result from a displacive structural modulation which most probably involves both the ReO₄⁻ anion and BEDT-TTF molecular sublattices.

Organic superconductivity has been observed in only two series of materials so far, namely, (TMTSF)₂X and (BEDT-TTF)_nX_m (where TMTSF is tetramethyltetraselenafulvalene, BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, and X can be various anions.¹ The (TMTSF)₂X compounds exhibit various types of phase diagrams with superconductor, magnetic insulator, or dielectric insulator ground states.^{1,2} When the anions X are noncentrosymmetric these compounds also often display structural phase transitions involving orientational ordering of the anions. In the high-temperature state, usually two orientations of the anions are randomly distributed on the anion sites, producing inversion centers at these sites. At low temperatures these different orientations order, giving rise to various superstructures.³ Depending on the particular wave vector characterizing the superstructure and on the strength of the coupling with the quasi-one-dimensional (1D) electronic system formed by the organic stacks of nearly flat TMTSF molecules, these ordering phase transitions may [as in (TMTSF)₂ReO₄] (Ref. 4) or may not [as in slowly cooled (TMTSF)₂ClO₄] (Ref. 5) lead to an insulator state. In the former case, superconductivity may be restored by applying pressure, and it is interesting to note that the low-temperature anion ordering is probably modified under these circumstances, although no experimental data are available at present.

In contrast, in the more recently discovered BEDT-TTF_nX_m series, noncentrosymmetric anions (for example, tetrahedra) are normally ordered at room temperature.⁶ In particular, this is the case for (BEDT-TTF)₂ReO₄, as found by x-ray structure determinations^{7,8} and as shown schematically in Fig. 1. The axes of the conventional crystallographic unit cell are labeled by (a, b, c).^{7,8} Within this unit cell the anion ordering contributes to Bragg reflections with odd k indices. In order to compare the type of anion ordering found in this material with those found in the parent (TMTSF)₂X compounds, it is useful to relate the (a, b, c) cell with that usually used to describe the parent compounds. These unit-cell axes are given in Fig. 1 by (a', b', c'), where $\mathbf{a} = -\mathbf{a}'$, $\mathbf{b} = -2\mathbf{b}'$, and $\mathbf{c} = \mathbf{c}' - \mathbf{b}'$. It can be seen that the two inverse orientations of the ReO₄ anions alternate in both the b' and c' directions. Accordingly, this

$(0, \frac{1}{2}, \frac{1}{2})'$ anion ordering wave vector in (BEDT-TTF)₂ReO₄ can be viewed as generating a (a', 2b', 2c') superstructure. In the following we shall use the conventional unit cell (a, b, c).

(BEDT-TTF)₂ReO₄ is metallic at room temperature [$\sigma \approx 200$ (Ω cm)⁻¹], and becomes superconducting below about $T_c = 1.5$ K under a pressure of 4 kbar.⁷ However, at ambient pressure this compound undergoes a sharp metal-insulator transition at about 80 K.⁷ In this paper we show that this transition is a structural phase transition consisting of a modulation of the (a, b, c) unit cell described by a wave vector $\mathbf{q} = (\frac{1}{2}, 0, \frac{1}{2})$. We suggest that this transition is very likely associated with a displacive modulation of the BEDT-TTF molecular and ReO₄⁻ anion sublattices.

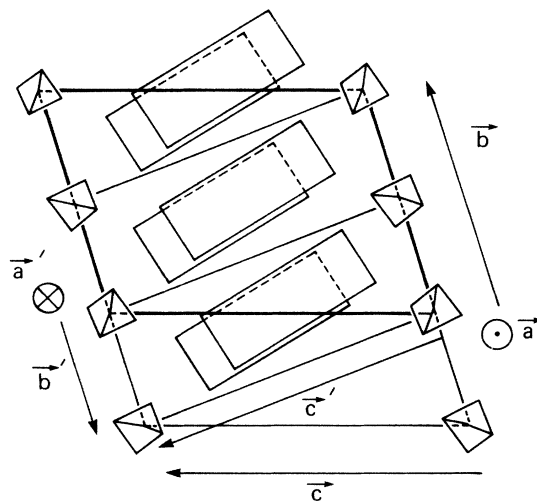


FIG. 1. Schematic view along the a axis of (BEDT-TTF)₂ReO₄. The BEDT-TTF molecules are symbolized by rectangles and the sides of the ReO₄ tetrahedra indicate their orientation. The light lines correspond to the cell axes (b', c') normally used to describe the structure of the related (TMTSF)₂X salts. In this description the ordering of the anions leads to the doubling of both the b' and c' translation periods. The heavy lines correspond to the (b, c) cell axes used in this study.

The $(\text{BEDT-TTF})_2\text{ReO}_4$ crystals (typical size $1 \times 0.25 \times 0.125 \text{ mm}^3$) used in this study were electrochemically synthesized according to Ref. 7. A preliminary photographic study showed new reflections appearing below about 80 K whose wave-vector component along a^* was $\frac{1}{2}$. However, primarily because of the large value of the b and c parameters, the monochromatic Laue photographs did not allow an accurate determination of the b^* and c^* components. Consequently, one crystal was selected for a diffractometer study. It was attached to the cold tail of a Displex-cryocooler installed on a Huber goniometer using the normal-beam lifting-detector geometry. The crystal was rotated around the chain axis a . The $\text{Cu } K\alpha$ x-ray beam was point focused by reflection from a doubly bent pyrolytic graphite monochromator.

At room temperature the cell parameters were found to be $a = 7.79 \text{ \AA}$, $b = 12.57 \text{ \AA}$, $c = 17.13 \text{ \AA}$, $\alpha = 72.95^\circ$, $\beta = 80.08^\circ$, $\gamma = 88.92^\circ$, $V = 1580 \text{ \AA}^3$,³ in satisfactory agreement with previous reports.^{7,8} At 12 K they were $a = 7.55 \text{ \AA}$, $b = 12.54 \text{ \AA}$, $c = 16.91 \text{ \AA}$, $\alpha = 73.23^\circ$, $\beta = 81.43^\circ$, $\gamma = 89.12^\circ$, $V = 1515 \text{ \AA}^3$. Note the very important thermal contraction along the a axis which may significantly increase the overlap integrals between neighboring BEDT-TTF molecules.

Supplementary low-temperature reflections with reduced wave vectors $(\frac{1}{2}, 0, \frac{1}{2})$ were readily detected, thus confirm-

ing the photographic results. Several of these reflections were examined as a function of temperature with the diffractometer. Figure 2 presents scans of the $(\overline{0.5}, 1, 0.5)$ reflection along the three reciprocal axes at $T = 76 \text{ K}$, showing that the wave vector of the modulation is commensurate, and that long-range order is established—the width of the satellite reflection being identical to that of the main Bragg reflections. Typical values of the half-width at half maximum are $\Delta Q_a^* = 0.014 \text{ \AA}^{-1}$, $\Delta Q_b^* = 0.004 \text{ \AA}^{-1}$, $\Delta Q_c^* = 0.002 \text{ \AA}^{-1}$ for the superstructure reflection shown in Fig. 2. The temperature dependence of the peak intensity of the $(\overline{1.5}, 3, 1.5)$ reflection is plotted in Fig. 3(a). The superstructure reflections appear very abruptly near 77 K (T_c) and their intensity almost levels off at about 76 K with only a weak increase on further cooling. This behavior is a clear signature of a strong first-order transition, for which the order parameter (proportional to the square root of the peak intensity) has at T_c nearly its value at saturation (deduced from the measurements at 12 K). Furthermore, cycling the sample temperature through the transition reveals an hysteresis of width $\sim 0.2 \text{ K}$ [Fig. 3(b)]. This first-order character is in agreement with conductivity measurements,⁷⁻⁹ which showed a discontinuous increase of the resistance by two orders of magnitude upon cooling through the transition. No sizable structural fluctuations have been detected above T_c , also in agreement with the strong first-order char-

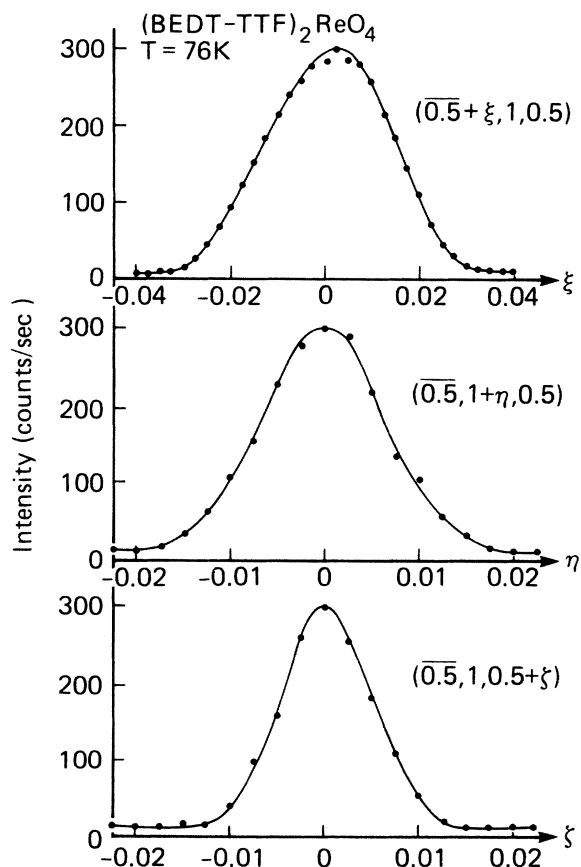


FIG. 2. Scans of the $(\overline{0.5}, 1, 0.5)$ reflection along a^* , b^* , and c^* just below T_c ($T = 76 \text{ K}$). The reduced wave vector of the superlattice reflections is therefore $(\frac{1}{2}, 0, \frac{1}{2})$.

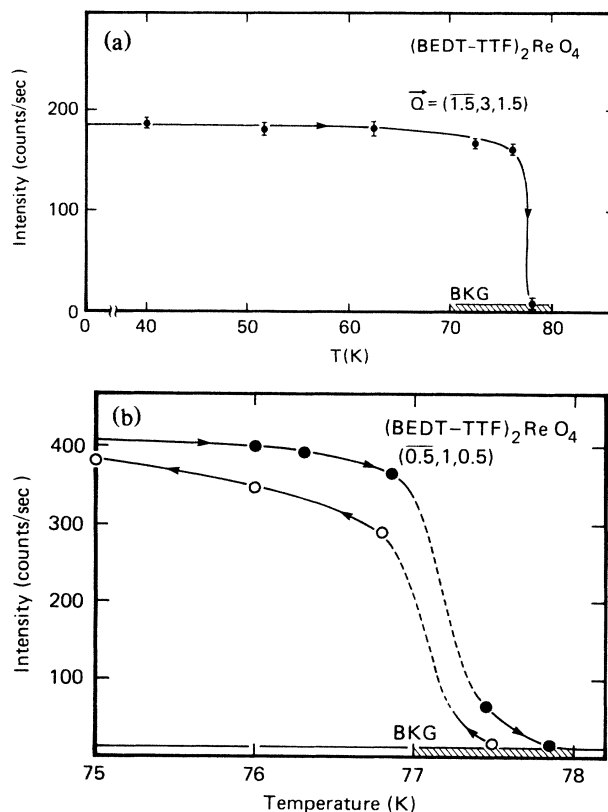


FIG. 3. (a) Temperature dependence of the $(\overline{1.5}, 3, 1.5)$ superlattice reflection peak intensity below 80 K showing the abrupt increase of intensity at $\sim 77 \text{ K}$. (b) Detailed peak intensity behavior of the $(\overline{0.5}, 1, 0.5)$ reflection around T_c under heating and cooling conditions showing an hysteresis of width $\sim 0.2 \text{ K}$. The lines are guides for the eyes.

acter of the transition.

We now discuss the structural nature of this transition. Since the ReO_4^- anions are already ordered at room temperature, one cannot attribute the transition to an anion ordering effect unless one allows that the type of ordering might change at T_c . However, this hypothesis can be ruled out for the following reasons. First, it is important to note that the intensity of the superstructure reflections is on the average between two and three orders of magnitude weaker than that of the main ones. This has to be compared to the case of anion ordering transitions in the $(\text{TMTSF})_2\text{X}$ series, such as in $(\text{TMTSF})_2\text{ReO}_4$ at the 177-K metal-insulator transition, where the intensity is only about one order of magnitude weaker.¹⁰ Second, the main reflections with odd k , which are directly related to the anion ordering present at room temperature in $(\text{BEDT-TTF})_2\text{ReO}_4$, would be strongly influenced by a change of order at T_c , but one does not observe any anomaly in the intensity, as can be seen in Fig. 4 for the $(\bar{1}, 3, 4)$ reflection.

The above data strongly suggest that $(\text{BEDT-TTF})_2\text{ReO}_4$ undergoes a displacive phase transition at 77 K. Such a hypothesis is supported by the occurrence of relatively strong reflections at fairly large wave vectors. There is also some indication of a significant component of the distortion along the three a, b, c directions, although again it must be emphasized that the amplitude of the displacements involved has to be small, given the overall weakness of the $(\frac{1}{2}, 0, \frac{1}{2})$ reflections. Both ReO_4^- and BEDT-TTF displacements can contribute to the superlattice reflection intensities, but without detailed structural refinements these two contributions cannot be separated. The formation of a large conductivity gap ($2\Delta \approx 1000$ K) below T_c (Ref. 7) suggests a sizeable distortion of the organic stack. In this regard that the a^* component of the superstructure reflection wave vector $(\frac{1}{2})$ corresponds to twice the Fermi wave vector $2\mathbf{k}_F = \frac{1}{2}\mathbf{a}^*$, within a quasi-1D description of the electron gas, so that the modulation of the organic stacks with this wave vector strongly perturbs the Fermi surface via the electron-phonon coupling. It is thus tempting to suggest that the $2k_F$ divergence of the charge-density wave (CDW) response function of the electron gas may drive this transition and open an electric gap resulting in the low-temperature insulating state. However, studies of the quasi-1D conductors of the TTF-TCNQ family have shown that the CDW instability usually leads to a second-order Peierls transition, announced above T_c by strong 1D structural fluctuations. The observation of a strong first-order phase transition in $(\text{BEDT-TTF})_2\text{ReO}_4$, which bears some

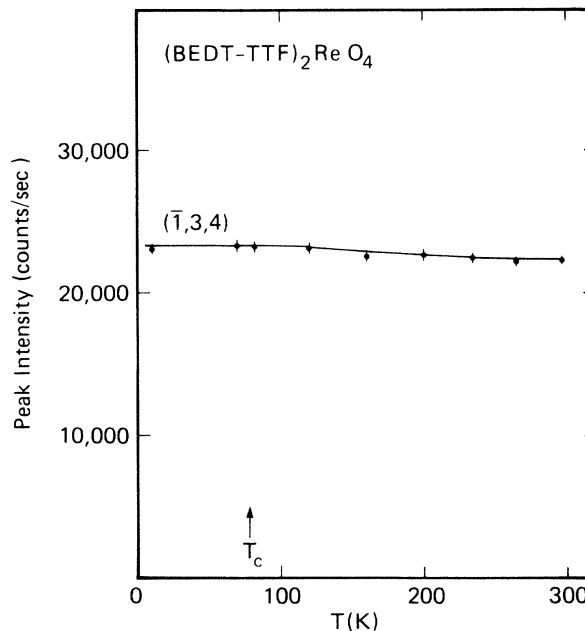


FIG. 4. Temperature dependence of the peak intensity of the $(\bar{1}, 3, 4)$ main reflection between 300 and 12 K. The absence of any significant anomaly at T_c in the intensity of this reflection rules out a change of the anion ordering.

similarities to that of VO_2 ,¹¹ suggests that additional features as, for example, the presence of a more complex Fermi surface (several contours, deviations from one dimensionality, etc.), together with electron-electron and electron-anion interactions, have to be incorporated in order to understand the first-order character of the low-temperature electronic and structural transition in this compound.

Finally, it is interesting to remark that the superconducting ground states of $(\text{BEDT-TTF})_2\text{ReO}_4$, $(\text{TMTSeF})_2\text{PF}_6$, and $(\text{TMTSF})_2\text{ReO}_4$ each compete under pressure with an insulating ground state, but that in each case the nature of the insulating ground state is different: namely, ground states stabilized by a displacive structural modulation, spin-density wave and anion ordering instabilities, respectively.¹

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