Anion-Ordering Phase Diagram of Di(tetramethyltetraselenafulvalenium) Perrhenate, $(TMTSF)_2ReO_4$

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We report high-pressure, low-temperature x-ray scattering measurements on the organic conductor $(TMTSF)_2ReO_4$. The anion-ordering phase diagram has been established up to 17 kbar. In addition to the low-pressure phase characterized by the wave vector $q=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, we have discovered a new high-pressure phase with an unexpected wave vector $q=(0,\frac{1}{2},\frac{1}{2})$. Coexistence of these two types of ordering has been observed in an intermediate pressure range.

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The interest in the $(TMTSF)_2X$ organic superconductors (TMTSF is tetramethyltetraselenafulvalene and X is one of various anions) resides for a large part in the unusual interplay of electronic, magnetic, and structural phenomena.[1] Structural properties are dominated by order-disorder transitions which involve the anion orientation in $(TMTSF)_2X$ salts containing noncentrosymmetric anions and which govern the nature of the low-temperature ground states. Orientational ordering of these anions originates from symmetry considerations. At room temperature the anions are found to be at inversion centers in the triclinic $P\bar{1}$ space group. This symmetry is actually an average one due to a random distribution of two inverse orientations. Upon cooling, anion-ordering (AO) transitions occur, leading to superstructures with either identical or alternate orientations of the anions along the three crystallographic axes. These superstructures are commonly characterized by the wave vector q of the new reflections which appear below T_{AO}.[2]

The AO transitions can induce contrasting low-temperature behaviors as in the case of the tetrahedral anions ClO_4^- and ReO_4^-. In $(TMTSF)_2ClO_4$, AO with $q_1=(0,\frac{1}{2},0)$ is obtained by slow cooling through the transition[3] ($T_{AO}\simeq 24$ K), leading to a superconducting state below 1.2 K,[4] while fast cooling quenches the anion disorder and a spin-density wave state is stabilized below 6 K.[5] In $(TMTSF)_2ReO_4$ the AO transition at $T_{AO}\sim 180$ K with $q_2=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$[6] leads to an insulating state[7] (in a 1D band model of the conducting organic stacks the band is half filled; therefore $2k_F=1/2a^*$, where k_F is the Fermi wave vector). However, the insulating state is suppressed under pressure above 12 kbar and superconductivity is recovered below 1.3 K.[8] In an intermediate pressure range 9–12 kbar) a complex situation is found with different low-temperature states depending on both thermal treatment and pressure.[9] This overall behavior seems to be typical of salts that present q_2-type AO transitions at atmospheric pressure like $(TMTSF)_2FSO_3$.[10]

In this Letter we report the first high-pressure, low-temperature x-ray study of an organic superconductor, $(TMTSF)_2ReO_4$. We establish the (P,T) AO phase diagram of this salt up to 17 kbar and discover a new phase, stable above 12 kbar, with an unexpected wave vector $q_3=(0,\frac{1}{2},\frac{1}{2})$.

The x-ray data were taken by use of a gasketed diamond-anvil pressure cell of the Merrill-Bassett type (as modified by Hazen and Finger[11]). The tiny crystal ($\sim 0.2\times 0.15\times 0.03$ mm^3) was cut from a needle taken from a batch grown by electrocrystallization and used independently for transport measurements. It was mounted in a 0.3-mm-diam hole in an Inconel gasket with ethanol as a pressure medium and oriented by eye so that the a axis was approximately normal to the diamond faces. The high-pressure cell was attached to the cold stage of a closed-cycle He refrigerator (minimum temperature ~ 10 K) installed on a normal beam-lifting-detector type diffractometer. The Mo $K\alpha$ x rays from a Rigaku 12-kW generator were focused by a vertically bent graphite monochromator and collimated to a cross section on the order of the gasket hole. *In situ* pressure determination by use of the measured cell parameters of NaCl powder added to the sample failed for technical reasons. The pressure was therefore estimated from measurement of the unit-cell dimensions of the $(TMTSF)_2ReO_4$ crystal by comparison with the available pressure data on $(TMTSF)_2PF_6$,[12] on the assumption of similar equations of state for the two salts. With this procedure we estimate an accuracy of ±0.5 kbar. The triclinic crys-

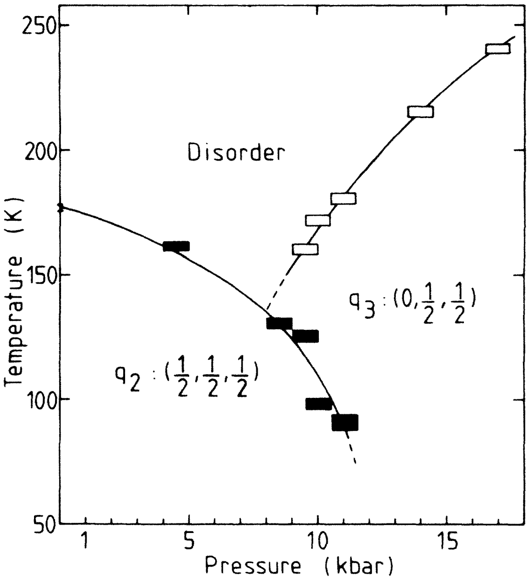

FIG. 1. Temperature-pressure anion-ordering phase diagram of $(TMTSF)_2ReO_4$. Note that the q_2 and q_3 phase boundaries overlap at $P = 9.5$, 10, and 11 (± 0.5) kbar and that they have opposite slopes.

tal was found to be twinned with a major component (more than 90% of the volume) which was used for the study.

The construction of the temperature-pressure phase diagram was achieved by the study of the characteristic superstructure reflections for different temperature cycles at several pressure values. The first problem at stake was the nature of the AO in the high-pressure conducting phase (above 12 kbar). We verified the absence of the $q_2 = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ type reflections which are present in the low-pressure insulating phase and we searched for supplementary reflections at low temperature with reduced wave vectors of the form $q = (0,n/2,m/2)$ ($n,m = 0$ or 1). Actually, rather strong expectations were in favor of the $q_1 = (0,\frac{1}{2},0)$ type of AO because its stabilization conditions the superconducting state in $(TMTSF)_2ClO_4$. However, no such reflections were observed while a set of reflections with $q_3 = (0,\frac{1}{2},\frac{1}{2})$ were detected. The phase boundaries of this high-pressure phase and of the low-pressure one were derived from the intensity versus temperature dependence of selected q_3- and q_2-type reflections, respectively, thus resulting in the phase diagram of Fig. 1.

In the low-pressure region ($P \lesssim 9$ kbar), results at 4.5 and 8.5 kbar together with the known atmospheric-pressure AO temperature ($T_{AO} \sim 180$ K) show that T_{AO} decreases with pressure. The phase boundary is in good agreement with that obtained for the metal-insulator transition.[8] However, no significant hysteresis is observed, contrary to previous resistivity data,[8] and Fig. 2 shows a reversible intensity-versus-temperature behavior for a typical reflection for slow cooling and heating rates (0.5 deg/min).

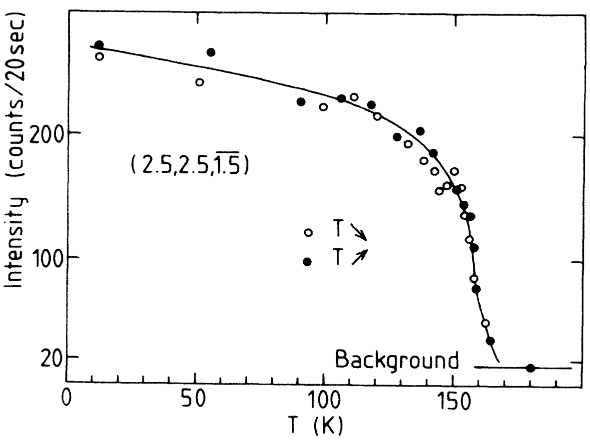

FIG. 2. Temperature dependence of the peak intensity of a q_2-type reflection at $P \sim 4.5$ kbar. Under slow cooling and heating rates (0.5 K/min) the transition shows no hysteresis.

The boundary of the q_3 phase presents, in contrast, a positive dT_c/dP slope (~ 10 K/kbar), reaching 240 K at 17 kbar. We note that there was no evidence for this phase boundary in transport properties,[8,13] while some puzzling conductivity anomalies had been observed at much lower temperatures.[13,14] The transition appears to be continuous, as seen from Fig. 3 (we recall that the peak intensity is proportional to the

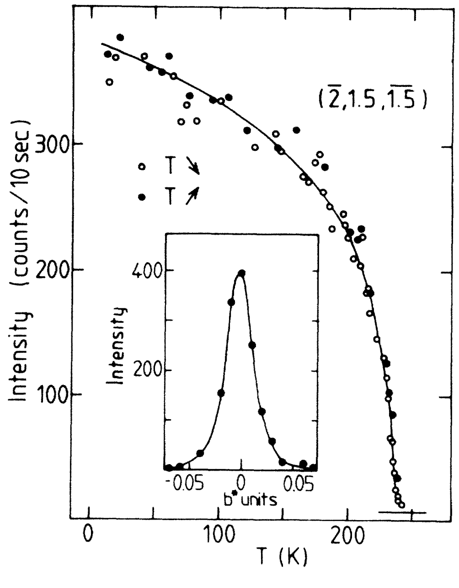

FIG. 3. Temperature dependence of the peak intensity of a q_3-type reflection at $P \sim 17$ kbar. Its profile (inset) is sharp and limited by experimental resolution.

square of the order parameter). Note also that the width of the q_3-type reflection is the same as that of the basic reflections indicating long-range order (Fig. 3, inset). Furthermore, the intensity of these reflections is, on the average, of the same order of magnitude as that of the q_2-type reflections, which supports our assignment of the q_3 superstructure to AO, although no structure refinement has been made.

Of particular interest is the intermediate-pressure range where the two phase boundaries overlap. Measurements have been made at three different pressures, 9.5, 10, and 11 (± 0.5) kbar in this region. Similar behaviors are found at 10 and 11 kbar, and Fig. 4(a) shows the results at $P = 10$ kbar. As the temperature decreases, the q_3-type reflection appears first at $T \sim 172$ K and grows in intensity; then the q_2-type reflection appears below $T \sim 98$ K but its intensity saturates at a low value of 2.7 counts/sec below about 85 K. This indicates that the corresponding q_2 order parameter does not develop completely. Note that the q_2 transition produces a dip in the intensity of the q_3-type reflection. The origin of these effects will be better understood after we look at the results obtained at $P = 9.5$ kbar for the same reflections [Fig. 4(b)]. In this case the intensity of the q_2-type reflection appears at $T \sim 130$ K and reaches a much higher low-temperature value than at 10 kbar (about 11 counts/sec). Correspondingly the intensity of the q_3-type reflection, after reaching a maximum at $T \sim 130$ K, starts decreasing and it eventually vanishes below 75 K. This apparent "exchange" of intensity between the two types of reflections is the signature of a transformation of the AO from q_3 into q_2 as the temperature is lowered. We also note that the effects of Fig. 4(b) are fully reversible in temperature and that profiles of the q_2- and q_3-type reflections measured at $T = 112$ K are sharp and resolution limited. The transition between the q_2 and q_3 AO should be first order because there is no group-subgroup relation between the two superstructures. Therefore we suggest that the coexistence region corresponds to a mixture of q_2- and q_3-type domains and that the AO switches between the two types as the temperature is varied, in a reversible process.

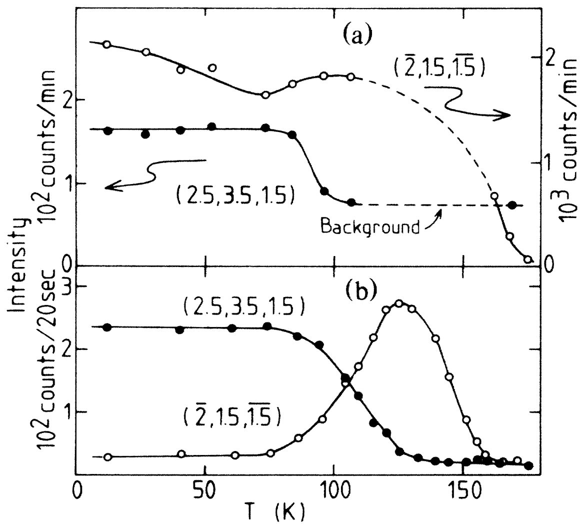

FIG. 4. Temperature dependence of the peak intensities of two typical q_2 (2.5,3.5,1.5) and q_3 ($\bar{2}$, 1.5, $\overline{1.5}$) reflections in the intermediate-pressure range. At 10 kbar, (a), the q_3-type reflection shows a weak anomaly corresponding to the incomplete q_2 AO below $T \sim 95$ K but at 9.5 kbar, (b), the q_3-type reflection disappears below $T \sim 75$ K while reordering with q_2 appears to be almost complete. Note the region of coexistence (~ 75–125 K) of the two AO's at $P = 9.5$ kbar.

The results of Fig. 4(a) ($P = 10$ kbar) can now be interpreted in terms of a partial transformation of the q_3 AO into q_2 AO as the temperature is reduced, as evidenced by the incomplete development of the q_2 order parameter. This phenomenon is also responsible for the small loss of intensity of the q_3-type reflection at $T \sim 80$ K, which is reminiscent of the corresponding disappearance observed at $P = 9.5$ kbar. The origin of this incomplete q_2 AO can be attributed to a freezing of the anion orientation below about $T_f = 85$ K, thus preventing a full reorientation from q_3 to q_2 AO. Such an effect with a freezing temperature $T_f \sim 60$ K at 12 kbar was suggested previously by Tomic, Jerome, and Bechgaard[9] from the analysis of resistivity data. Our results confirm this effect, although it is observed at higher temperatures, all the more so since T_f should increase with pressure. On the other hand, at $P = 9.5$ kbar the $q_3 \rightarrow q_2$ transition takes place at a temperature high enough for the q_2 AO to be completed just above T_f.

The most intriguing result of this study is the q_3 AO observed in the high-pressure region, as it raises questions about the relation between AO and superconductivity. First it is obvious that the potential associated with the q_3 AO does not open a $2k_F$ gap at the Fermi level since the a^* component of q_3 is 0 and not $\frac{1}{2}$. This property also holds for the q_1 AO in $(TMTSF)_2ClO_4$. However, if one considers the coupling between the anions and the conducting organic stacks, then the influence of the q_1 and q_3 AO's can be distinguished, as first suggested by Emery.[15] In the case of the q_1 AO the inversion centers which relate the TMTSF molecules along the chains are preserved. Thus the molecules experience the same potential and the $4k_F$ dimerization gap as well as the closely related electron-electron umklapp-scattering coupling constant g_3 should not vary.[16] On the other hand, the q_3 AO removes the inversion centers on the stacks and the molecules see different potentials. The $4k_F$ dimerization gap and the g_3 coupling should be enhanced. In this case a spin-density-wave rather than superconducting ground state has been predicted to be favored.[15] (TMTTF)$_2$SCN[17] follows this model with a q_3 AO transition at 160 K corresponding to a $4k_F$ localization and a magnetic state below 7 K.[18] In contrast, the present results show that in the high-pressure phase of (TMTSF)$_2$ReO$_4$ the same q_3 AO keeps the metallic state and leads to superconductivity. This may indicate that the g_3 coupling is not pertinent in the TMTSF series. The nature and the strength of the electron-anion interaction is also an important parameter which is still poorly assessed. Information on this coupling may be gained by the determination of possible structural distortions associated with the AO. A preliminary analysis of the superstructure reflection intensities in (TMTSF)$_2$ReO$_4$ at 17 kbar indicates that such distortions probably occur with significant displacements along the stacking axis *a*.

The knowledge of the AO phase diagram allows us to understand more clearly the anomalous resistivity behavior of (TMTSF)$_2$ReO$_4$ in the intermediate-pressure region.[8,9,13] Cooling-rate effects are particularly dramatic in the low-pressure part of this region (just above 9 kbar) leading to either an insulating or a superconducting low-temperature state. Although our results were obtained with slow cooling or heating rates (~ 0.5 K/min), the partial q_3-q_2 AO transformation observed at 10 and 11 kbar and the peculiar broad coexistence region at 9.5 kbar strongly support a high sensitivity of the AO to the thermal treatment. It is therefore very likely that the $q_3 \rightarrow q_2$ AO transition, which appears to be complete at $P = 9.5$ kbar under slow cooling, can be quenched by fast cooling, thus preserving a conducting behavior at low temperature.

Finally we mention that recent magnetoresistance measurements at about 11 kbar have shown Shubnikov–de Haas oscillations which indicate the existence of a magnetic-field–induced transition.[19] This should be analyzed in the light of the mixed q_2 and q_3 AO state that we have observed below 90 K under the same pressure.

In conclusion, the present study provides the first direct experimental evidence of a pressure-induced change of the orientational anion ordering in the (TMTSF)$_2X$ series. Moreover, the construction of the phase diagram up to $P = 17$ kbar reveals a competition between the q_2 $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ order and the q_3 $(0,\frac{1}{2},\frac{1}{2})$ unexpected one with a coexistence of both orders in an intermediate pressure region. Theoretical models should be extended to account for these results.

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