

A hidden low-temperature phase in the organic conductor $(\text{TMTSF})_2\text{ReO}_4$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 4451

(<http://iopscience.iop.org/0953-8984/1/27/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:26

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

A hidden low-temperature phase in the organic conductor $(\text{TMTSF})_2\text{ReO}_4$

S Tomić† and D Jérôme

Laboratoire de Physique des Solides, Université de Paris-Sud, 91405 Orsay, France

Received 10 April 1989

Abstract. We prove, using an appropriate pressure–temperature cycling, that it is possible to maintain the non-centrosymmetric anion ReO_4 in an ordered configuration that does not give rise to an induced insulating phase at low temperatures. If such a cooling procedure is followed, the low-temperature phase diagram of $(\text{TMTSF})_2\text{ReO}_4$ is very reminiscent of the diagram observed with centrosymmetric anions such as PF_6^- , AsF_6^- and so on. The semi-conducting phase, which is stabilised below 15 K at ambient pressure, is suppressed above 8 kbar and gives rise to a superconducting ground state. The re-entrance of the superconducting phase is observed close to the critical pressure. We identify the low-temperature state as a spin-density-wave phase and discuss the phase diagram of $(\text{TMTSF})_2\text{ReO}_4$ in the framework of a unique model for $(\text{TMTSF})_2\text{X}$ organic conductors.

The broad interest in the $(\text{TMTSF})_2\text{X}$ organic conductors is certainly due to a large variety of electronic, magnetic and structural phenomena (see, for example [1]). Basically, they are single-chain materials in which a nominally quarter-filled band is created by a charge delocalisation on the organic chain. However, the three-dimensional environment of a stack makes the band half-filled. The spatial anisotropy of the overlapping molecular orbitals leads to an open Fermi surface and to a strong anisotropy in the electronic properties. At low temperatures, the ground states can be either insulating, metallic or superconducting (SC). The origin of the insulating ground state appears to be closely related to the choice of anion X. In the case of centrosymmetric anions such as PF_6^- , AsF_6^- and SbF_6^- , the insulating ground state is due to the formation of a spin-density-wave (SDW) phase ($T_c \approx 12$ K), while in the compounds with non-centrosymmetric tetrahedral anions, such as ReO_4 , FSO_3 and BF_4 , the metal-to-insulator transition is driven by an ordering of the anions according to the wavevector $q_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($40 \text{ K} \leq T_c \leq 180 \text{ K}$). A finite external pressure suppresses the insulating phase and leads to a metallic behaviour in the whole temperature region and eventually to a SC ground state if there is no disorder left in the structure. Moreover, at approximately the same critical pressure, a new anion-ordered superstructure (AO) is induced with a different wavevector: $q_3 = (0, \frac{1}{2}, \frac{1}{2})$ in $(\text{TMTSF})_2\text{ReO}_4$ above 10 kbar [2].

However, the specific role of anions with respect to the ground state is far from being understood. Two examples are indicative of the behaviour outlined above: (i) the Q -states of $(\text{TMTSF})_2\text{ClO}_4$ (where the low-temperature state is antiferromagnetic (AF)) and $(\text{TMTSF})_2\text{NO}_3$, in which in spite of the AO with a wavevector $(\frac{1}{2}, 0, 0)$, the ground state is

† Permanent address: Institute of Physics of the University, 41001 Zagreb, Yugoslavia.

also AF [3, 4] and (ii) there is also some experimental evidence for the existence of the SDW phase at low temperatures close to the critical pressure in the $(\text{TMTSF})_2\text{ReO}_4$ compound—namely, in the narrow pressure region where two anion orders q_2 and q_3 coexist, the low-temperature state is shown to be highly sensitive to thermal treatments [5, 7].

The aim of the present work on $(\text{TMTSF})_2\text{ReO}_4$ is to search for a genuine ground state of the electron gas in the low-pressure region ($p < p_c$, where p_c is the critical pressure required to reach SC). In order to achieve this it was necessary to make the otherwise-strong anion–electron $2k_F$ coupling irrelevant, and thus to prevent the metal-to-insulator phase transitions occurring in the high-temperature region. Therefore we have undertaken a new investigation of the phase diagram of $(\text{TMTSF})_2\text{ReO}_4$ using the helium-gas-pressure technique at up to 10 kbar, following a well chosen pressure–temperature procedure. We have established a pressure–temperature phase diagram that confirms the main qualitative features already found at high temperatures [2, 6, 7]. Moreover, we have discovered a metastable state stabilised at low temperatures at up to 8 kbar, which might be identified as a SDW phase. Also, the pressure dependence of the SDW phase is identical to that found for an AF ground state in $(\text{TMTSF})_2\text{X}$ compounds with centrosymmetric anions. Finally, we argue that the electronic interactions responsible for the stabilisation of the ground state (AF or SC) in the family of $(\text{TMTSF})_2\text{X}$ organic conductors depend essentially on the organic stack and are only very weakly affected by the anion sublattice.

Resistivity measurements were performed using a low-frequency lock-in technique with a measuring current of 10 mA. The resistivity was measured along the high-conductivity a axis using the four-probe arrangement. Electrical contacts were made with silver paint on previously evaporated gold pads. Typical dimensions of the samples used in this study were $3 \times 0.2 \times 0.1 \text{ mm}^3$. In particular, most measurements were performed on one high-quality single crystal and verified as perfectly reproducible on several others. In order to avoid the q_2 AO at high temperatures, we performed our experiment in the following way. First, we increased the pressure up to 10 kbar at room temperature and then we cooled the system down to 72 K. During this procedure the material retains its metallic behaviour. Moreover, the AO with wavevector $q_3 = (0, \frac{1}{2}, \frac{1}{2})$ discovered in the x-ray scattering measurements by Moret [2] is evidenced by a kink in the resistivity below which a more rapid decrease is observed [8]. Then, we released the pressure and at the same time we decreased the temperature so that the sample followed a well defined p – T line L (see figure 1). The position of the line is, in practice, fixed by the melting curve of helium 4 (line H in figure 1).

In order to check the stability of the low-temperature phases, we used two distinct approaches. First, we chose a particular pressure and varied the temperature, and secondly we cycled the pressure keeping the temperature constant. In this way, we have observed the low-temperature p – T phase diagram that is displayed in figure 1. The most important properties are certainly the preservation of the high-pressure metallic phase in the low-pressure–temperature region ($p < 10$ kbar) and a new metastable semi-conducting state that is established at pressures up to 8 kbar. Note that a critical pressure ($p_c \approx 8$ kbar) above which a SC ground state is established is somewhat lower than the one previously reported [6, 7, 9]. In the following paragraphs, we will describe typical T and p cyclings that led to the final presentation of the phase diagram in figure 1.

The initial position is defined by coordinates (p_i, T_i) on the line L previously described. From here on we keep the pressure constant and decrease the temperature.

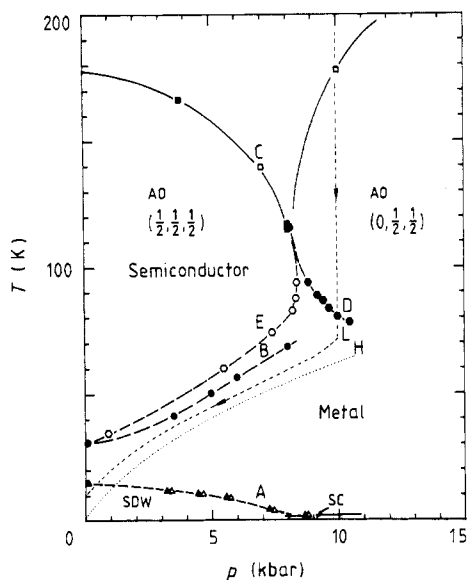


Figure 1. The pressure-temperature phase diagram of $(\text{TMTSF})_3\text{ReO}_4$. Open and full squares: cooling and warming, respectively. After p - T cycling path L: open triangles for cooling; full triangles, circles and squares for warming. Open and full hexagons for decreasing and increasing pressure, respectively.

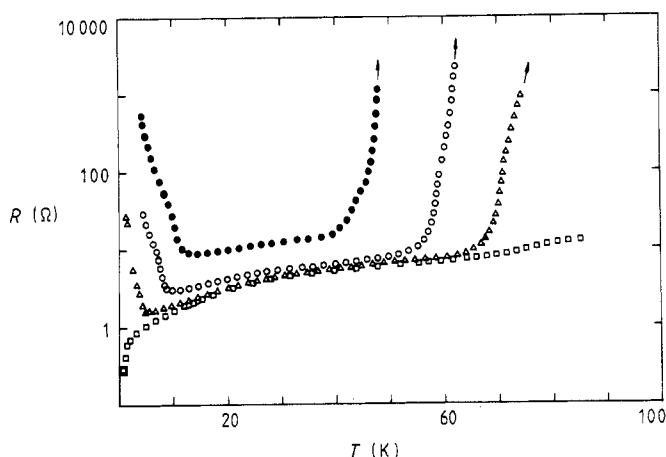


Figure 2. Resistance against temperature after p - T cycling L on warming up to 100 K at four different pressures: full and open circles, triangles and squares for 3.5, 6, 8 and 9 kbar, respectively.

(i) On cooling down, the material retains its metallic behaviour down to the transition line A (open triangles). Below this line, the material enters a semiconducting state.

(ii) On warming, the material leaves the semiconducting state crossing the same line A (closed triangles) and stays metallic up to the transition line B (full circles). Above this line, the material enters the insulating high-temperature region.

The behaviour of the sample at different pressures and on warming is shown in figure 2. If the sample is heated further it becomes metallic again on crossing the line C (full squares). This phase boundary is in good agreement with the one obtained before. The overall temperature behaviour at a pressure of 3.5 kbar is shown in figure 3.

The temperature is fixed below 120 K in the high-temperature insulating phase.

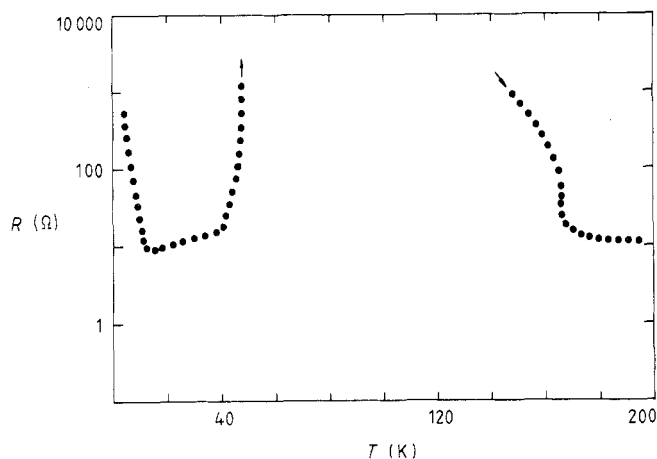


Figure 3. Overall temperature behaviour of resistance at $p = 3.5$ kbar after p - T cycling L on warming.

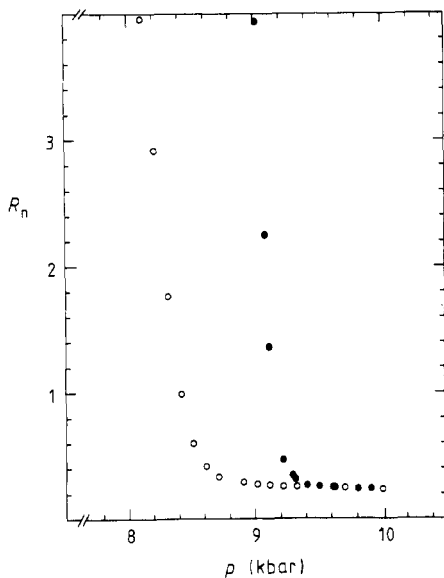


Figure 4. Resistance versus pressure at $T = 87.5$ K. Open and full circles: decreasing and increasing pressure, respectively.

(i) On increasing the pressure the material leaves the insulating phase by crossing the line D (full hexagons).

(ii) On releasing the pressure, the material stays metallic until the line E (open hexagons) is crossed, where it enters the insulating phase. The behaviour of the sample at $T = 87.5$ K is displayed in figure 4.

It is worth noting the existence of a strong hysteretic behaviour when the material is cycled between the insulating and metallic phase at low temperatures (lines D and E, B and E). The line D indicates the limit of the $q_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ AO stabilised on cooling at low pressures. The lines B and E define the limit of the metastability of the $q_3 = (0, \frac{1}{2}, \frac{1}{2})$ AO stabilised by a pressure-temperature cycling. The conversion of one anion order into

another, as well as disorder–order transition lines, can be phenomenologically described in terms of a Landau expansion of the free energy. An appropriate choice for the pressure and temperature dependence of the second- and fourth-order terms of the expansion should be similar to what has been already proposed for the phase diagram of β -(BEDT-TTF)₂I₃ that reveals the existence of a tricritical point [10] and that may be understood by a simple mean-field model [11]. It is also worth noting that the partial transformation of the q_3 AO into q_2 AO previously observed in the x-ray scattering and resistivity measurements attributed to a freezing of the anion orientation coincide rather well with the conversion lines B and E defined in our experiment [2, 5, 7].

Taking into account our new results we can summarise the pressure–temperature phase diagram of (TMTSF)₂ReO₄ as follows. The metal-to-insulator phase transition due to q_2 AO that exists at ambient pressure is suppressed to pressures below 8 kbar in favour of a metallic phase in which anions are ordered with a wavevector q_3 . The respective ground states are a non-magnetic anion-driven insulator and a superconductor. However, if the q_3 AO is maintained at pressures lower than 8 kbar, so that the density of states at the Fermi level is preserved, a new semiconducting phase is stabilised as the ground state. The pressure dependence of the transition temperature strongly resembles that of the SDW ground state found in (TMTSF)₂X compounds with centrosymmetric anions and also that of (TMTSF)₂NO₃ [12, 13]. Furthermore, the border line with the SC ground state occurs at about the same critical pressure. Moreover, in the narrow pressure region around the critical pressure ($p = 8 \pm 0.25$ kbar), the re-entrance of the SC phase is observed similarly to that found for (TMTSF)₂AsF₆. Therefore, it rather appears justified to identify the low-temperature semiconducting state in (TMTSF)₂ReO₄ with an antiferromagnetic phase, although no direct proof has yet been given with magnetic experiments. Since similar low-temperature (AF–SC) phase diagrams are found for the centrosymmetric anions PF₆, AsF₆ [12, 13] and q_3 AO states in (TMTSF)₂ReO₄, the anion-ordering phenomenon has probably a much weaker impact on the physics of the organic stacks than what was believed from a theoretical viewpoint [13] (except for the anion ordering giving rise to a $2k_F$ potential along the stacking axis with the concomitant opening of a gap at the Fermi level). We may recall that the q_3 AO that removes the inversion centre between molecules in the same stack and the g_3 coupling should be enhanced [13, 14, 15]. Also, as we already mentioned, the anion disorder (the Q -state of (TMTSF)₂ClO₄) and the AO of type $(\frac{1}{2}, 0, 0)$ ((TMTSF)₂NO₃) do not prevent the stabilisation of the SDW phase. Nevertheless, a necessary condition for SC (stressed in our earlier work) requires long-range uniformity of the potential created by anions along conducting chains [5].

In conclusion, a unique theoretical model may be used to explain the electronic structure and the stabilisation of a particular ground state (AF or SC) in the organic conductors (TMTSF)₂X at low temperatures. The theory proposed by Bourbonnais and co-workers [16] seems to be quite appropriate at the moment. In this picture the inter-chain AF exchange mechanism might be responsible for the stabilisation of the SDW phase at low pressures. Moreover, this coupling generates inter-chain pairing fluctuations over a wide range of temperatures in the one-dimensional region. The applied pressure should suppress the nesting conditions of the Fermi surface with the concomitant frustration of the SDW state, leading therefore to superconducting long-range order in the system.

We wish to acknowledge the skilful technical assistance of J C Ameline. We thank K Bechgaard, C Lenoir and P Batail for providing us with good quality single crystals. One of us (ST) would like to acknowledge CNRS for financial support during a stay at Orsay.

References

- [1] Jérôme D and Caron L D (ed.) 1987 *Low-Dimensional Conductors and Superconductors*, NATO ASI Series B (New York: Plenum)
- [2] Moret R, Ravy S, Pouget J P, Comes R and Bechgaard K 1986 *Phys. Rev. Lett.* **57** 1915
- [3] Walsh W M, Wudl F, Aharon-Shalom E, Rupp L W, Vandenberg J M, Andres K and Torrance J B 1982 *Phys. Rev. Lett.* **49** 885
- [4] Tomic S, Jérôme D, Cooper J R and Bechgaard K 1988 *Synth. Met.* **27** B645
- [5] Tomic S, Jérôme D and Bechgaard K 1984 *J. Phys. C: Solid State Phys.* **17** L11
- [6] Parkin S S P, Jérôme D and Bechgaard K 1981 *Mol. Cryst. Liq. Cryst.* **79** 21
- [7] Tomic S, Jérôme D and Bechgaard K 1987 *Low-Dimensional Conductors and Superconductors*, NATO ASI Series B ed. D Jérôme and L G Caron (New York: Plenum)
- [8] Brossard L, Tomic S, Mailly D, Jérôme D, Ribault M and Bechgaard K 1986 *Physica B* **143** 409
- [9] Tomic S, Jérôme D and Bechgaard K 1985 *Mol. Cryst. Liq. Cryst.* **119** 241
- [10] Kang W, Creuzet G, Jérôme D and Lenoir C 1987 *J. Physique* **48** 1035
- [11] Ravy S, Moret R and Pouget J P 1988 *Phys. Rev. B* **38** 4469
- [12] Brussetti R, Ribault M, Jérôme D and Bechgaard K 1982 *J. Physique* **43** 801
- [13] Emery V J 1983 *J. Physique Coll.* **44** C3 977
- [14] Barisic S and Brazovskii S 1981 *Recent Developments in Condensed Matter Physics* vol 1, ed. J P Devreese (New York: Plenum) p 327
- [15] Emery V J, Bruinsma R and Barisic S 1982 *Phys. Rev. Lett.* **48** 1039
- [16] Bourbonnais C 1987 *Low-Dimensional Conductors and Superconductors*, NATO ASI Series B ed. D Jérôme and L G Caron (New York: Plenum)