

Superconductivity in a BEDT-TTF organic conductor with a chloromercurate anion

R. N. Lyubovskaya, R. B. Lyubovskii, R. P. Shibaeva, M. Z. Aldoshina, L. M. Gol'denberg, L. P. Rozenberg, M. L. Khidekel', and Yu. F. Shul'pyakov
Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

(Submitted 3 October 1985)

Pis'ma Zh. Eksp. Teor. Fiz. **42**, No. 9, 380–383 (10 November 1985)

A new organic superconductor has been synthesized: $(\text{BEDT-TTF})_4\text{Hg}_3\text{Cl}_8$ [BEDT-TTF bis(ethylenedithiolo)tetrathiafulvalene]. This material goes superconducting at $T_c = 1.8$ K at a pressure of 12 kbar. An x-ray structural analysis has been carried out. This conductor exhibits a resistance anisotropy which is exceedingly pronounced for an organic conductor. A phase transition occurs near 40 K.

Two classes of organic superconductors have been identified. The basic component of the first class is the molecule¹ TMTSeF, while that of the second class is² the molecule BEDT-TTF. The BEDT-TTF salts are of particular interest for studies, since this group includes the superconductors with the highest transition temperatures³ T_c . Superconducting salts of BEDT-TTF have been produced with three anions: I_3^- (a set of phases arises, with superconducting transition temperatures ranging from 1.5 to 7.5 K at atmospheric pressure),⁴ IBr_2^- (Ref. 5), and ReO_4^- (Ref. 6; this material goes superconducting at pressures above 6 kbar). In the present letter we report results on the structure and properties of a new BEDT-TTF superconductor, with a chloromercurate anion. The data from an x-ray structural analysis, an elemental analysis, and an analysis by a local-microprobe method reveal the composition of the ion radical salt to be $(\text{BEDT-TTF})_4(\text{Hg}_2\text{Cl}_6)\text{HgCl}_2$.

The crystals of the $(\text{BEDT-TTF})_4(\text{Hg}_3\text{Cl}_8)$ salt are synthesized by an electrochemical technique as diamond-shaped crystals with dimensions of $1.5 \times 1.0 \times 0.05$ mm and in the form of elongated plates with dimensions of $2.0 \times 0.2 \times 0.05$ mm. The x-ray structural studies show that there are two incommensurate sublattices in these crystals, with subperiods $a' \sim 11$ Å and $a'' \sim 12$ Å. The layer lines corresponding to the subperiod a' consist of clearly defined Bragg reflections and are attributed to the BEDT-TTF cation sublattice; the layer lines corresponding to the subperiod a'' are diffuse, with Bragg reflections. The basic crystallographic data on the cation sublattice are $a = 11.062(3)$, $b = 8.754(2)$, $c = 35.92(14)$ Å, $\beta = 91.01(3)^\circ$, and $V = 3478$ Å³. The space group is $I2/c$, $Z = 2$. The anion sublattice is apparently of symmetry $I2$. The structure was deciphered through an analysis of Patterson functions and refined to $R = 0.11$ by the method of least squares. Figure 1 shows a projection of the structure along the a direction. A characteristic feature is the presence of BEDT-TTF cation-radical layers, oriented parallel to the ab plane. The layer is made up of parallel BEDT-TTF pairs with a pronounced overlap within a pair and with a rather short distance between adjacent BEDT-TTF planes: 3.59 Å. Furthermore, there is a shortened S...S contact in a pair: 3.49 Å. Each cation radical also has four shortened (3.40, 3.51, 3.60, and 3.67 Å) S...S contacts on both "sulfur" sides with neighboring BEDT-

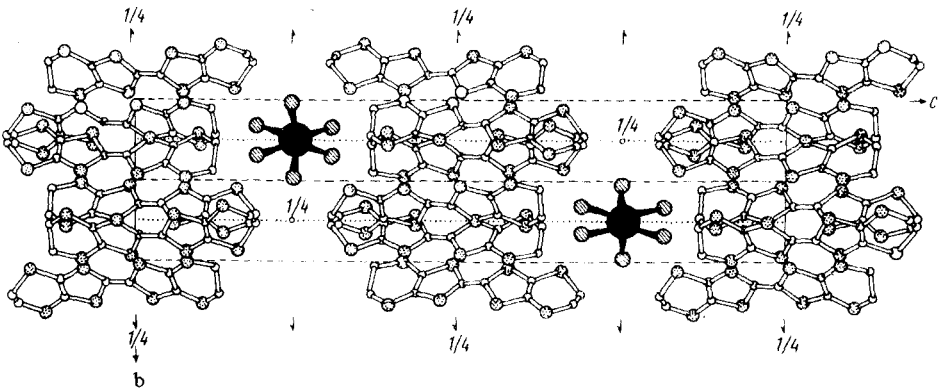


FIG. 1. Projection of the structure along the a direction.

TTF, bound to them by a grazing-reflection plane. The dihedral angle between the median planes of these molecules is $\sim 84^\circ$. Chains of mercury chloromercurate anions lie in channels parallel to the a axis between the cation-radical layers.

The conductivity of the single crystal is measured by a dc four-contact method. These crystals are quite brittle, and each time the temperature is lowered we observe discontinuities in the resistance if the single crystal is cemented to annealed platinum wires $10\ \mu\text{m}$ in diameter. These discontinuities in the resistance can be avoided entirely by assembling a module with clamped contacts in which the crystal, on a movable copper substrate, is lightly pressed against the four platinum conductors by a spring.

To study the conductivity at high pressures, we use a toroidal chamber of lithographic rock. At the center of the toroid, there is a small cup, made of Teflon, containing the liquid GKZh-94. This arrangement makes it possible to measure the conductivity of the single crystals during hydrostatic compression up to 60 kbar at room temperature. For the thermal measurements of the conductivity at high pressures, we use a squirrel-cage chamber, which makes it possible to measure the resistance of the single crystals down to 1.5 K at a fixed pressure up to 40 kbar. At room temperature the resistance varies in inverse proportion to the pressure, and it falls off by a factor of about 16 at 50 kbar.

The conductivities of the crystals synthesized separately at room temperature lie in the interval 5–30 S/cm. Measurements of the anisotropy of the conductivity show that in a plane of the crystal coinciding with the crystallographic ab plane this anisotropy is insignificant (no greater than 2), while in the perpendicular plane it is very large, $\sim 5 \times 10^4$. There has been no previous observation of such a pronounced anisotropy in an organic conductor. Figure 2 shows the temperature dependence of the resistance of the $(\text{BEDT-TTF})_4\text{Hg}_3\text{Cl}_8$ single crystals. As the temperature is lowered, the resistance of the sample falls, by a factor 2–2.5 at $T = 100$ K, then remaining nearly constant over the interval 50–100 K (for some of the crystals, the resistance remains constant down to liquid-helium temperatures). Below 40 K the resistance begins to decrease again, as the carriers are localized in the region of liquid-helium temperatures; the localization temperature differs from crystal to crystal.

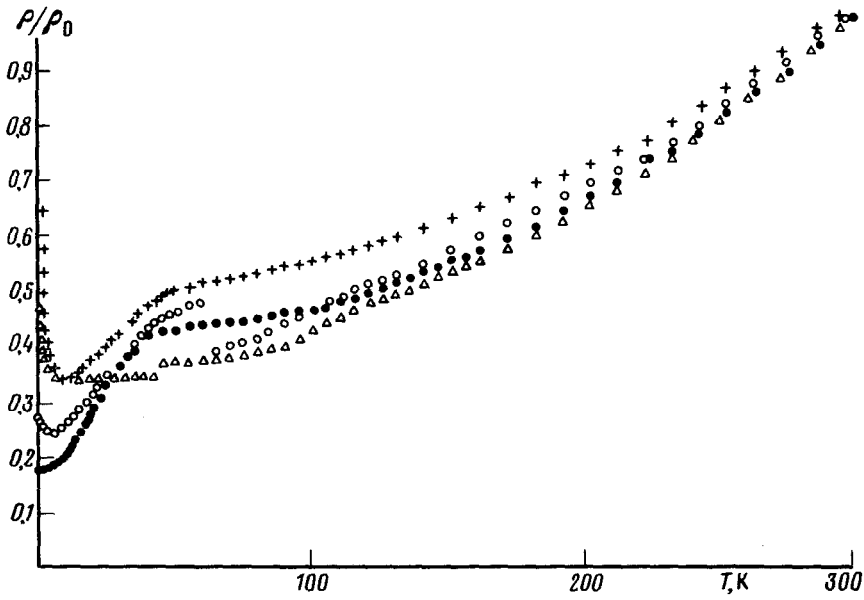


FIG. 2. Temperature dependence of the resistance of various single crystals.

Figure 3 shows the temperature dependence of the resistance at various pressures. We see that at pressures up to 9 kbar in the interval 300–25 K, the temperature dependence of the resistance becomes weaker than at atmospheric pressure. At tem-

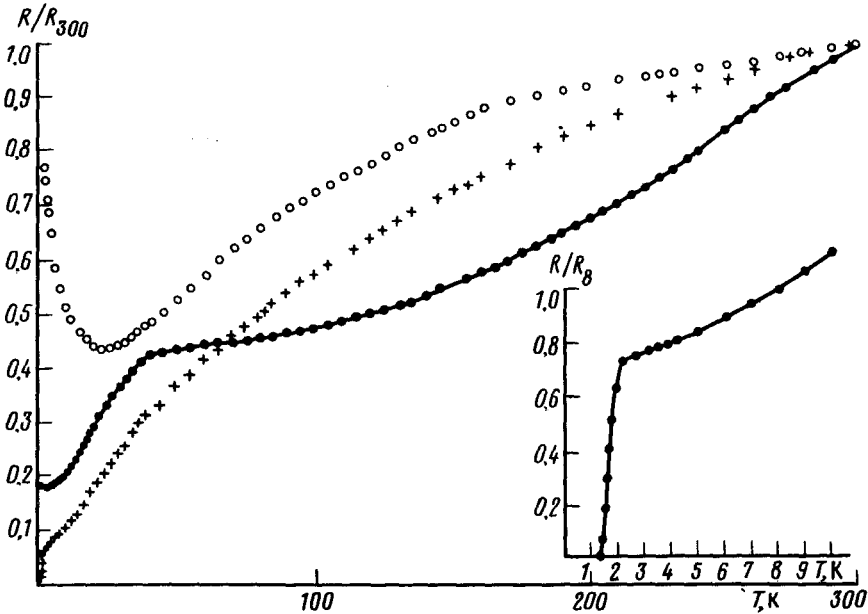


FIG. 3. Temperature dependence of the resistance at various pressures. ●—Atmospheric pressure; ○—9 kbar; +—12 kbar. The inset shows the low-temperature part of the temperature dependence of the resistance at 12 kbar.

peratures below 25 K, the resistance begins to increase. As the pressure is raised to 12 kbar, the low-temperature increase in the resistance disappears, and at 2.2 K there is an abrupt superconducting transition, which terminates at 1.5 K. The normal resistance before this transition does not reach saturation at low temperatures; it continues to fall off monotonically all the way to the beginning of the transition. The temperature T_c , found from the middle of the transition, is 1.8 K.

We are naturally interested in whether the observed superconductivity results from the anion sublattice or the cation sublattice. We do not rule out the possibility that the superconductivity occurs along chains of mercury atoms, as in the case of Ref. 7, which are arranged in an uncorrelated way with respect to each other, according to the structural data. However, the absence of an anisotropy of the conductivity in the plane of the cation layer at room temperature apparently rules out such an extremely interesting one-dimensional superconductivity.⁸ We can apparently also rule out a superconductivity of mercury, possibly extruded from the surface because of the different compressibilities of the cation and anion sublattices,⁹ since the observed temperature of the superconducting transition is quite different from the corresponding temperature for mercury under pressure.¹⁰ The superconductivity most probably involves the cation sublattice, but here there are some features that distinguish this compound from other organic superconductors of this class. In the first place, the packing of the cation radicals in the layer is atypical of organic superconductors.^{6,11} Second, for the organic superconductors that have been identified, there is a correlation between the decrease in the resistance of the samples as they are cooled from room temperature to liquid-helium temperature and the width of the superconducting transition: Specifically, the transition is relatively narrow where the decrease is relatively pronounced. In the compound studied in the present experiments, the relative decrease in the resistance is slight: $R_{300}/R_{4.2} \approx 6$ at atmospheric pressure and $R_{300}/R_{4.2} \approx 15$ at 12 kbar. On the other hand, the superconducting transition is quite sharp, having a width of 0.7 K.

Finally, we should point out that this compound goes into another state (a metallic state in terms of the conductivity) below 40 K at atmospheric pressure. It is completely possible that the superconducting transition occurs in a lattice differing considerably from that at high temperatures.

We are deeply indebted to I. F. Shegolev for constant interest in this study and for support, A. I. Larkin and S. A. Brazovskii for a useful discussion, and I. S. Krainskii for assistance in the study and for furnishing the cryostat for the high-pressure measurements.

¹S. S. Parkin, M. Ribault, D. Jerome, and K. Bechgaard, *J. Phys. C*, **14**, 5305 (1981).

²É. B. Yagubskii, I. F. Shegolev, V. N. Laukhin, *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 12 (1984) [*JETP Lett.* **39**, 12 (1984)].

³V. N. Laukhin, E. É. Kostyuchenko, Yu. V. Sushko, I. F. Shegolev, and É. B. Yagubskii, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 68 (1985) [*JETP Lett.* **41**, 81 (1985)].

⁴É. B. Yagubskii, I. F. Shegolev, V. N. Topnikov, *et al.*, *Zh. Eksp. Teor. Fiz.* **88**, 244 (1985) [*Sov. Phys. JETP* **61**, 142 (1985)].

⁵J. M. Williams, H. H. Wang, *et al.*, *Inorg. Chem.* **23**, 3839 (1984).

⁶S. S. Parkin, *et al.*, *Phys. Rev. Lett.* **50**, 270 (1983).

⁷D. Moses, A. Denenstein, and M. Weger, *Phys. Rev. B* **28**, 6324 (1984).

⁸W. A. Little, *Phys. Rev. A* **134**, 1416 (1964).

⁹W. R. Datars, A. van Schyndel, J. S. Lass, D. Chartier, and R. J. Gillespie, *Phys. Rev. Lett.* **40**, 1184 (1978).

¹⁰L. D. Jennings and C. A. Swenson, *Phys. Rev.* **112**, 31 (1958).

¹¹R. P. Shibaeva, V. F. Kaminskiĭ, and V. K. Bel'skiĭ, *Kristallografiya* **24**, 1088 (1984) [*Sov. Phys. Crystallogr.* **24**, 624 (1984)].

Translated by Dave Parsons