Superconducting transition at $T_c = 5.3$ K in the high-pressure phase of the organic metal (BEDT-TTF)$_4$Hg$_3$Cl$_2$

R. B. Lyubovskiĭ, R. N. Lyubovskaya, and N. V. Kapustin[1)]

Division of Institute of Chemical Physics, USSR Academy of Sciences
(Submitted 25 February 1987)
Zh. Eksp. Teor. Fiz. **93**, 1863–1869 (November 1987)

The conductivity of the organic metal (BEDT-TTF)$_4$Hg$_3$Cl$_8$ (BEDT-TTF-bis-(ethylenedithiolo)-tetrathiafulvalene) in the temperature range 1.4–300 K and at pressures from 1 to 30 kbar was investigated. It is shown that at 12 and 39 kbar this compound becomes superconducting with $T_c = 1.8$ K and 5.3 K, respectively. The conductivity at room temperature was investigated under pressures up to 50 kbar. Apparatus is described for the measurement of the conductivity of organic conductors at pressures up to 50 kbar and temperatures from 1.4 to 300 K.

The first organic superconductors were obtained by applying pressures up to 12 kbar to the single-crystal systems (TMTSeF)$_2$X.[1] Pressure leads in these compounds to suppression of the spin-density wave, or prevents, in the anion chain, the order-disorder phase transition connected with the ordering of the low-symmetry anion.[2] The superconductivity of the organic salt (TMTSeF)$_2$ClO$_2$ at atmospheric pressure is due to the unique packing of the anion and to the appearance, in the lattice, of a "chemical compression" equivalent to pressure.

The first organic superconductor, based on another donor BEDT-TTF was also obtained after applying to the (BEDT-TTF)$_2$ReO$_4$ salt a pressure up to 6 kbar.[4] This results in an abrupt metal-insulator transition at 81 K and the metallic state can be preserved down to helium temperatures, where a superconducting transition takes place at 1.5 K. Soon after the synthesis of a superconductor with this cation under pressure, the salt (BEDT-TTF)$_2$I$_3$ was synthesized, which becomes superconducting at atmospheric pressure and at $T_{c_-} = 1.5$ K (Ref. 5). An extremely interesting feature of this salt is that application of even a rather small pressure (~ 1.3 kbar) leads to the appearance of a new superconducting phase with $T_c = 7.5$ K (Ref. 6). It is interesting that this phase is preserved in a metastable state after

vacuum heat trement of iodine-rich ε-phase crystals[7] or after a special working of the β-phase crystals by pressure.[8] It is natural to assume that application of pressure to other BEDT-TTF salts also leads to stabilization of the metallic state in them and, as a possible consequence, to a superconducting transition.

We have obtained a new organic superconductor based on this cation, (BEDT-TTF)$_4$Hg$_3$Cl$_8$ (Ref. 9), which becomes superconducting at 1.8 K and 12 kbar. We report in the present paper the existence in this compound of a high-pressure phase that becomes superconducting with $T_c = 5.3$ K in the region of 29 kbar. This is the second largest T_c of the now known organic superconductors.

MEASUREMENT PROCEDURE

Crystals of the investigated salt were obtained electrochemically in the form of thin rhombic plates with typical dimensions $1.5 \times 1.0 \times 0.05$ mm. Their conductivity was measured by the dc four-contact method, after sputtering four gold strips on the crystal and securing it with silver or graphite paste to platinum leads of 10 μm diameter. This measurement method, however, yields as a rule a conductivity curve with jumps in the temperature range 150–50 K. It was possible to eliminate these resistivity jumps by constructing a clamping module (Fig. 1).[10]
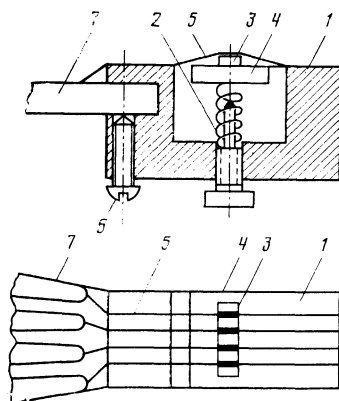

FIG. 1. Clamping module for the measurement of conductivity (top and side views): 1—housing of module, 2—spring, 3—measured single crystal, 4—movable lug, 5—platinum electric leads, 6—retainer screw, 7—housing holder.
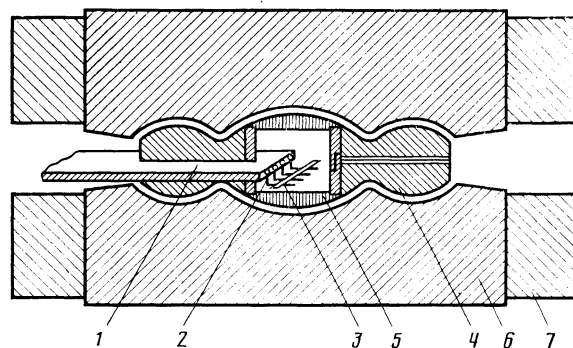

FIG. 2. High-pressure unit of chamber. 1—four-contact lead-in module, 2—platinum contacts, 3—single crystal (samples), 4—lithographic-limestone toroid; 5—teflon slotted vessel with removable covers, 6—punches made of har alloy, 7—supporting rings.
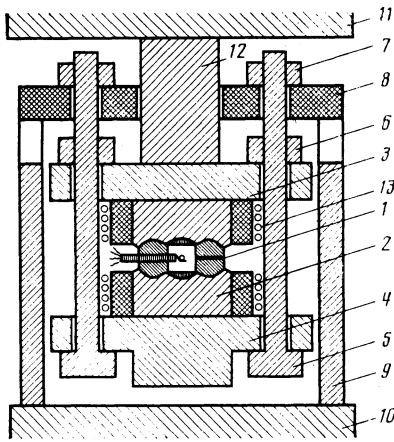
FIG. 3. Device for loading the high-pressure chamber into the hydrostatic press and fixing the pressure on the sample: 1—toroid with four-contact lead-ins and sample, 2—punches of hard alloy, 3 and 4—support plates for the punches, 5—tightening bolts, 6—adjusting nuts, 7—suspension nuts, 8—support plate of suspension, 9—support cylinder, 10 and 11—base and cross-piece of hydraulic press, 12—pusher rod, 13—solenoid.

To measure the pressure dependence of the conductivity we used a high-pressure chamber in the form of a lithographic-limestone toroid. The high-pressure installation constructed by us permits application of pressures up to 50 kbar to organic single crystals and cooling of the compressed samples to 1.5 K.

Crystal 3 (Fig. 2) is glued to 10 μm diam platinum wires 2 which are soldered beforehand to the module 1. The module consists of four manganin wires of 0.7 mm diameter, secured with epoxy resin to one strip. A hole of 6 mm diameter is drilled in the center of the lithographic-limestone toroid 4 to admit a slotted teflon vessel, and the toroid itself is cut in two halves, to be able to place between them the module 1 with the crystal. Organosilicon liquid GKZh-94 was used to produce the hydrostatic pressure. The useful working volume of the vessel is 120 mm³ and can hold simultaneously two modules with crystals or with pressure sensors.
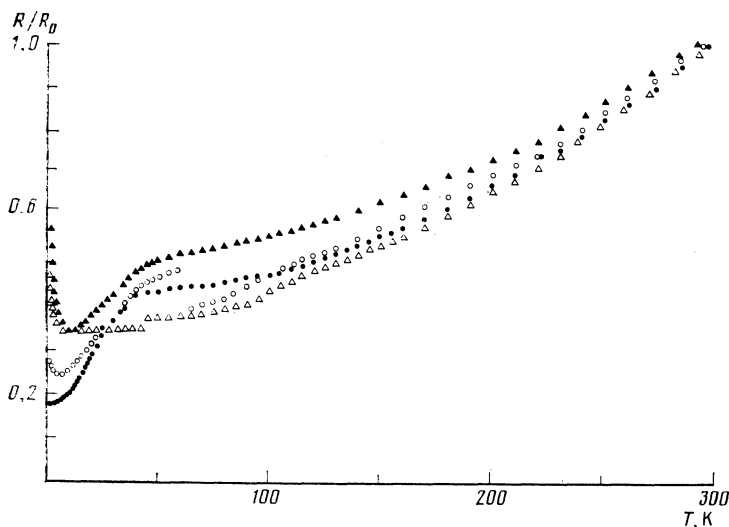
Temperature measurements of the conductivity were made with a fixing clamp of the "squirrel-cage" type[11] (Fig. 3). In this structure, simultaneously with increasing the force of the press (10,11) and compression of the high-pressure chamber with sample 1, six securing bolts are tightened by nuts 6 to produce the required force in the press. Such a construction makes it possible to maintain almost constant the pressure on the sample after extracting the apparatus from under the press. The thermal expansions of these parts of the apparatus which operate in tension and in compression are cancelled out. A check against the superconducting transition of tin has shown that at helium temperatures the initial pressure is preserved in the chamber with accuracy 5%.

RESULTS OF EXPERIMENT

The room-temperature conductivity of the different synthesized crystals ranged from 5 to 30 $(\Omega \cdot cm)^{-1}$. Measurement of the conductivity along different rhomb diagonals corresponding to the axes a and b of the crystal structure[9] of the complex have shown that the conductivity anisotropy in the ab plane of the crystal is small (<2), but on the other hand it follows from the measurements of the conductivity in the perpendicular plane that the anisotropy here is very large and amounts to $(3-5) \cdot 10^4$. No such an anisotropy was ever reported for in organic conductors. Figure 4 shows the temperature dependence of the resistance of a number of single crystals at normal pressure. It can be seen that up to 100 K the resistance decreases by 2–2.5 times, after which the decrease slows down and in the region of 40 K, after a small kink, the drop of the resistance of most crystals is again accelerated. The resistance of many crystals reaches a minimum at temperatures from 4 to 20 K, after which it begins to increase insignificantly. No low-temperature increase of resistance was observed for certain crystals at helium temperatures.

Figure 5 shows the dependence of the room-temperature resistance on pressure up to 50 kbar. The procedure used, with lithographic limestone used to maintain the pressure in the working chamber, makes measurements at low pressures impossible. The force applied to the press will be

FIG. 4. Atmospheric-pressure resistances of various single crystals, normalized to room-temperature resistance.
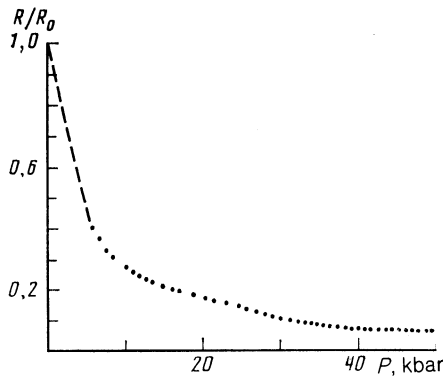
R/R₀
1,0

FIG. 5. Single-crystal resistance vs pressure at room temperature, normalized to the resistance at atmospheric pressure.

adequately transmitted to the sample after the stone becomes ductile. For lithographic limestone this pressure is of the order of 5 kbar. It can be seen from Fig. 5 that the resistance decreases with increase of pressure and that at 50 kbar it is 16 times smaller than the resistance at normal pressure. Notice must be taken of the substantially smaller compressibility of the investigated crystals compared with the organic superconductor β-(BEDT-TTF)$_2$I$_3$, whose resistance decreases by a factor of 10 at 8 kbar pressure.[6] The resistance of the investigated crystals decreases at this pressure by a factor 2.5–3.

The temperature dependences of the resistance at different pressures are shown in Fig. 6. It can be seen from this figure that at pressures up to 9 kbar the resistance change in the temperature range 25–300 K is weaker than at atmospheric pressure. Below 25 K, carrier localization sets in and the resistance begins to increase. A pressure of 12 kbar suppresses the low-temperature localization, and the resistance continues to decrease monotonically to 2.2 K. At this temperature, a strong superconducting transition sets in and terminates at 1.5 K. The pre-transition normal resistance does not reach saturation at low temperatures, but continues to decrease monotonically all the way to the start of the transition. The temperature T_c estimated from the center of the

transition corresponds to 1.8 K. Note that in a number of complexes the transition does not go all the way: it stops apparently at a temperature below 1.4 K.

The temperature dependence of the resistance changes qualitatively at 29 kbar. Whereas at lower temperature, starting approximately with 40 K, the decrease of the resistance was accelerated, at 29 kbar the resistance varies linearly starting with this temperature region and at 5.4 K it decreases abruptly to one-half in a 0.1 K interval and to one-quarter at 4.2 K. The subsequent decrease is somewhat slower and at 1.5 K the resistance is one-sixteenth its value at 6 K.

DISCUSSION OF RESULTS

The structure of the investigated complex,[9] just as the structure of other complexes based on BEDT-TTF (Ref. 12), consists of layers of the BEDT-TTF$^+$ cation and layers of the (Hg$_3$Cl$_8$)$^{2-}$ anion. A feature of this compound is the existence of two incommensurate sublattices along the a axis, and the force lines connected with the anion sublattice have a diffuse character. The cation sublattice contains shortened contacts between the sulfur atoms of the nearest BEDT-TTF molecules, both along the a and along the b axis.

The presence of incommensurate sublattices and of disorder in the anion sublattice explains apparently the considerable scatter of the crystal resistivities at room temperature (5–30 $\Omega \cdot cm^{-1}$) and certain difference between the temperature dependences of their resistivities, especially at helium temperatures (Fig. 4). According to x-ray structural data, the crystallographic ab plane coincides with the crystal plane, so that the almost complete absence, in experiment, of conductivity anisotropy in this plane is apparently due to the presence of shortened contacts in both directions of the cation layer. The presence of large anisotropy in the transverse lane, in turn allows us to state that the anion sublattice in the conductivity does not participate in the conduction and serves so to speak as an insulating layer between the conductor layers.

It must be noted that the conductivity measured across the crystal plane duplicates exactly the behavior of the conductivity measured along the crystal plane. This is quite strange, since the transverse conductivities of the investigated crystals were smaller by more than four orders of magni-
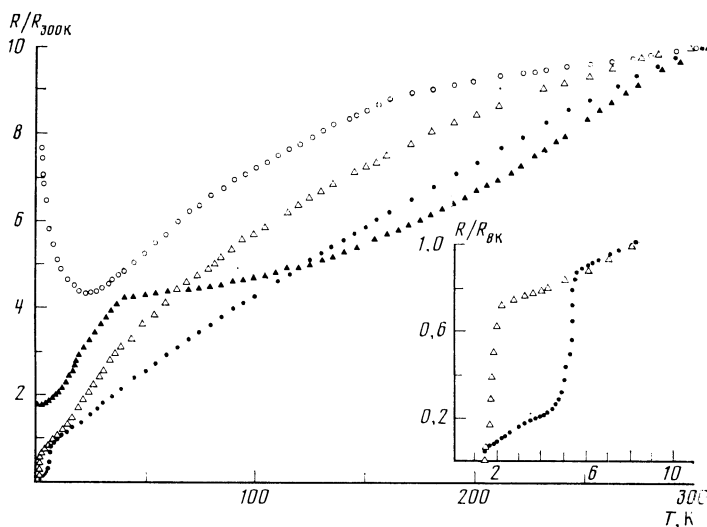
R/R₃₀₀K

FIG. 6. Resistance vs temperature at different pressures: ▲—1 bar, ○—9 kbar, △—12 kbar, ●—29 kbar. The inset shows the superconducting transition at pressures 12 (△) and 29 (●) kbar.
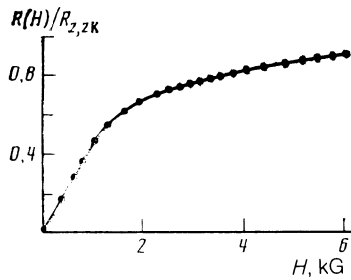
FIG. 7. Crystal resistance vs the magnetic field at $T = 1.4$ K.

tude than the longitudinal. At helium temperatures and at such low conductivities, electrons should move in the transverse direction by hopping. It is therefore natural to assume that the conduction across the crystal plane is determined by short circuits (due to structure defects) between the conducting layers. The intrinsic anisotropy of the crystal conductivity is therefore apparently much higher than the measured value. Note that a similar picture was observed for the longitudinal and transverse conductivities in layered TaS_2 compounds intercalated with iridium.[13] The high anisotropy, together with the possible inhomogeneties of the crystals, leads sometimes, in four-contact measurements of the conductivity, to a current-channel distribution such that the measured voltage, starting with certain temperatures, becomes negative, and sometimes voltages appear accross parts of the crystal where there should be none whatever.[14] It must be noted, however, that these voltages vanish for the superconducting transitions and reappear when a magnetic field is applied to the sample.

Particularly interesting in the investigated complex is the appearance of superconductivity at 12 kbar. The transition is quite abrupt, rather unusual for organic metals at a small overall resitance drop ($R_{300\,K}/R_{4.2\,K} = 15$ for a sample cooled from room to helium temperature). At 12 kbar pressure, the resistance begins to decrease precipitously starting with 2.2 K and vanishes completely at 1.5 K. At higher pressures the superconducting transition is shifted to a region of lower temperatures; at the minimum measurable temperature 1.4 K only its start can be observed, while at 23 kbar it vanishes completely. To determine dT_c/dP we used the temperature of the start of the transition, determined from the intersection of the tangents to the curve. Such a calculation yielded $dT_c/dP = -5 \cdot 10^{-2}$ K/kbar. It should be noted that dT_c/dP in an organic superconductor $(BEDT-TTF)_2I_3$ is about -1 K/kbar (Ref. 6), while in TMTSeF-based superconductors dT_c/dP is approximately $(6-9) \cdot 10^{-2}$ K/kbar (Ref. 2).

To determine the nature of the transition at 12 kbar we applied a magnetic field to the samples. To this end, we placed in the small gap between the punches and the retaining bolts (Fig. 3) a solenoid made up of four layers of superconducting wire, which produces at the sample a magnetic field ≈ 6 kG at a current 30 A. The study of the field characteristics by this method entails certain difficulties, for each passage of current through the solenoid leaves in the sample a magnetic field due to the residual magnetization of the

partial cycle. To eliminate this field it is necessary to demagnetize the magnetic circuit after each measurement by using a damped alternating current.

Figure 7 shows the dependence of the crystal resistance at a pressure 12 kbar on the field at 1.4 K. The magnetic field is directed along the easy axis perpendicular to the crystallographic ab plane. The observed increase of the resistance with increase of the magnetic field makes it possible to state with assurance that we are dealing with a superconducting transition. It should be noted that a field ~ 6 kG does not destroy the superconductivity completely at 1.4 K.

It can be definitely assumed that the observed superconductivity is due to the anion lattice, which contains mercury atoms, just as in the case of $Hg_{2.86}AsF_6$ (Ref. 15). The absence of conductivity anisotropy in the cation-layer plane seems to exclude this possibility. Nor can we exclude superconductivity via the mercury squeezed out to the sample surface on cooling, owing to the different compressibilities of the cation and anion sublattices.[16] The substantial difference, however, between the observed temperature of the superconducting transition and the value of T_c of mercury under pressure[17] seems likewise to exclude this possibility. It must be noted in addition that, in contrast to $Hg_{2.86}AsF_6$, the mercury in this compound is in a bound state and the probability of its appearance in a free state is low. It is most likely that the observed superconductivity is realized by the cation sublattice.

The most interesting feature of the investigated complex is the existence of a high-pressure phase at 29 kbar. The onset of a new phase is indicated not only by the superconducting transition at $T_c = 5.3$ K, but the qualitative change of the temperature dependence of the resistance, which exhibits a kink at 40 K and a linear dependence of the resistance way down to the superconducting transition. The incomplete superconducting transition can apparently be attributed to the solidification of the pressure-transmitting liquid.

The authors are deeply grateful to I. F. Shchegolev and M. L. Khidekel' for constant interest and support, to V. A. Merzhanov and I. S. Krapinskiĭ for help with the work, and to V. N. Laukhin and V. A. Litvin for helpful consultations in the course of construction of the high-pressure apparatus.

[1)]Institute of Experimental Mineralogy, USSR Academy of Sciences.

[1]D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. de Phys. Lett 41, L95 (1980).
[2]A. I. Buzdin and L. N. Bulaevskiĭ, Usp. Fiz. Nauk 144, 415 (1984) [Sov. Phys. Usp. 27, 830 (1984).
[3]S. S. P. Parkin, M. Ribault, D. Jerome, and K. Bechgaard, J. Phys. 14C, 5305 (1981).
[4]S. S. P. Parkin, E. M. Engler, and R. P. Schumaker, Phys. Rev. Lett. 50, 270 (1983).
[5]E. B. Yagubskiĭ, P. F. Shchegolev, V. N. Laukhin et al., Pis'ma Zh. Eksp. Teor. Fiz. 39, 12 (1984) [JETP Lett. 39, 12 (1984)].
[6]V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko et al., ibid. 41, 68 (1985) [41, 81 (1985)].
[7]V. A. Merzhanov, E. E. Kostyuchenko, V. N. Laukhin et al., ibid. 41, 146 (1985) [41, 179 (1985)].
[8]M. Tokumoto, K. Murata, H. Banda et al., Sol. St. Commun. 54, 131 (1985).
[9]R. N. Lyubovskaya, R. B. Lyubovskiĭ, R. P. Shibaeva et al., Pis'ma Zh. Eksp. Teor. Fiz. 42, 380 (1985) [JETP Lett. 42, 468 (1985)].
[10]R. B. Lyubovskiĭ, Prib. Tekh. Eksp. No. 3, 227 (1986).
[11]F. P. Bundy and K. J. Dunn, Rev. Sci. Instr. 51, 753 (1980).
[12]R. P. Shibaeva, V. F. Kaminskii, and V. K. Bel'skiĭ, Kristallografiya 29,

1089 (1984) [Sov. Phys. Crystallogr. **29**, 638 (1984)].

[13]A. H. Thompson, F. R. Gamble, and R. F. Koehler, Phys. Rev. **135**, 2811 (1972).

[14]D. E. Schafer, F. Wudl, G. A. Thomas *et al.*, Sol. St. Comm. **14**, 347 (1974).

[15]D. Moses, A. Denenstein, and M. Weger, Phys. Rev. **B28**, 6324 (1984).

[16]W. R. Datar, A. Van Schundel, J. S. Lass *et al.*, Phys. Rev. Lett. **40**, 1184 (1978).

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

Translated by J. G. Adashko