Low-temperature resistance anomaly in a new organic metal $(TSeT)_4Hg_4I_9$ (tetraselenotetracene iodomercurate) under pressures exceeding 5 kbar

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At pressures exceeding 5 kbar in the temperature range 0.4–100 K, the temperature behavior of the resistance of the quasi-one-dimensional organic metal $(TSeT)_4Hg_4I_9$ is nonmonotonic: The resistance increases weakly with cooling from 100 to ~ 10 K and drops slightly below 10 K. The application of a transverse magnetic field decreases the nonmonotonicity indicated.

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Tetraselenotetracene iodomercurate with the composition $(TSeT)_4Hg_4I_9$ is a new organic metal, whose crystals were obtained with oxidation of tetraselenotetracene (TSeT) by mercury iodide (HgI_2) in a solution of benzonitrile. The synthesis was performed with a molar ratio $TSeT/HgI_2$ equal to 1:5 in an inert atmosphere at a temperature of 76 ± 2 °C. The conductivity of the complex at normal pressure and room temperature is of the order of $10^3\ \Omega^{-1}\ cm^{-1}$, which is typical for most organic metals.

Figure 1 shows a projection of the structure of the complex on the ac plane. The rhombic lattice of the complex has the following parameters: $a = 28.85$ (1), $b = 13.431$

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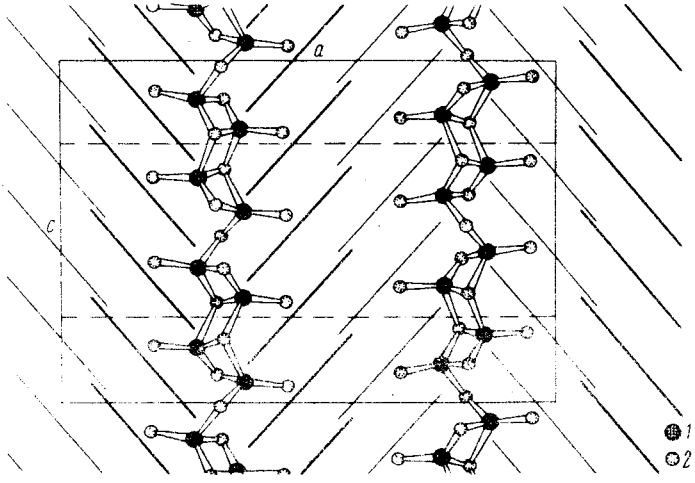

FIG. 1. Projection of the structure on the ac plane. TSeT ions at a height $(1/4)b$ are indicated by the thin lines and at a height $(3/4)b$ by the dark lines. 1) Hg; 2) I.

(4), $c = 20.66$ (1) Å, $V = 8006$ Å^3, the space group is $P2_1cn$, and the unit cell contains four formula units of the composition indicated. The crystalline structure of the complex characteristically contains cation-radical stacks of TSeT stretched along the c axis and continuous anionic chains, consisting of Hg and I atoms, in which there are no separated molecular clusters. The unit cell contains in all two nonequivalent pairs of cationic stacks and two anionic chains. There are four TSeT molecules in the cationic stacks per period c and, in addition, in one of the two nonequivalent stacks the average interplanar TSeT–TSeT distance is 3.31 Å, while in the other, it is 3.39 Å. The TSeT molecules in the stacks form angles of 40 and 41°, respectively, with the c direction. It should be noted that the peaks in the electron density, which correspond to mercury and iodine atoms, are small. This problem may be attributable to some disorder in the anionic chain and requires special analysis.

We measured the conductivity of the complex along the c axis in the temperature range 0.4–300 K under hydrostatic pressures up to 22 kbar and in magnetic fields up to 20 kOe. The conductivity was measured by a four-contact method at constant current with the measuring current varying from 10 to 100 μA. Platinum wires ∅ 20 μm were pasted with silver paste to gold strips, ~0.1 mm wide, sputtered in a vacuum onto the surface of the crystals beforehand. With this method of mounting the contacts, the resistance of the contacts over the entire range of temperatures and pressures did not exceed several ohms. The pressure was created in a piston-cylinder apparatus using a technique analogous to that described in Ref. 1. Temperatures below 1.2 K were obtained in an He^3 bath and were measured according to the elasticity of He^3 vapor. Special experiments, in which the temperature within the high pressure cylinder was monitored by the superconducting transition in a cadmium film mounted at the location of the specimens, showed that for the values of the resistance of the

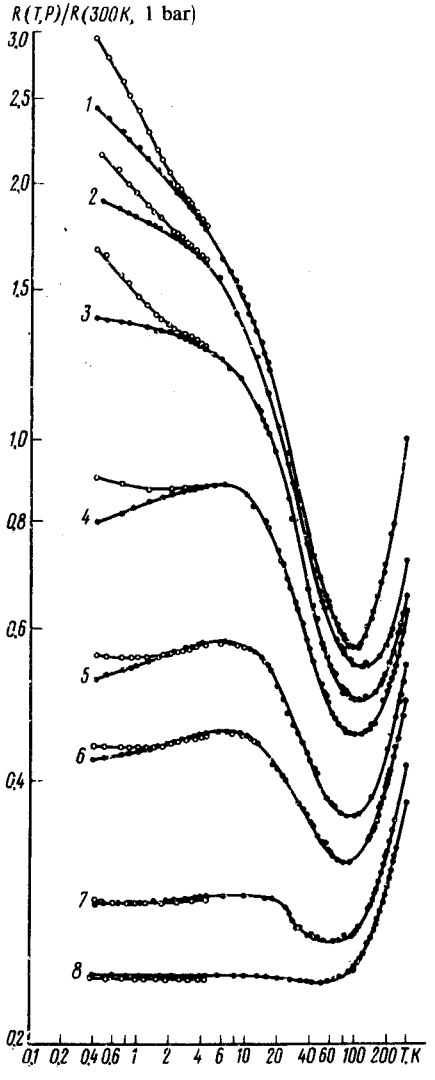

FIG. 2. Temperature dependence of the resistance. ● are for $H_\perp = 0$; ○ are for $H_\perp = 18$ kOe. 1) 1 bar; 2) 4 kbar; 3) 5 kbar; 4) 6 kbar; 5) 8 kbar; 6) 10 kbar); 7) 14 kbar; 8) 22 kbar.

contacts and the measuring current indicated, there is no overheating of the specimens and their temperature coincides with the temperature of the bath.

Figure 2 shows typical temperature dependences of the resistance of $(TSeT)_4Hg_4I_9$ along the c axis at different pressures and two values of the transverse magnetic field: $H_\perp = 0$ and $H_\perp = 18$ kOe. This figure presents data for three different single crystals. We should point out that at an identical pressure, the spread in the temperature behavior of the resistance of different crystals from a single synthesis does not exceed $\sim$10–15%. It is possible to separate three temperature regions, characterized by different behavior of the resistance. In the interval between 300 and $\sim$100 K, the resistance of the complex drops with a decrease in temperature, indicating the metallic nature of its resistance. Between $\sim$100 and $\sim$10 K, the resistance slowly increases

nearly logarithmically. Below 10 K, the increase in the resistance decreases and under pressures exceeding 5 kbar, it begins to decrease. All low temperature variations in the resistance decrease with increasing pressure. At a maximum pressure of 22 kbar, the resistance, after reaching a minimum value near 50 K, increases slightly as the temperature is decreased from ~ 50 to ~ 10 K and then remains constant with further cooling.

A transverse magnetic field at pressures below 5 kbar increases the resistance. The effect of a 18-kOe field becomes appreciable at temperatures below ~ 5 K and by the minimum temperature 0.4 K, the magnitude of the magnetoresistance reaches 10–15%. At pressures above 5 kbar, the relative change in the resistance in a magnetic field, depending on the temperature and pressure ranges, can be both positive and negative. At the maximum pressure of 22 kbar, it is negative in the entire range of temperatures investigated and constitutes about 1%. On the other hand, in the region $5 < P < 22$ kbar, the sign of the magnetoresistance changes at a temperature that decreases with increasing pressure.

The nonmonotonic behavior of the resistance described above at low temperatures and at pressures exceeding 5 kbar, as well as the change in sign of the magnetoresistance, constitute a new phenomenon, which has not been observed before in organic quasi-one-dimensional metals. At present, it is difficult to propose a unique interpretation of this phenomenon. It is possible that for $P > 5$ kbar and $T < 100$ K, the complex makes a transition into a new state. This is supported by the curves $R(P)$, shown for two different temperatures in Fig. 3. It is evident that at temperatures below 100 K, something like a jump in resistance, which increases with decreasing temperature, is observed on these curves in the pressure range from 5 to 10 kbar. It has not been ruled out that this transition is an Anderson type transition and then the nonmonotonic behavior of the resistance at low temperatures and high pressures could be attributed to quantum corrections with different signs,[2] arising from scattering by impurities and spin-orbit interaction. In this case, the role of the magnetic field, which destroys inter-

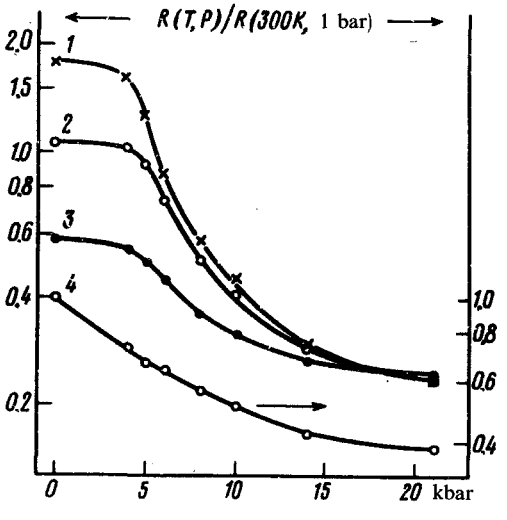

FIG. 3. Pressure dependence of the resistance at different temperatures: 1) 4 K; 2) 20 K; 3) 100 K; 4) 300 K.

ference[2] and decreases the magnitude of both corrections, would be qualitatively understandable.

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