Iodocuprate bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)$_2$Cu$_5$I$_6$—the first quasi-two-dimensional organic metal with a polymer anion layer

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(Submitted 30 May 1986)
Zh. Eksp. Teor. Fiz. **92**, 594–599 (February 1987)

The structure and physical properties of a new organic metal were studied. The substance is iodocuprate bis(ethylenedithio)tetrathiafulvalene or (BEDT-TTF)$_2$Cu$_5$I$_6$, which contains a polymer metal-complex anion. The character of the crystal structure, the temperature dependences of the resistance and of the paramagnetic susceptibility, as well as data on the conductivity anisotropy of (BEDT-TTF)$_2$Cu$_5$I$_6$ crystals indicate that this compound is a quasi-one-dimensional narrow-band organic metal stable at least down to 1.3 K.

INTRODUCTION

The discovery of superconductivity of β-(BEDT-TTF)$_2$I$_3$ at normal pressure[1,2] has stimulated a search, among the BEDT-TTF salts, for new organic metals that are stable to metal–insulator transitions. One of the necessary conditions for the stabilization of their metallic state at low temperatures is apparently the presence of a quasi-two-dimensional electronic system that is formed by the specific arrangement of the BEDT-TTF cation-radicals in the crystal.[3] At the same time, an important role is assumed also by the anion-part structure that influences the character of the packing and the electronic characteristics of the conducting cation–radical system in these compounds. In addition, the presence of a rigid polymer anion core in crystals of small-size organic conductors can impede the onset of structural Peierls instabilities that lead to a metal–insulator transition.[4] It is therefore of interest to obtain BEDT-TTF salts with metal-complex monovalent copper anions, free to produce polymer chains in which the metal atoms are bound to one another by halogen-atom bridges.[5,6]

We have investigated the structure and properties (conductivity along various crystallographic directions and at various pressures, magnetic susceptibility, thermoelectric power) of a new organic metal, iodocuprate of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)$_2$Cu$_5$I$_6$, which contains a polymer metal-complex anion.

SAMPLES AND MEASUREMENT PROCEDURE

The (BEDT-TTF)$_2$Cu$_5$I$_6$ crystals were synthesized by electrochemical oxidation of BEDT-TTF in a solution of trichloroethane ($c_1 = 2.10^{-3}$ mol/l) on a plantinum anode with direct current ($I = \mu A$) at $T = 323$ K. The electrolyte was Bu$_3$NCuI$_2$ ($c_2 = 2\cdot 10^{-2}$ mol/l). The resultant crystals were mainly of two types: needles elongated along a or plates. Typical dimensions were $1\times 0.05\times 0.03$ mm for the needles and $1.5\times 1\times 0.02$ mm for the plates. X-ray diffraction has shown these crystals to be identical.

The experimental x-ray data (1450 independent reflections with $I \geqslant 2\sigma(I)$) was obtained with a "Syntex $P\bar{1}$" automatic diffractometer with monochromatized Mo $K\alpha$ radiation in the interval up to $(\sin\theta/\lambda)_{\max} = 0.790$ from a crystal measuring $0.6\times 0.2\times 0.1$ mm. The structure was determined from an analysis of the Paterson function and refined by least squares in anisotropic–isotropic approximation to $R = 0.062$.

All the electric conductivity measurements were made with direct current in the temperature range 1.3–295 K. The electric conductivities of the crystals in different crystallographic directions in the ac plane were measured by the traditional four-probe method. The conductivity anisotropy in the ab plane was measured by the Montgomery method.[7] The crystals were secured to 10-μm platinum wires by a graphite paste. Pressure was produced in apparatus of the piston-cylinder type and recorded at room temperature. The pressure-transmitting medium was the organosilicon liquid. GHZh-94. The pressure at liquid-helium temperatures was determined from the shift of the superconducting-transition temperature of an Sn film.

The magnetic susceptibility was measured with a Faraday balance in the temperature range 1.5–300 K. The samples were placed in a small quartz vessel and comprised a set of randomly oriented single crystals with total mass 20–30 mg.

The thermoelectric power was measured by a standard method in the temperature interval 1.5–300 K along the a direction of needle-shaped single crystals. The temperature drop along the sample did not exceed 0.5 K. The measured values of the thermoelectric power were corrected by comparison with the absolute thermoelectric power of gold electrodes.

RESULTS AND DISCUSSION

The main crystallographic data for (BEDT-TTF)$_2$Cu$_5$I$_6$ are: $a = 4.326 \pm 0.003$ Å, $b = 21.29 \pm 0.02$ Å, $c = 22.41 \pm 0.02$ Å, $\alpha = 91.31 \pm 0.07°$, $V = 2063$ Å^3, space group $P\,2_1/c$, and $Z = 2$. Typical of the structure of the compound are cation-radical layers alternating along [010] and honeycomblike polymer grids of (Cu$_5$I$_6$)$^-$ anions (Figs. 1 and 2). The cation-radical layer is made up of regular BEDT-TTF stacks in the a direction. The (BEDT-TTF) – (BEDT-TTF) interplanar distance in the stack is 3.80 Å, and the neighboring cation-radicals overlap with a transvers shift relative to one another. The middle BEDT-TTF planes in stacks A and B (Fig. 1) are parallel, and the dihedral angle between the middle BEDT-TTF planes of stacks A and C is 125°. All the contacts S . . . S within the

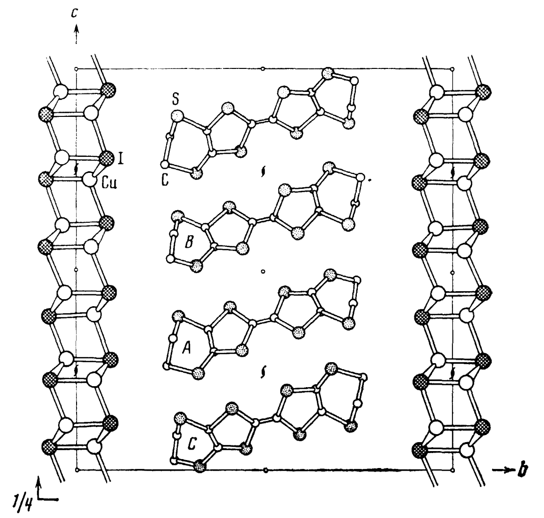

FIG. 1. Projection of $(\mathrm{BEDT\text{-}TTF})_2 \cdot \mathrm{Cu_5I_6}$ crystal structure along the *a* direction.

stacks are not less than the sum of the van der Waals radii (3.70 Å). At the same time, there are a number of shorted interstack contacts S . . . S, viz., 3.36–3.42 Å (between *A* and *B*) and 3.43–3.63 Å (between *A* and *C*).

Each Cu atom in the polymer anion grid (Fig. 2) has a tetrahedral surround of I atoms with Cu–I distance 2.555–2.751 Å. The interatomic Cu . . . Cu distances vary in the range 2.94–3.10 Å, and the I . . . I distances in the range 4.24–4.42 Å. It should be noted that the population of the Cu atoms in each position is 5/6. It appears that the vacancies in the Cu atom positions are somewhat disordered in the crystal, as attested by the presence of weak diffuse line in the 0*kl* Weisenberg diagrams; Some difference in the diffuseness is observed in different crystals.

The conductivity of the $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu_5I_6}$ single crystals in the *ac* plane at $P = 1$ bar and $T = 295$ K is 15–45 $\Omega^{-1}\mathrm{cm}^{-1}$ for both plates and needles. At lower temperatures the resistance decreases by a factor 10–25, reaching a minimum in the temperature interval 2–15 K for different crystals. At lower temperatures, the resistance increases slightly, apparently because of localized effects. The latter may be due to scattering by impurities and/or lattice defects, due in paraticular to the mentioned disorder in the anion part of the crystal. Figure 3 shows the temperature dependences of the resistance of one of the crystals along *a* at various pressures. Note that the resistance of the investigated assembly is decreased by application of pressure much more slowly in the investigated temperature range than the resistance of the β-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{I_3}$ crystals.[8] The minimum resistance, observed for the given crystal at atmospheric pressure near 13 K, becomes less pronounced with increase of pressure and shifts towards lower temperatures. At $P = 18$ kbar the low-temperature growth of the resistance is almost completely suppressed.

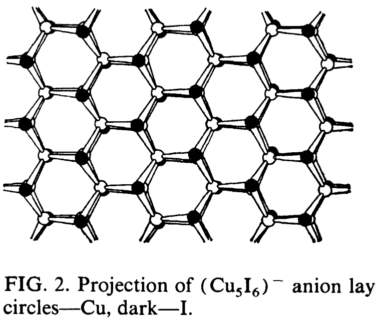

FIG. 2. Projection of $(\mathrm{Cu_5I_6})^-$ anion layer along the *b* direction: light circles—Cu, dark—I.

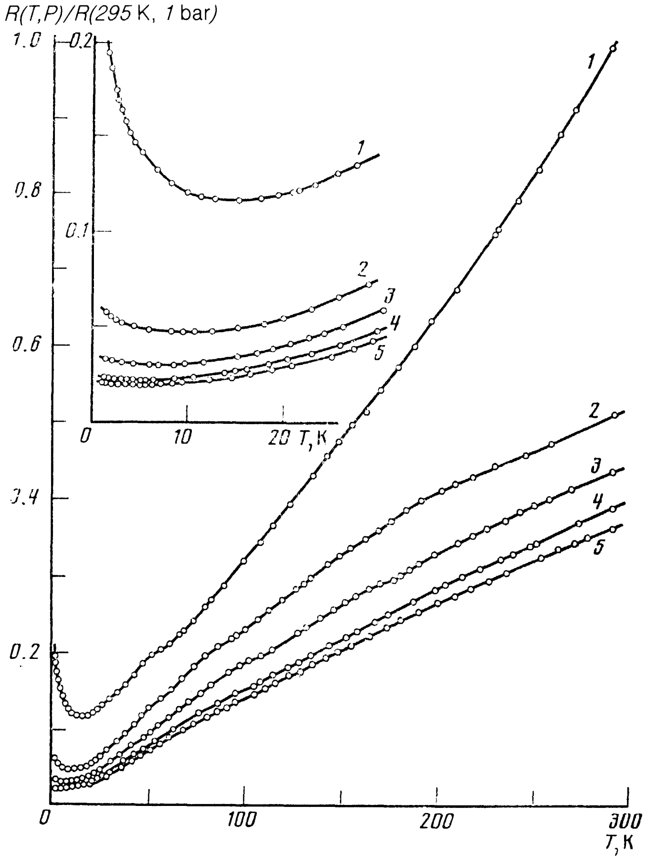

FIG. 3. Temperature dependences of relative resistance along the a direction of one of the crystals for different pressures: 1—1 bar; 2—7,8 kbar; 3—11,2 kbar; 4—15 kbar, 5—17,2 kbar. The inset shows the low-temperature parts of the corresponding curves.

A similar behavior was observed earlier in the $(\mathrm{TSeT})_4\mathrm{Hg_4I_9}$ complex, a feature of whose crystal structure is the presence of polymer anion chains.[4] As already noted, the anion structure in the investigated samples takes a polymer layer-grid form. This circumstance, namely the presence of rather rigid polymer anion part, is apparently the reason why there are no substantial changes in the conducting properties of the complexes when high pressures are applied.

There is practically no conductivity anisotropy in the ac plane at atmospheric pressure: its value is $\sigma_a/\sigma_c = 1 - 2$ and remains essentially constant in the entire investigated temperature range. The conductivity anisotropy in the *ab* plane, to the contrary, is quite large, $\sigma_a/\sigma_b \sim 10^4$ at $T = 295$ K, and increases monotonically by several times at $T \approx 2$ K. So high a conductivity anisotropy is obviously due to the absence of shorted intermolecular contacts in a direction perpendicular to the conducting layer.

The temperature dependence of the paramagnetic part χ_S of the susceptibility is shown in Fig. 4. Curve 1 was obtained by subtracting from the measured susceptibility the small contribution of the ferromagnetic impurities and the

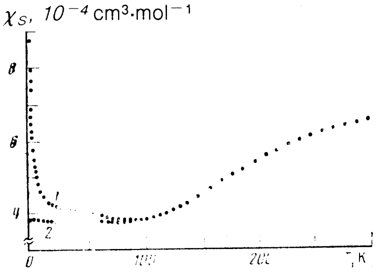

FIG. 4. Temperature dependence of the paramagnetic susceptibility (1—initial curve, 2—after subtracting the contribution of the paramagnetic impurities.

diamagnetic contribution of the lattice.

The ferromagnetic-impurity content was determined from the dependence of the susceptibility χ on $1/H$ at $T = 295$ and 4.2 K, and corresponds to 45 *ppm* of iron in the sample. The diamagnetic contribution was determined in accordance with the Pascal rules and amounted to $7.52 \cdot 10^{-4}$ cm^3·mol^{-1}. A susceptibility increase in accordance with the Curie law, frequently observed in organic conductors and due to impurities or structure defects, becomes noticeable at 20 K. It corresponds in this case to 0.26 mol.% of paramagnetic impurities with spin $S = 1/2$. Substracting this contribution from the susceptibility, we get the conduction-electron paramagnetic contribution represented by curve 2 of Fig. 4. Note that the observed rather high Pauli paramagnetism ($6.5 \cdot 10^{-4}$ cm^3·mol^{-1} at $T = 300$ K) corresponds to a density of states 10 eV^{-1}·spin^{-1}. This means that (BEDT-TTF)$_2$Cu$_5$I$_6$, as well as α – and β-(BEDT-TTF)$_2$I$_3$ (Refs. 9 and 10) is a narrow-band organic crystal.

The temperature dependence of the absolute thermoelectric power S is plotted in Fig. 5 which shows it to be negative in the entire investigated temperature range. Contrary to expectations for a metal, the plot is not a staright line but shows a deep minimum near $T \approx 100$ K. This nonmonotonic dependence of the thermoelectric power is not yet clearly understood. A similar anomalous behavior was observed earlier in β-(BEDT-TTF)$_2$I$_3$ (Refs. 9 and 11), and may be a common property of quasi-two-dimensional metals based on BEDT-TTF.

Thus, the character of the crystal structure, the temperature dependence of the resistance, and also the data on the conductivity anisotropy of (BEDT-TTF)$_2$Cu$_5$I$_6$ indicate clearly that this compound is a quasi-two-dimensional organic metal. The fact that the paramagnetic susceptibility remains finite in the entire investigated temperature interval agrees with the behavior of the conductivity and indicates that this compound remains in a metallic state down to the lowest temperatures.

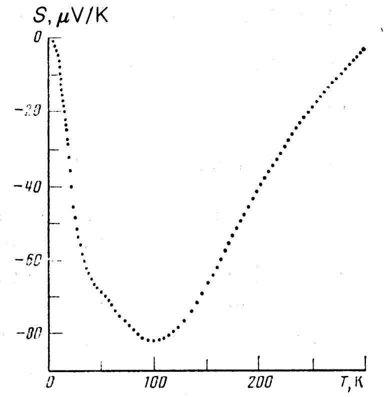

FIG. 5. Temperature dependence of the absolute thermoelectric power.

In conclusion, we thank I. F. Shchegolev for constant interest and for a discussion of the result, and L. P. Rozenberg for a preliminary x-ray-diffraction study of the crystal.

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Translated by J. G. Adashko