Organic conductors and superconductors: mixed (IBr_2^-) polyhalides BEDT-TTF

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Three mixed (IBr_2^-) polyhalides BEDT-TTF (α, β, and γ phases) with different conducting properties have been obtained. The α and β phases, which are polymorphic modifications, have the same composition $(BEDT\text{-}TTF)_2IBr_2$. The α phase is a semiconductor with $E = 0.25$ eV and the β phase is a metal which undergoes a transition to the superconducting state at $T_c = 2$ K and at normal pressure.

The discovery of superconductivity of bis-(ethylene dithiolo) tetrathiofulvalene polyiodides (BEDT-TTF) with record critical temperatures for organic superconductors,[1–9] $T_c = 1.4$–7 K, has stimulated a search for new superconductors among the cation-radical salts BEDT-TTF with anions—structural analogs of triiodide. Of greatest interest in this connection is the use of mixed polyhalide anions: BrI_2^-, IBr_2^-, ICl_2^-, and $IClBr^-$ as counter ions.

In this letter we report the synthesis of three mixed (IBr_2^-) polyhalides, BEDT-TTF (α, β, γ phases) and describe their structure and conducting properties. The crystals of these phases were obtained by electrocrystallization in benzonitrile by analogy with the synthesis of BEDT-TTF triiodides.[10] As the electrolyte we used Et_4NIBr_2 ($c = 10^2$ moles/l). The α and β phases, which are polymorphic modifications, have the same composition $(BEDT\text{-}TTF)_2IBr_2$.

β-$(BEDT\text{-}TTF)_2IBr_2$ is isostructural[10] with the β-$(BEDT\text{-}TTF)_2I_3$ compound and its cell parameters correspond to those reported in a recently published paper.[11] At room temperature, the conductivity of the crystals of this phase along the "a" axis is ~ 20 mho/cm and is approximately equal to the conductivity of the isostructural triiodide.[1] The temperature curves for the resistance of two β-phase samples are shown in Fig. 1. The curves exhibit a metallic nature, $R_{300K}/R_{4.2K} \simeq 1000$–$200$, although small, abrupt changes in the resistance, due probably to the cracking of the sample, have been observed in the latter case during cooling. A transition to the superconducting state occurs below 2.5 K. The inset in Fig. 1 shows the superconducting-transition curves. The critical temperatures (T_c), determined from the midpoints of the corresponding curves, are the same for each sample: 2 K. This temperature is higher than that of isostructural triiodide[1] ($T_c = 1.4$ K) obtained by electrocrystallization.[10] Furthermore, in contrast with triiodide which at a pressure of ~ 1 kbar undergoes a transition to a high-temperature superconducting phase[5] with a maximum $T_c = 7.5$ K, β-$(BEDT\text{-}TTF)_2IBr_2$ has no such transition up to pressures of ~ 8 kbar.

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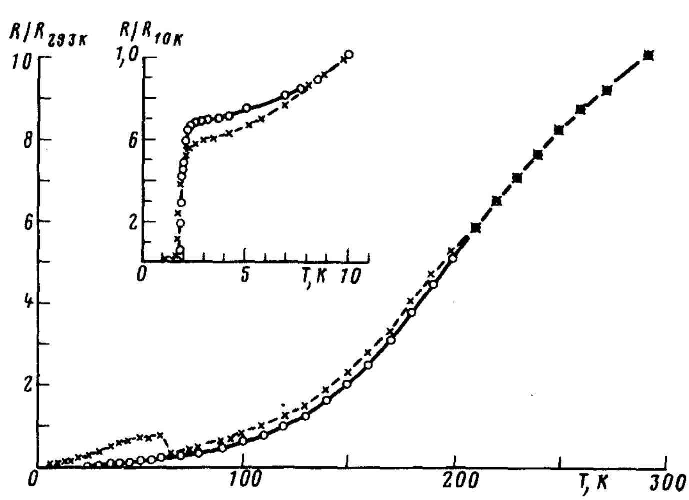

FIG. 1. Temperature dependence of the resistance of β-(BEDT-TTF)$_2$IBr$_2$ crystals.

A higher T_c for β-(BEDT-TTF)$_2$IBr$_2$, in the range 2.5–2.7 K, was reported by Williams *et al.*[11] This discrepancy is probably due to the difference in the measurement methods: Williams *et al.*[11] detected the superconducting transition from the screening signal. A value of T_c approximately equal to our result, $T_c = 2.2$ K, was recently reported in a study,[12] in which the superconducting transition was recorded from the resistance.

The α-phase of (BEDT-TTF)$_2$IBr$_2$ obtained by us is not isostructural with the α-(BEDT-TTF)$_2$I$_3$ compound (Refs. 3 and 13), and its crystal parameters are nearly equal to the parameters reported in Ref. 11. We carried out a complete x-ray structural analysis of this phase. The main crystallographic data are: $a = 12.005(3)$, $b = 8.898(3)$, $c = 16.410(5)$ Å, $\alpha = 88.71(3)$, $\beta = 85.15(2)$, $\gamma = 7P, 76(3)$ Å, $V = 1649.1(9)$ Å (Ref. 3), space group $P\bar{1}$, and $Z = 2$. (We used Syntex $P\bar{1}$ diffractometer, MoK$_\alpha$ emission, 3918 independent reflections, with $1 \geqslant 2\sigma$, method of least squares to obtain more accurate data, and $R = 0.062$). Figure 2 shows the projection of the structure along the a axis. The structure typically has BEDT-TTF layers alternating along the c axis and layers consisting of nearly linear (the angle of Br-I-Br is 179.36°) IBr$_2$ anions with atomic separations I-Br 2.709(1) and 2.715(1) Å. The cation-radical layer is constructed from two types of BEDT-TTF stacks, whose dihedral angle between the central planes of BEDT-TTF is ~48°.

At room temperature the conductivity of the α phase along the a axis (the main direction of crystal growth) is ~1 mho/cm. This value falls off immediately as the temperature is lowered at the activation energy of $\simeq$0.25 eV.

The composition and crystal structure of the third synthesized phase, γ-(BEDT-TTF)$_x$ (IBr$_2$)$_y$, are currently not known, so that high-quality crystals of this phase cannot yet be obtained. A preliminary x-ray diffraction study has shown that orthorhombic γ-phase crystals have the following approximate parameters: $a = 13.6$, $b = 14.3$, $c = 34.1$ Å. The room-temperature conductivity of these crystals along the a

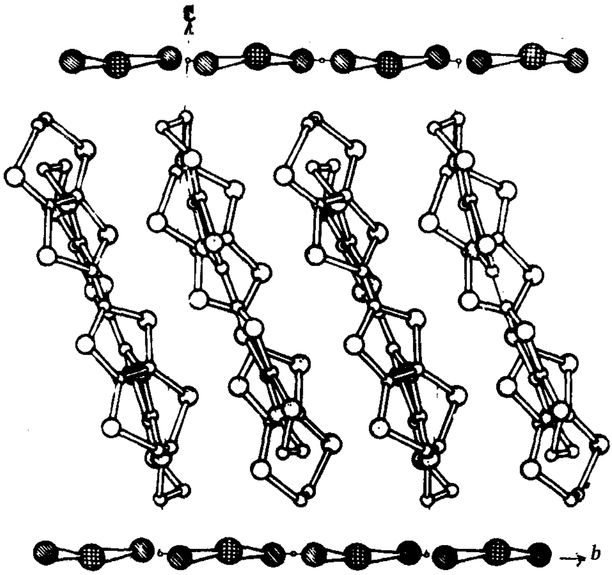

FIG. 2. Projection of the crystal structure of α-(BEDT-TTF)$_2$IBr$_2$ along the a axis.

axis is $\sim$100 mho/cm. The temperature dependence of the conductivity is of a metallic nature: σ increases with decreasing temperature and at $\sim$5 K reaches a permanent value, $\sigma_{4.2K}/\sigma_{300K} \simeq 40$. A superconducting transition in γ-phase crystals has not been observed down to 1.3 K.

[1]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].
[2]É. B. Yagubskiĭ, I. F. Shchegolev, S. I. Pesotskiĭ, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 275 (1984) [JETP Lett. **39**, 328 (1984)].
[3]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 387 (1984) [JETP Lett. **40**, 1201 (1984)].
[4]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Topnikov, *et al.*, Zh. Eksp. Teor. Fiz. **88**, 244 (1985) [Sov. Phys. JETP **61**, 142 (1985)].
[5]V. N. Laukhin, E. É. Kostyuchenko, Yu. V. Syshko, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 81 (1985) [JETP Lett. **41**, 81 (1985)].
[6]V. A. Merzhanov, E. É. Kostyuchenko, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 146 (1985) [JETP Lett. **41**, 179 (1985)].
[7]I. F. Schegolev, É. B. Yagubskiĭ, and V. N. Laukhin, Mol. Cryst. Lig. Cryst., in press.
[8]R. P. Shibaeva, V. F. Kaminskiĭ, and É. B. Yagubskiĭ, Mol. Cryst. Lig. Cryst. **119**, 361 (1985).
[9]L. I. Buravov, M. V. Kartsovnik, V. F. Kaminskiĭ, *et al.*, Synthetic Metals, in press.
[10]V. F. Kaminskiĭ, T. G. Prokhorov, R. P. Shibaeva, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 15 (1984) [JETP Lett. **39**, 17 (1984)].
[11]J. M. Williams, H. H. Wang, M. A. Beno, *et al.*, Inorg. Chem. **23**, 3839 (1984).
[12]M. Tokumoto, H. Anzai, H. Bando, *et al.*, Preprint, 1985.
[13]K. Bender, I. Hennig, D. Schweitzer, *et al.*, Mol. Cryst. Lig. Cryst. **108**, 359 (1984).

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