The conductivity anisotropy of the quasi-two-dimensional organic metal β-(BEDT-TTF)$_2$I$_3$

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(Submitted 30 May 1986)
Zh. Eksp. Teor. Fiz. **91**, 2198–2203 (December 1986)

The anisotropy of the conduction properties of crystals of the organic superconductor β-(BEDT-TFF)$_2$I$_3$ with $T_c \approx 1.5$ K (β-1.5) and with $T_c \approx 7.5$ K (β-8) has been studied. The ratio $\rho_c^*/\rho_a = 380 \pm 50$ at $T = 293$ K and increases to ≈ 500 at $T \approx 50$ K; the ratio $\rho_{b'}/\rho_a$ has the value ≈ 1.5–2 at all temperatures. For β-8 crystals, $\rho_{c*}/\rho_a = 200 \pm 50$ at $T = 293$ K and changes little with temperature down to the superconducting transition. It was found that there are often superconducting formations present in β-1.5 crystals with $T_c \approx 6$–7.5 K, extended in planes close to the **bc** plane. There is, apparently, a superconduction network of such formations in β-8 crystals.

The organic layered metal β-(BEDT-TFF)$_2$I$_3$ is a superconductor with $T_c \approx 1.5$ K (Refs. 1–3) (specimens of the β-1.5 type), if they are obtained by chemical[4] or electrochemical[2,5] means, and acquire $T_c \sim 7.5$ K if they are obtained by an appropriate heat treatment and partial removal of iodine from the iodine-richer ε phase[6,7] (β-8 specimens). The appearance of this transition is sometimes also observed in β-1.5 crystals in the form of a noticeable step on the temperature dependence of the resistivity at 7–8 K (Refs. 8–10). Raising of T_c to 7.5 K takes place in β-1.5 specimens if the crystal is under a pressure of ≈ 1.3 kbar (Ref. 11). Zvarykina *et al.*[7] showed that β-8 specimens differ from the more perfect β-1.5 specimens in that mosaic twinned crystals occur and they consist of blocks with the β-1.5 structure somewhat misoriented relative to one another.

An investigation of the temperature dependences of the paramagnetic susceptibility in the range 8–293 K shows that this characteristic is the same for specimens of both types,[6,12] and does not give the answer to the question of the reasons for the raising of T_c.

In the present work, the conductivity anisotropy of crystals of both types has been studied by measuring the temperature dependences of the resistivity for the directions **a**, **b**$'$ and **c*** by a method similar to that used by Montgomery.[13] In each experiment two quantities were determined simultaneously for a given crystal[1)]: either ρ_a and ρ_{c*}, or $\rho_{b'}$ and ρ_{c*} or ρ_a and $\rho_{b'}$. In addition, as evidence of the superconducting nature of the features of R_{c*} found near 7–8 K in a direction perpendicular to the layers of BEDT-TFF molecules, it was also measured by β-1.5 crystals at low temperatures by a direct four-probe method in a magnetic field as a function of its magnitude for the orientations $\mathbf{H} \| \mathbf{c}^*$ and $\mathbf{H} \| \mathbf{a}$.

The crystals used for the measurements were thin prisms with the base in the form of an elongated hexagon with characteristic dimensions $\approx 1 \times 0.5 \times 0.06$ mm^3, with the large dimension corresponding to the direction of the **a** axis (Refs. 2 and 3).

The arrangement for mounting the contacts to measure ρ_a and ρ_{c*} is shown in Fig. 1a. It differs from that of Montgomery[13] (Fig. 1b) in that the contacts, which are glued on with a conducting paste, are not point contacts and are not positioned at the corners of the crystal in view of its nonstandard shape and the thinness of the specimens. However, model experiments in an electrolytic bath with the appropriate geometry showed that the formulae and graphs given by Montgomery[13,2)] could be used to calculate the anisotropy and the resistivity, if correction coefficients are introduced to take account of the displacement of the contacts from the ends of the crystal. These coefficients, which determine the relation between the voltages for different arrangements, were measured in advance with the help of an electrolytic bath and were used in the calculations for all specimens.

The mounting system for direct measurement of the transverse conductivity in the **c*** direction is shown in Fig. 1c. Four deposited gold contacts were used for this, to which 4 10 μm diameter platinum wires were stuck with conducting paste. Measurements were made in a magnetic field up to 48 kOe.

RESULTS OF THE MEASUREMENTS

The study of the temperature dependences of the resistance showed that the conductivity of β-1.5 and β-8 crystals in all directions is of metallic type, and the fall in resistivity

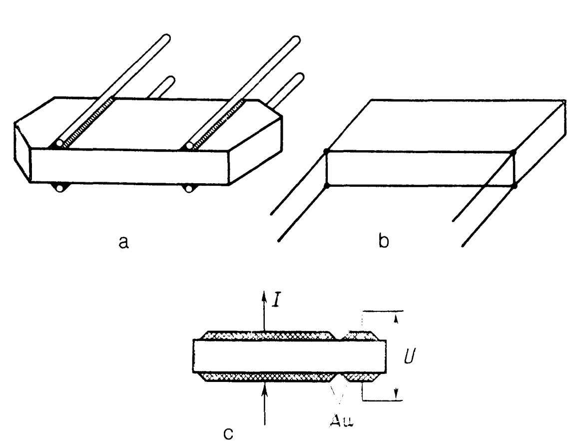

FIG. 1. Systems for mounting the contacts.

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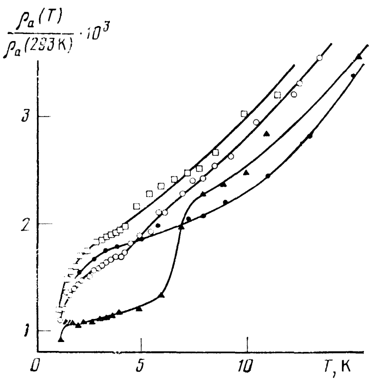

FIG. 2. The temperature dependence $\rho_a(T)$ for β-1.5 crystals.

in the range 10–293 K is on average ~400, 250, and 300 respectively for the directions **a**, **b**′, and **c*** in β-1.5 crystals and ~250 for the **a** and **c*** directions in β-8 crystals. It should be noted that the results of the measuremtns of ρ_a made by the method described here agree with results obtained in the usual way.[1,6]

The results of measuring the specific resistivity ρ_a, ρ_b, and ρ_{c^*} (by a system of the type of Fig. 1a) are shown in Figs. 2–5 for the range 1.2–15 K. As can be seen from Figs. 3 and 4, for β-1.5 crystals $\rho_{b'}$ and ρ_{c^*}, as a rule, decrease more sharply at a temperature below 7–8 K in the form of a more or less pronounced stap, at the same time that such a feature is more rarely met for ρ_a (Fig. 2).

The behavior of the temperature dependences of the resistivities ρ_a and ρ_{c^*} for β-8 crystals (Fig. 5) differs from that for β-1.5 in that both resistivities along the directions given fall sharply on cooling, starting from 8.5 K, with ρ_{c^*} falling somewhat faster than ρ_a.

The features of the behavior of the resistivity at low temperatures for crystals of both types show up clearly in the temperature dependence of the anisotropy of the resistivity.

These dependences ρ_{c^*}/ρ_a, $\rho_{c^*}/\rho_{b'}$ and $\rho_{b'}/\rho_a$ are shown in Figs. 6 and 7 for β-1.5 crystals, joining them on to the mean values at $T = 293$ K: $[\rho_{c^*}/\rho_a]_{293} \approx 380 \pm 50$, $[\rho_{c^*}/\rho_{b'}]_{293} \approx 230 \pm 50$, $[\rho_{b'}/\rho_a]_{293} \approx 1.6 \pm 0.5$. The anisotropy ρ_{c^*}/ρ_a (curve 1 of Fig. 6) changes only weakly in the range 180–293 K. On lowering the temperature further, this quantity grows by about 30% with a maximum at $T \approx 50$ K, with a subsequent small reduction in the range 8.5–50 K.

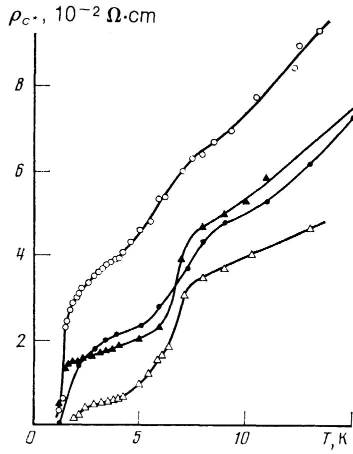

FIG. 4. The temperature dependence $\rho_{c^*}(T)$ for β-1.5 crystals.

Two consecutive falls in the anisotropy are observed in the range 1.2–8.5 K: one in the range 4–8.5 K, the other in the range 1.2–2 K, which is evidently a reflection of two superconducting transitions in the system[8–10]; they are shown in more detail on the inset to Fig. 6 (curves 1′, 1″, 1‴). The quantity $\rho_{c^*}/\rho_{b'}$ changes with temperature in a qualitatively similar way (curve 2 of Fig. 6) with some difference in the details. The anisotropy in the **ab**′ plane changes within the limits of ≈ 1.5–2 over the temperature range 7–293 K (Fig. 7); two consecutive drops in this dependence are observed at $T < 7$ K, similar to the change in ρ_{c^*}/ρ_a in this temperature region.

The anisotropy ρ_{c^*}/ρ_a for β-8 crystals amounts to ≈ 200 on average at $T = 293$ K and almost doesn't change in the range 200–293 K (curve 3 of Fig. 6). A small rise in the ratio ρ_{c^*}/ρ_a is observed on lowering the temperature further with a maximum of about 15% at 50 K. The sharp fall in anisotropy in these crystals in the range 7.5–9 K is associated with a faster fall in ρ_{c^*} compared with the fall in ρ_a (Fig. 5).

The results of studying the transverse resistance R_{c^*} for β-1.5 crystals by the direct method in a magnetic field are shown in Fig. 8 (for **H**‖**c***). These results show that the fall in the transverse resistivity in β-1.5 crystals for $T \lesssim 8$ K is a superconducting transition, with the temperature derivative of the critical field at $T \approx T_c$, which characterizes this transition, equal to $H'_a \approx 23.5$ kOe/K and $H'_{c^*} \approx 3$ kOe/K (the inset to Fig. 8). These values are close to those found earlier

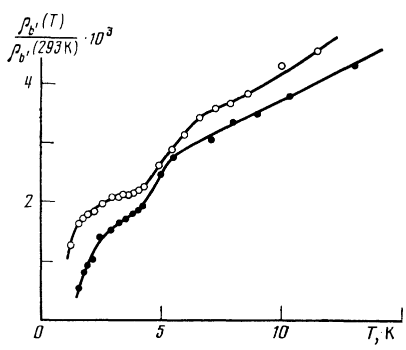

FIG. 3. The temperature dependence $\rho_{b'}(T)$ for β-1.5 crystals.

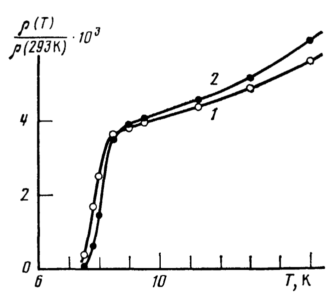

FIG. 5. The temperature dependences $\rho_a(T)$ (curve 1) and $\rho_{c^*}(T)$ (curve 2) for β-8 crystals.

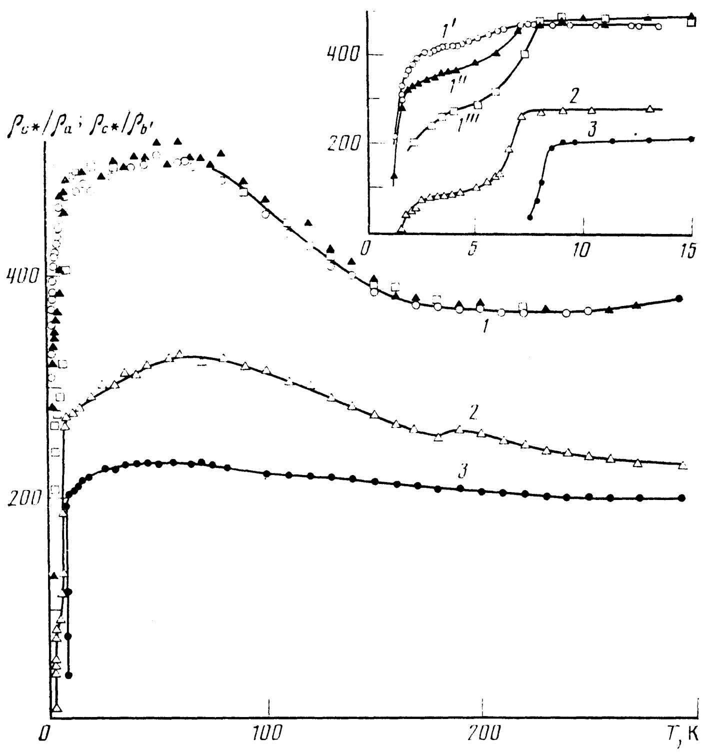

FIG. 6. The temperature dependence of the resistivity anisotropy: 1) ρ_{c*}/ρ_a for β-1.5 crystals; 2) $\rho_{c*}/\rho_{b'}$ for a β-1.5 crystal; 3) ρ_{c*}/ρ_a for β-8 crystal: 1', 1'', and 1''' are ρ_{c*}/ρ_a for different β-1.5 crystals.

for β-8 crystals[7]: ~27.5 kOe/K and ~3.5 kOe/K respectively for H'_a and H'_{c*}.

DISCUSSION OF THE RESULTS

The resistivity anisotropy of β-(BEDT-TFF)$_2$I$_3$ crystals is thus high in the **ab**' plane, reaching values of $\rho_{c*}/\rho_a \approx 500$ for β-1.5 crystals and ~250 for β-8 crystals, at the same time that it is of the order of 1.5–2 in the **ab**' plane. This shows that crystals of both types are quasi-two-dimensional conductors, and confirm similar conclusions drawn for β-1.5 crystals on the basis of x-ray structural results[2,3] and of the anisotropy of the critical magnetic fields.[14,15]

It should be noted that the value found for the anisotropy ρ_{c*}/ρ_a for β-1.5 crystals at $T \gtrsim 9$ K agrees with that calculated from the formula[16]: $\rho_{c*}/\rho_a = (H'_a/H'_{c*})^2$ for a so-called "dirty" superconductor, if we use values of the critical fields obtained by Tokumoto *et al.*[14] and by Ginodman *et al.*[15]

The growth in the anisotropy ρ_{c*}/ρ_a, $\rho_{c*}/\rho_{b'}$, and $\rho_{b'}/\rho_a$ at $T \lesssim 200$ K is evidently related to the start of the structural transition found by Leung *et al.*[17]

It was established that although the behavior of ρ_{c*} and $\rho_{b'}$ for β-1.5 specimens often points to a partial superconducting transition, which starts around 7–8 K, such a transition does not always show up in the behavior of ρ_a. On the contrary, the superconducting transition in β-8 specimens with $T_c \approx 7.5$ K is observed in both temperature dependences $\rho_a(T)$ and $\rho_{c*}(T)$.

It was suggested earlier[8–10] that the steps in the region of 7–8 K on the temperature dependence of ρ_a in β-1.5 crystals arise from the existence of shunting superconducting formations with the appropriate T_c. It is now clear that the dimensions of such formations in the direction of the **a** axis are usually small, at the same time that they can be extended in planes close to the **b'c** plane to an extent comparable with the transverse dimensions of the crystal. Since these inclusions have the derivatives H'_a and H'_c and the anisotropy of the critical fields close to those found for β-8 crystals, it is natural to suggest that there are also similar formations in β-8 specimens, but in larger numbers. Such superconducting inclusions in a β-8 crystal evidently form a spatial network with $T_c \approx 7.5$ K, leading to superconductivity in all directions.

The observed nature of the anisotropy of the critical magnetic fields for the steps near 7–8 K show that the superconducting formations with $T_c \approx 7.5$ K in β-1.5 crystals

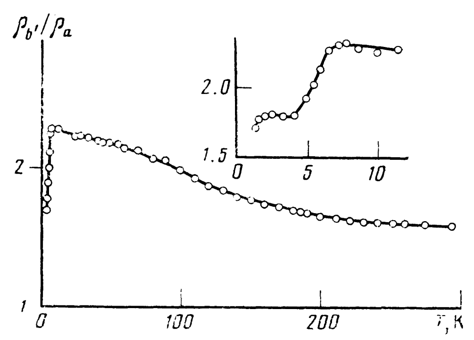

FIG. 7. The temperature dependence of the anisotropy ρ_{b*}/ρ_a for β-1.5 crystal.

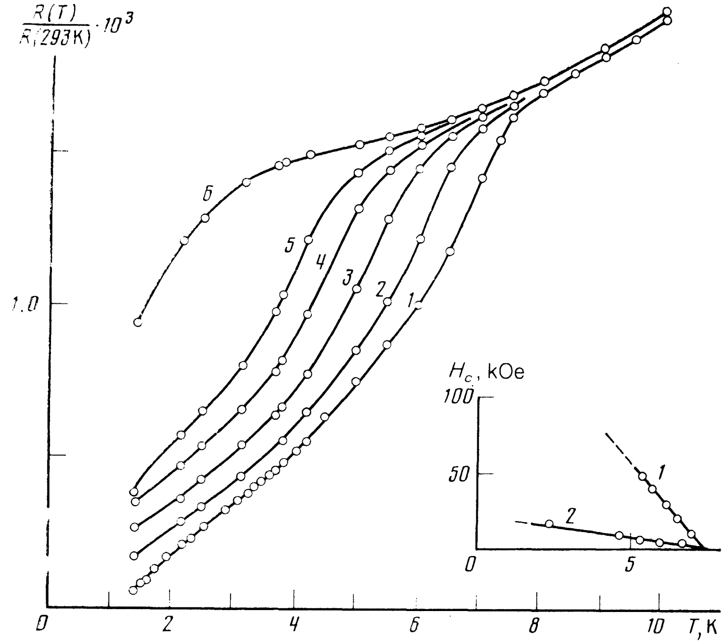

FIG. 8. The temperature dependence of the resistance $R_{c^*}(T)$ in a magnetic field $\mathbf{H}\|\mathbf{c}^*$: curve 1) 0 kOe, 2) 2 kOe, 3) 4 kOe, 5) 8 kOe, 6) 16 kOe; inset, the dependence of the critical fields on T: curve 1) $\mathbf{H}\|\mathbf{a}$, 2) $\mathbf{H}\|\mathbf{c}^*$. The superconducting transition temperature was determined from the start of the transition.

have a layer structure, as occurs in the basic material.

The authors are grateful to S. A. Brazovskiĭ and A. I. Larkin for discussion of the results, to É. B. Yagubskiĭ, E. É. Laukhina and A. I. Kotov for providing the specimens and to A. V. Zvarykina for help with the experiments.

[1)]**b**′ is the direction perpendicular to the **ac*** plane.

[2)]In the present work we have used the approximation to the calculated curves of Montgomery[13]: $y = 0.1963^{\pi x}$ for $x \geqslant 1$, $y = 0.1963 \times \exp(3.2x - 0.0584/x)$ for $x < 1$ for Fig. 1 and $y = \exp[3.2(x - 1/x)]$ for Fig. 3.

[1]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].

[2]V. F. Kaminskiĭ, T. G. Prokhorova, R. P. Shibaeva, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 15 (1984) [JETP Lett. **39**, 17 (1984)].

[3]R. P. Shibaeva, V. F. Kaminskiĭ, and V. K. Bel'skiĭ, Kristallografiya **29**, 1089 (1984) [Sov. Phys. Crystallogr. **29**, 638 (1984)].

[4]E. É. Kostyuchenko, É. B. Yagubskiĭ, O. Ya. Neĭland, and V. Yu. Khodorkovskiĭ, Izv. Akad. Nauk SSSR Ser. Khim. **12**, 2834 (1984).

[5]J. M. Williams, T. J. Emge, H. H. Wang, M. A. Beno, P. J. Copps, K. D. Carlson, and G. W. Crabtree, Inorg. Chem. **23**, 2558 (1984).

[6]V. A. Merzhanov, E. É. Kostyuchenko, V. N. Laukhin, R. M. Lobkovskaya, M. K. Makova, R. P. Shibaeva, I. F. Shchegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 146 (1985) [JETP Lett. **41**, 179 (1985)].

[7]A. V. Zvarykina, P. A. Kononovich, V. N. Laukhin, V. N. Molchanov, S. I. Pesotskiĭ, V. I. Smirnov, R. P. Shibaeva, I. F. Shchegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 257 (1986) [JETP Lett. **43**, 329 (1986)].

[8]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Topnikov *et al.*, Proc. 23rd All-Union Conf. on Low Temperature Physics, Tallin (1984) Part I, p. 124.

[9]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Topnikov, S. I. Pesotskiĭ, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, S. I. Dedik, and L. I. Buravov, Zh. Eksp. Teor. Fiz. **88**, 244 (1985) [Sov. Phys. JETP **61**, 142 (1985)].

[10]L. I. Buravov, M. V. Kartsovnik, V. F. Kaminskiĭ *et al.*, Synth. Metals **11**, 207 (1095).

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

[12]V. A. Merzhanov, E. É. Kostyuchenko, O. E. Faber, I. F. Shchegolev, and É. B. Yagubskiĭ, Zh. Eksp. Teor. Fiz. **89**, 292 (1985) [Sov. Phys. JETP **62**, 165 (1985)].

[13]H. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).

[14]N. Tokumoto, H. Bando, H. Anzai, G. Saito, K. Murata, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. **54**, 869 (1985).

[15]V. B. Ginodman, A. V. Gudenko, and L. N. Zherikhina, Pis'ma J. Eksp. Teor. Fiz. **41**, 41 (1985) [JETP Lett. **41**, 49 (1985)].

[16]A. I. Buzdin and L. N. Bulaevskiĭ, Usp. Fiz. Nauk **144**, 415 (1984) [Sov. Phys. Usp. **27**, 830 (1984)].

[17]P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, and J. M. Williams, J. Am. Chem. Soc. **106**, 7644 (1984).

Translated by R. Berman