Superconducting properties of the orthorhombic phase of bis-(ethylenedithiolo)tetrathiofulvalene triiodide

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The orthorhombic modification of the system (BEDT-TTF)-I_3 undergoes a superconducting transformation under normal pressure and at the temperature of the center of the superconducting transition $T_c = 2.5$ K. The large anisotropy of the critical fields and the proximity of their magnitudes in the *ab* plane to the magnitude of the paramagnetic limit suggests a two-dimensional nature of the superconducting state.

It was reported in Ref. 1 that the system (BEDT-TTF)-I_3 includes a triclinic modification with the composition $(BEDT\text{-}TTF)_2\text{-}I_3$, which transforms into the superconducting state under normal pressure with $T_c = 1.5$ K. Information on the crystal-

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line structure of this compound is presented in Ref. 2. Variation of the conditions of electrochemical synthesis by using different solvents and selecting the working current leads to the growth of crystals of a number of other crystalline modifications of the same system. In this paper we present data on the properties of the orthorhombic phase of the system (BEDT-TTF)-I_3, which undergoes a superconducting transformation at normal pressure with $T_c = 2.5$ K.

The crystalline structure of this compound has not yet been identified, so that we do not know its exact composition. At the present time, we only have data on the parameters of the orthorhombic unit cell, which contains eight I_3^- anions: $a = 13.8$Å, $b = 14.7$Å, $c = 33.6$Å. The crystals grow in the form of thin plates, extended along the a axis. The characteristic dimensions of the plates are of the order of $1 \times 0.1 \times 0.01$ mm.

The conductivity of the crystals was measured by a four-contact method with dc current. Platinum electrodes ϕ 10 $\Phi\mu$m were glued with the help of a silver paste to four gold strips, deposited beforehand on the crystal. The resistance of the contacts did not exceed several tens of Ω. The magnitude of the measuring current was chosen to equal 10 μA. *The sensitivity of the measuring setup amounted in this case to* 10^{-3} Ω. The resistance along the a axis as measured in all experiments.

Figure 1 shows the temperature dependence of the resistance of several specimens in the entire temperature range investigated. The average value of the room-temperature conductivity of the crystals was $\sigma_{300} = 20 \pm 5\ \Omega^{-1} \cdot \text{cm}^{-1}$. The behavior of the resistance at temperatures between 160 and 100 K in the curves in Fig. 1 is interesting. The resistance of crystals 1, 2, and 3 in this temperature interval increases with decreasing temperature, although to a different degree. For crystal 4, there is no growth but the growth of the resistance slows down; the curve for crystal 5 has a small break, almost unnoticeable in Fig. 1, at 125 K. The change in resistance in the temperature region examined occurs with a small hysteresis, shown in the curve of crystal 1.

The presence or absence of a "hump" near 120 K on the temperature dependence of the resistance leads to appreciable changes in the magnitude of the resistance of the crystals at 4.2 K. The ratio $R_{300}/R_{4.2}$ for crystals 1, 2, 4, and 5 amounts to 6.6, 16, 26, and 150, respectively. Nevertheless, all of them transform into the superconducting state essentially with an identical transition temperature.

The low-temperature parts of the curves in Fig. 1 are shown in greater detail in the inset. It is evident that the temperature of the superconducting transition T_c, which was determined from the centers of the corresponding curves, lies in the interval 2.4–2.6 K for different crystals. It is interesting that the beginning of the transition (with $T > T_c$) is smeared most in the most perfect specimen 5 with $R_{300}/R_{4.2} = 150$. At the same time, completion of the transition (at $T < T_c$) is extended most for specimen 1 with the lowest ratio $R_{300}/R_{4.2}$.

To obtain the curves of a transition in a magnetic field, the module with the specimen was mounted in a special rotatable setup inside a superconducting solenoid. This permitted changing the orientation of the specimen relative to the magnetic field and setting the specimen in the desired position to within $\pm 1°$. In this case, the fact that the field was parallel to the ab plane was easily ascertained from the sharp mini-

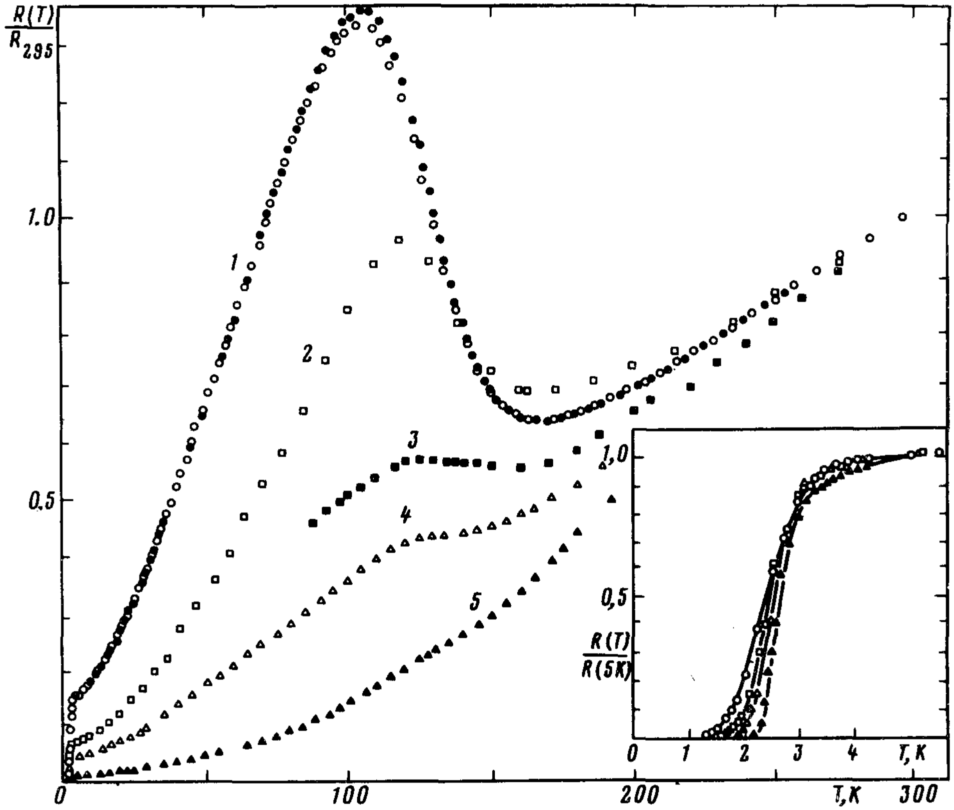

FIG. 1. Temperature dependence of the resistance for five specimens. Curves of the superconducting transition of these specimens are shown in the inset.

mum in the angular dependence of the resistance, measured in a fairly high magnetic field at $T < T_c$. An example of this dependence is shown in Fig. 2.

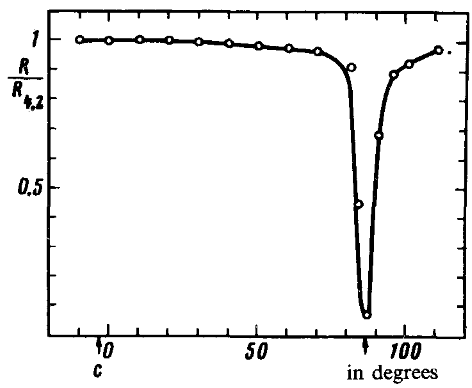

FIG. 2. Angular dependence of the resistance of the specimen in a magnetic field $H = 20$ kOe at $T = 1.5$ K.

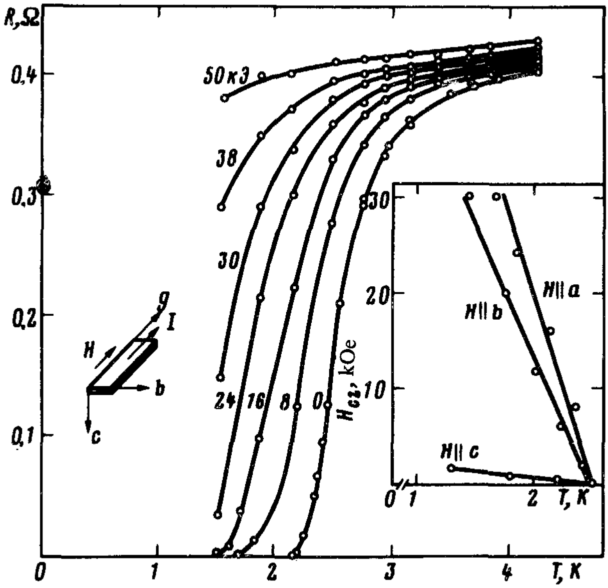

FIG. 3. Suppression of the superconducting transition in specimen 5 by a magnetic field $H\parallel a$. The temperature dependence of the critical fields is shown in the inset.

The curves of the superconducting transition of specimen 5 in a magnetic field oriented along the a axis are shown in Fig. 3. The temperature dependence of critical fields, applied along the direction of each of the crystallographic axes, is shown in the inset in this figure. The lowest critical fields are obtained when the field is oriented perpendicular to the ab plane. The critical fields in directions parallel to this plane are one to one and one half orders of magnitude greater, and their values turn out to be on the order of magnitude of the paramagnetic limit. At $T_c = 2.5$ K the magnitude of the gap is $\Delta \sim 10$ K ~ 70 kOe. Whereas the magnitude of the longitudinal critical fields is on the order of 30 kOe at temperatures only 1.5 times lower than the critical value. We note also that the destruction of superconductivity by a longitudinal field at $T = 1.5$ K proceeds extremely sluggishly: traces of resistance appear at 15–20 kOe, and the transition terminates at $H > 50$ kOe. All of this evidence suggests a two-dimensional nature of the superconductintg state.

As is evident from Fig. 3, the magnetic field suppresses the drop in resistance, beginning with a temperature on the order of 4 K. This is especially clearly manifested in fields parallel to the easy axis c. Figure 4 shows the field dependences of the resistance of specimen 5 at $T = 4.2$ K with different orientations of the magnetic field. The 5% increase in resistance in a field of ~ 15 kOe with H$\parallel c$ is too large for the usual galvanomagnetic effect. With a conductivity of $\sigma_{4.2} = 3\times 10^3\ \Omega^{-1}\cdot \text{cm}^{-1}$ and a stoichiometric concentration $n \simeq 10^{21}$ cm^{-3}, the quantity $\Delta\rho/\rho \sim (\omega\tau)^2 = (eH\tau/mc)^2 \sim (H\sigma/nec)^2 \sim 10^{-5}$ would have to be three orders of magnitude smaller. It thus appears that the superconducting transition begins at temperatures ~ 4 K.

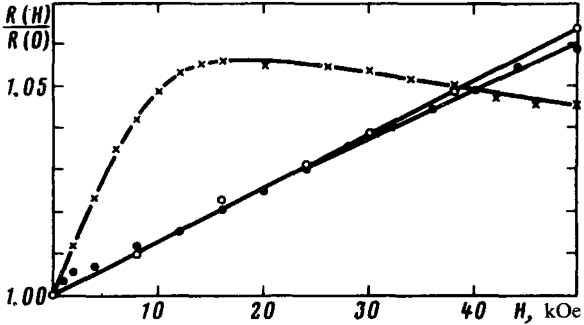

FIG. 4. Field dependences of the resistance of specimen 5 at $T = 4.2$ K: $H \| a$ (○), $H \| b$ (●), $H \| c(x)$.

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[1]É. B. Yagubskiĭ, I. F. Shegolev, 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**, to be published].
[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**, to be published].

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