# Superconducting transition in the dielectric $\alpha$ phase of iodine-doped $(BEDT–TTF)_2I_3$ compound

É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, R. P. Shibaeva,
E. É. Kostyuchenko, A. G. Khomenko, Yu. V. Sushko, and A. V. Zvarykina
*Institute of Chemical Physics, Academy of Sciences of the USSR*

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When crystals of the $\alpha$ phase of $(BEDT–TTF)_2I_3$ are doped with iodine, the metal–insulator transition is partially suppressed and a transition to the superconducting state with $T_c = 3.1–3.3$ K occurs.

The compound $(BEDT–TTF)_2I_3$ exists in two polymorphic modifications, one of which (the $\beta$ phase) transforms to the superconducting state at $T_c = 1.5$ K (Ref. 1) and the other (the $\alpha$ phase) undergoes a sharp metal–insulator transition near 140 K (Ref. 2) We have found that doping the $\alpha$ phase with iodine partially suppresses the metal–insulator transition and causes a superconducting transition at $T_c = 3.1–3.3$ K.

The structure of the $\alpha$ phase, like the structure of the $\beta$ phase, is two-dimensional in nature which typically has layers that consist of BEDT–TTF molecular units separated by $I_3^-$-anion layers. However, in contrast to the analogous layer of the $\beta$ phase that consists of the BEDT–TTF units of one type, the $\alpha$-phase layer contains two types of differently oriented BEDT–TTF units.

The parameters of the triclinic unit cell of $\alpha$-$(BEDT-TTF)_2I_3$ are $a = 10.785$ (7), $b = 9.172$ (7), $c = 17.39$ (1) Å, $\alpha = 82.08$ (3), $\beta = 96.92$ (3), $\gamma = 89.13$ $(3)^0$, $V = 1690.3$ Å$^3$, $Z = 2$; and the space group is $P\bar{1}$. Figure 1 shows its projection along the diagonal $\mathbf{a}' = \mathbf{a} + \mathbf{b}$. The BEDT–TTF molecules that occupy the common positions III, III', and III" form a single stack, while the molecules I and II with a center of inversion form another stack. The distribution of bond lengths in the units I and II is nearly the

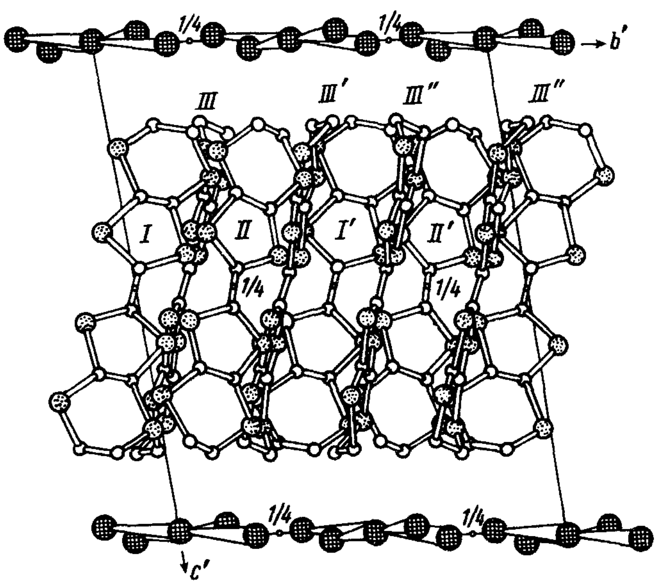

FIG. 1. Projection of the structure of $\alpha$- $(BEDT-TTF)_2I_3$ along the direction $\mathbf{a} = \mathbf{a} + \mathbf{b}$.

same as the distribution characteristic for neutral BEDT–TTF molecules, whereas the unit III is characterized by a bond-length distribution typical of cation radicals.[3] The molecules I and II are not completely parallel to each other (the dihedral angle is ~ 11°) and their planes form angles of 109.5° and 120.3°, respectively, with the plane of unit III. The cation-radical layer contains slightly shortened contacts S . . . S. There are more of such contacts in the $\alpha$ phase than in the $\beta$ phase, and their length varies from 3.468 to 3.669 Å.

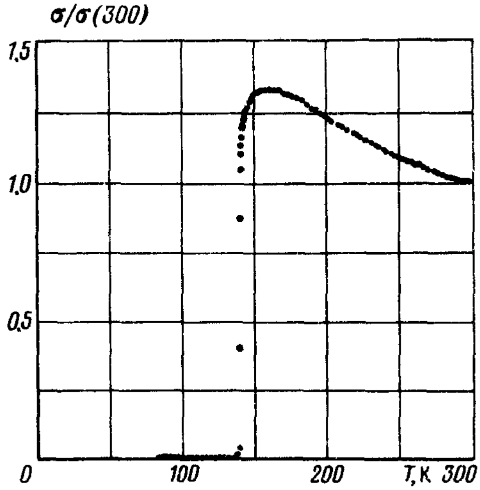

FIG. 2. Temperature dependence of the conductivity of $\alpha$-$(BEDT-TTF)_2I_3$ crystals.

The conductivity of $\alpha$-(BEDT–TTF)$_2$I$_3$ crystals was measured with direct current by a four-contact method along the $\mathbf{b}' = \mathbf{b} - \mathbf{a}$ axis. At room temperature the conductivity on the order of 20–30 mho/cm and it generally increases very slightly at first (by ~20–40%) as the temperature is reduced. A sharp metal–insulator transition occurs at $T = 137$ K: The conductivity in the range 2–3 degrees decreases approximately by two orders of magnitude and continues to decrease rapidly as the temperature is further reduced (Fig. 2). This transition proceeds without hysteresis.

The temperature dependence of the conductivity, which changes considerably after holding the crystals in the saturated iodine vapor for one hour at $T = 25$ °C (Fig. 3) begins to resemble the temperature evolution of the resistance of the second superconducting modification ($\gamma$ phase) of the system (BEDT-TTF)–I.[4] However, the "hump" here is much higher: The resistance at the peak can be several orders of magnitude greater than at room temperature. The very diffuse superconducting transition begins near 4.5 K, so that at 1.3 K it is still not completed (see inset in Fig. 3). The center of the transition for the two measured samples lies at $T = 3.1$ and 3.3 K. X-ray diffraction analysis shows that the parameters of the unit cell remain unchanged after iodine doping.

Before the superconducting transition, the samples are in a high-resistance state:

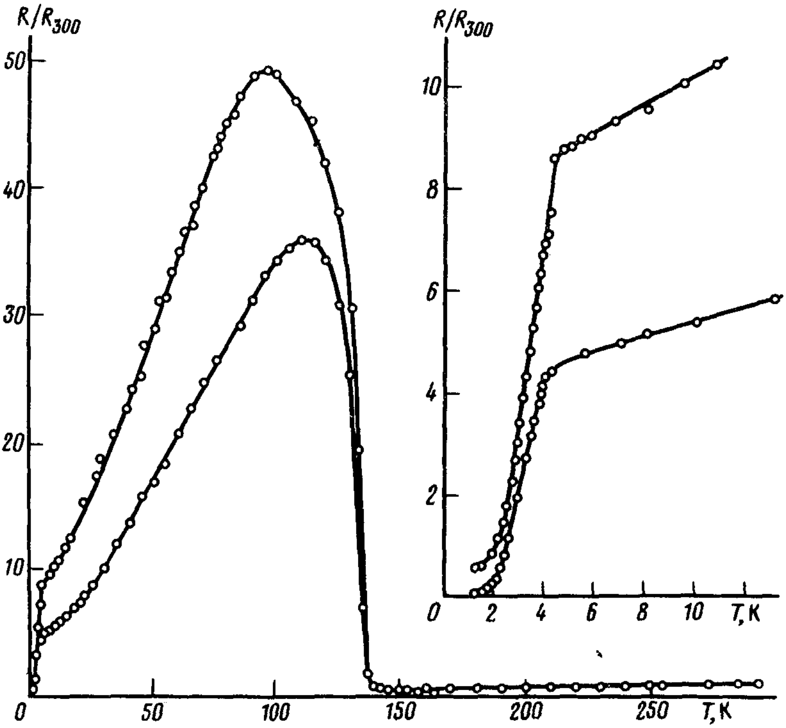

FIG. 3. Temperature dependences of the resistance of two iodine-doped samples of $\alpha$-(BEDT–TTF)$_2$I$_3$. The inset shows the curves of the superconducting transition in these samples.

At $T = 4.5$ K the resistance can be almost an order of magnitude higher than at room temperature, i.e., before the superconducting transition, the conductivity is only 2–5 mho/cm. What is the nature of the superconducting state under these conditions?

It is possible that iodine doping is nonuniform and only part of the sample (not revealed by x-ray structural analysis) transforms to another conducting state that undergoes a superconducting transition. The formation of this new conducting phase could be associated with the fact that after the excess iodine enters the space between the layers of BEDT–TTF molecules it increases their degree of oxidation. This is entirely possible, because some of the molecules in the undoped crystals are apparently neutral (see the discussion above). In this case, doping can increase the state density and can therefore lead to the appearance or intensification of superconductivity. By adding the conductivities of this new modification and of the starting $\alpha$ phase, we obtain the curves shown in Fig. 3. Because of the formation of boundaries inside the crystal, the superconducting transition may not reach its completion, and the resistance of the samples can be quite high before the transition.

On the other hand, it is conceivable that we are dealing here with a superconducting transition associated with a degenerate impurity band which is formed when the crystals are doped with iodine. Superconductivity of this type has been observed in ordinary semiconductors,[5] although the superconducting transition in such materials occurs at temperatures below 1 K.

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