Transformation of the α-phase $(BEDT\text{-}TTF)_2I_3$ to the superconducting β phase with $T_c = 6\text{–}7$ K

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(Submitted 20 August 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 6, 293–294 (25 September 1986)

The crystals of the α-phase $(BEDT\text{-}TTF)_2I_3$, which become a dielectric at 137 K, undergo a transition to the superconducting β phase with $T_c = 6\text{–}7$ K when they are heated to 70° C or better and then held at this temperature. The transformation is accomplished by the appearance of features on the temperature-resistance curve of the original crystal and by the heat absorption.

1. Two crystalline polymorphic modifications of an organic metal $(BEDT\text{-}TTF)_2I_3$ are now known: the α phase, which undergoes a sharp metal-insulator transition[1–3] at 137 K, and the β phase, which goes superconducting[4,5] at $T_c = 1.5\text{–}8$ K.

We have established that α-phase crystals (which are grown electrochemically)

 0021-3640/86/180376-03$01.00

become β-phase crystals upon heating. An x-ray diffraction analysis of α-phase samples, after being heated, revealed the presence in the Weissenberg rotating-crystal photographs of reflections characteristic of the β phase. The transformation rate, which is already appreciable at 70 °C, increases considerably with increasing temperature. For example, the time necessary for a transition to occur at 80 °C is 10–15 hours and at 100 °C it decreases to 5 or 6 hours, slightly varying from one sample to the next.

2. The conductivity of the crystals was measured with a direct current according to the four-contact method; the samples were placed in helium. The contacts were established with a graphite paste. The temperature dependences of the resistance at $T<300$ K of the original α-phase samples and of the β-phase formed after heating the samples are in good agreement with the temperature dependences reported previously.[2–5] The structural features associated with the transformation, $\alpha \rightarrow \beta$, are seen in these samples at $345\ \text{K} < T < 370$ K. A slow increase in temperature (in ~ 5 h) in this region gives rise to the appearance on the $R(T)$ curve for the α-phase crystal of a region in which the resistance decreases appreciably (to 40%), which then gives way to a region in which it increases (Fig. 1). A subsequent cooling of the sample causes its resistance to decrease monotonically, culminating below 8 K with a rather prolonged superconducting transition.

The crystals heated, as indicated in Sec. 1, at 100 °C for six hours had the highest critical temperature, $T_c \cong 7$ K, which was determined from the midpoint of the superconducting transition (see the inset in Fig. 1). Even in this case, however, the transition width is appreciable, $\Delta T \cong 3$ K, which seems to indicate that the inhomogeneity of the heat-treated β-phase crystals is considerable. The same situation applies to β-phase samples obtained in the thermolysis of the ϵ phase.[5]

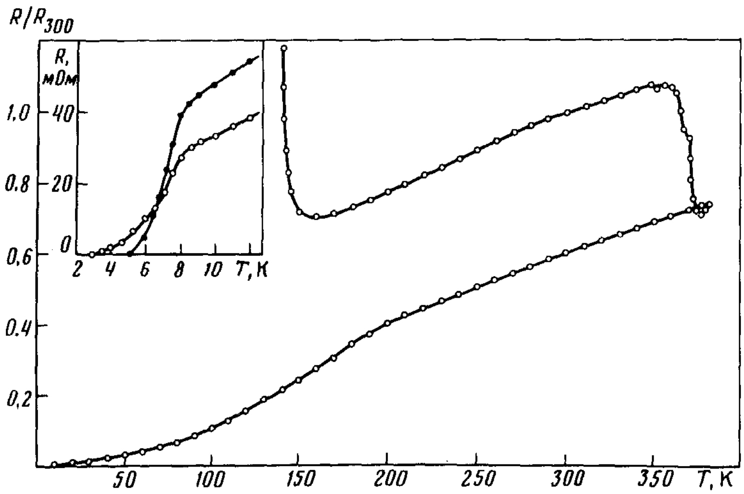

FIG. 1. Temperature dependence of the resistance of a α-(BEDT-TTF)$_2$I$_3$ crystal during the cooling-heating-cooling cycle involving a transformation to the β phase. The inset shows the superconducting transition of this crystal (○) and of the β-phase sample obtained by heat treatment of α-(BEDT-TTF)$_2$I$_3$ (●).

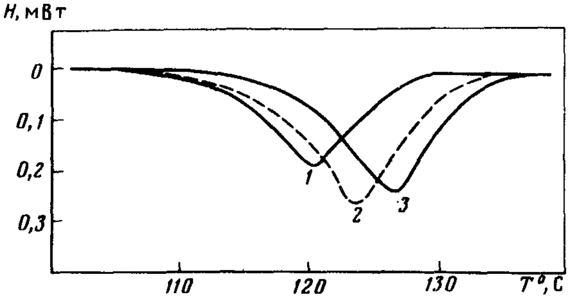

FIG. 2. Thermograms of α-$(BEDT\text{-}TTF)_2I_3$ crystal in the region of $\alpha \rightarrow \beta$ phase transformation at the following heating rates: 1—6.9 °C/min; 2—10.4 °C/min; 3—15.6 °C/min. H is the heat flux.

3. The thermograms in the region 30°–300 °C were recorded with a DuPont 1090 thermoanalyzer. These thermograms showed that a considerable amount of heat (up to 8 J/g) is absorbed in the region of phase transformation. This process reaches its peak at 120°–130° at heating rates of 7°–15° C/min (Fig. 2). Decreasing the latter leads to a smearing of the maximum and to its shift toward the low-temperature region. Upon heating to 150 °C, no change in the mass of the substance was detected. The thermal effect which we detected apparently stems from the increase in the energy of the crystal lattice, which occurs irreversibly when the stable α modification of $(BEDT\text{-}TTF)_2I_3$ exceeds the temperature limits.

We wish to thank L. P. Rozenberg for furnishing the x-ray photographs and I. F. Shchegolev for useful discussions.

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Translated by S. J. Amoretty