Nature of the high-temperature superconducting state with $T_c = 7–8$ K in β-(BEDT-TTF)$_2$I$_3$

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Crystals of β-(BEDT-TTF)$_2$I$_3$ synthesized by the $\epsilon \rightarrow \beta$ conversion have T_c values up to 7.5 K at standard pressure and are mosaic twins. The approximate equality of T_c and the upper critical field of these crystals to the corresponding properties of the high-pressure phase can be explained on the basis of a suppression in each case of a superstructural transition which lowers T_c to 1.5 K.

1. Seven different compounds have at present been identified in the system of iodides of BEDT-TTF. The composition and structure of five of them are described in Ref. 1; the structure and properties of the other phases will be reported in the near future. Some of these compounds are superconductors at standard pressure.[2–4]

It was originally found that β-(BEDT-TTF)$_2$I$_3$ crystals go superconducting at $T_c \simeq 1.5$ K (we will call these "β-1.5 crystals"). It was later found[5,6] that in certain samples of this phase a diffuse superconducting transition begins at 7–8 K, and crystals with a sharp partial transition at the same temperatures were found.[7] The latter result was subsequently reproduced in Ref. 8.

It was suggested in Refs. 5–7 that this behavior stems from the existence of yet another superconducting phase in the (BEDT-TTF)-I system, with T_c at 7–8 K. It was found, however, that values $T_c = 7$–8 K are also characteristic of crystals of the same β phase but produced by the conversion[9] $\epsilon \to \beta$ ("β-8 crystals").

In an effort to determine the reasons for the fivefold increase in T_c in these crystals, we have carried out a detailed step-by-step x-ray diffraction analysis of one of them during the $\epsilon \to \beta$ conversion, and we have measured the anisotropy of their upper critical fields.

2. For the x-ray diffraction, we selected a single crystal of the ϵ phase with dimensions of $0.5 \times 0.7 \times 0.1$ mm. The integral intensities of 14 strong reflections of the ϵ phase[1] are measured at room temperature at the end of each cycle of crystal heating at 70 °C for 1.5–2 h. After 5.5 h of heating, the intensities of the reflections decrease by a factor ~20, and their half-widths increase from 0.22 °C to 1.24 °C. There is no substantial change in the orientation of the crystal in the process. After 8.5 h of heating, the ϵ-phase reflections can no longer be detected.

In their place we find some new reflections, all of which can be identified as reflections of the β-phase[1] under the assumption that the crystal is a twin with a twofold axis coinciding with a monoclinic axis of the original ϵ phase. The ratio of the volumes of the two individuals in the twin is 3:2. The twin junction lies in the (001) plane, coinciding with the (001) plane of the initial ϵ phase. The orientation of the axes ($\mathbf{a}_1$, $\mathbf{b}_1$,$\mathbf{c}_1$) and ($\mathbf{a}_2$, $\mathbf{b}_2$, $\mathbf{c}_2$) of the unit cells of the β phase, which forms with respect to the axes ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) of the cell of the ϵ phase, is determined by the following relations:

$$\begin{aligned}
\mathbf{a}_1 &= 0.339\,\mathbf{a} + 0.263\,\mathbf{b} + 0.004\mathbf{c} & \qquad \mathbf{a}_2 &= 0.339\mathbf{a} - 0.263\mathbf{b} - 0.004\mathbf{c}\\
\mathbf{b}_1 &= 0.583\mathbf{a} - 0.114\mathbf{b} + 0.002\mathbf{c} & \qquad \mathbf{b}_2 &= 0.583\mathbf{a} + 0.114\mathbf{b} - 0.002\mathbf{c}\\
\mathbf{c}_1 &= 0.017\mathbf{a} + 0.229\mathbf{b} - 0.872\mathbf{c} & \qquad \mathbf{c}_2 &= 0.017\mathbf{a} - 0.229\mathbf{b} + 0.872\mathbf{c}.
\end{aligned}$$

3. The small number of reflections and their very diffuse nature (their half-width is ~5°) are evidence that the conversion $\epsilon \to \beta$ produces low-quality mosaic crystals. The average room-temperature conductivity of these crystals is on the order of 15 ± 5 S/cm, slightly lower than that of β-1.5 crystals.[2] The decrease in the resistance toward 10 K is characterized by the values $R_{300}/R_{10} \simeq 150$–200 instead of 350–460.

The superconducting transition is noticeably stretched out, to a width which depends strongly on the temperature and the duration of the $\epsilon \to \beta$ conversion. The beginning of the transition, on the other hand, essentially always occurs at 8–8.5 K (Fig. 1).

Figure 2 shows the temperature dependence of the upper critical field corresponding to the middle of the resistive transition of one of the β-8 crystals in a field of given magnitude and direction. The crystals studied exhibit a characteristic two-dimensional

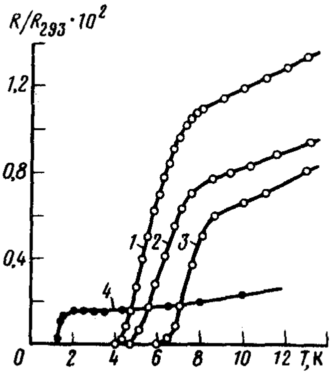

FIG. 1. 1–3—Representative resistive superconducting transitions in β-8 crystals obtained by the conversion $\epsilon\rightarrow\beta$ under various conditions; 4—the transition in the β-1.5 crystal, for comparison.

anisotropy, with $H_{c2}^{(a)}\simeq H_{c2}^{(b*)}\gg H_{c2}^{(c*)}$. The values of the derivative $(dH_{c2}/dt)_{T_c}$ in the a, $b*$, $c*$ directions are 27.5, 25, and 3.4 kOe/K, respectively.

4. The transition temperature and the values of $(dH_{c2}/dT)_{T_c}$ of these crystals are very close to the corresponding characteristics of the high-pressure phase which exists in β-(BEDT-TTF)$_2$I$_3$ at $P\gtrsim 1$ kbar at low temperatures.[10] According to the measurements of Ref. 11, for example, at $P=1.6$ kbar we have $(dH_{c2}^{(c*)}/dT)_{T_c}=2.9$ kOe/K and $(dH_{c2}^{(a)}/dT)_{T_c}=33$ kOe/K. These results suggest that the reason for the increase in the transition temperature from 1.5 to 7.5 K in β-(BEDT-TTF)$_2$I$_3$ is that at least part of the sample attributable to the $\epsilon\rightarrow\beta$ conversion is in a state which is ordinarily stable only at high pressures. The same factor can lead to the existence at 7–8 K of partial superconducting transitions in β-1.5 crystals.[7]

In this connection, it might be suggested that the initially high value of T_c in β-(BEDT-TTF)$_2$I$_3$ decrease to 1.5 K because of a superstructural transition which occurs at 180 K (Refs. 12 and 13), while the increase in T_c to 7.5 K in the high-pressure

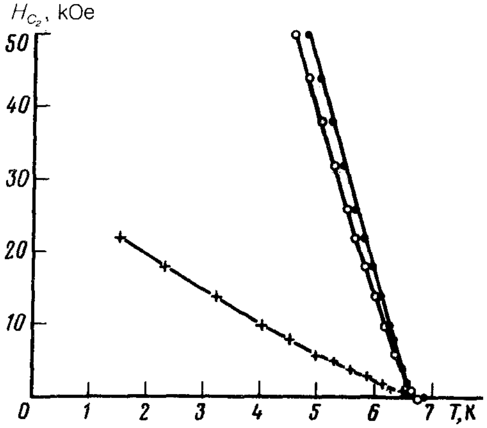

FIG. 2. Dependence of the upper critical field on the temperature of the middle of the superconducting resistive transition in one of the β-8 crystals. ●—$H\parallel a$; ○—$H\parallel b*$; ×—$H\parallel c*$.

phase[10] stems from the suppression of this transition. The disorder which is characteristic of β-8 crystals may itself, like the stresses that it causes, be another factor that leads to the suppression of such a transition.[2)] We would then find a natural explanation for the agreement of the superconducting characteristics of these crystals and of the high-pressure phase.

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[2)] Analogous phenomena have been observed[14] in layered superconductors of the TaS_2 type.

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