Study of the superconducting transitions in two modifications of β-$(\mathrm{BEDT{-}TTF})_2I_3$ on the basis of the diamagnetic-screening signal

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(Submitted 18 December 1985)
Zh. Eksp. Teor. Fiz. **90**, 2172–2175 (June 1986)

A study is made of the superconducting transition in two modifications of β-$(\mathrm{BEDT{-}TTF})_2I_3$ with $T_c \approx 1.5$ K and $T_c \approx 7.5$ K. The results indicate that the superconductivity is of a bulk nature in both types of crystals. An anisotropy of the diamagnetic susceptibility is detected in the directions a and c^*. It is found that the diamagnetic transition is appreciably shifted toward lower temperatures from the resistive transition. Possible causes of such behavior are discussed.

At least five crystalline modifications of the system (BEDT–TTF)–I are known,[1] some of which are superconducting at normal pressure, with transition temperatures T_c ranging from 1.4 to 7.5 K.[2–6] Of particular interest in this system is the β phase of the compound $(\mathrm{BEDT{-}TTF})_2I_3$. Crystals of this phase can be obtained by two methods. First, they can be grown by ordinary chemical or electrochemical means.[7,8] We shall call these crystals type β-1.5. The other method[6] of obtaining them is the vacuum sublimation of iodine from crystals of the ε phase at a temperature of around 100 °C. Here the beginning of the superconducting transition is shifted to 8–9 K, and in the case of the most complete $\varepsilon \rightarrow \beta$ transformation the center of the transition lies at $T_c = 7.5$ K. These crystals will be called type β-7.5.

The reasons for such a marked difference in T_c in crystals that would seem to be of the same composition and structure are not completely clear. One hypothesis attributes the increase in T_c to the stabilization, in at least part of the crystal, of a high-pressure phase having a T_c in the range 7–7.5 K at pressures $\gtrsim 1$ kbar.[9] Such a stabilization could be stimulated by local lattice distortions arising during the conversion $\varepsilon \rightarrow \beta$ on account of the marked difference of the structures of these phases. This hypothesis would seem to be supported also by the presence of steps on the resistance-versus-temperature curves $R(T)$ in the 7–8 K region in some of the type β-1.5 crystals, indicating a partial superconducting transition.[4,5]

In this connection it is of interest to elucidate the question of the completeness of the superconducting transition in β-$(\mathrm{BEDT{-}TTF})_2I_3$ crystals obtained by different methods and characterized by different superconducting properties. For this purpose we have studied the superconducting transition in type β-1.5 and β-7.5 crystals on the basis of the diamagnetic-screening signal, the size of which gives an idea of the fraction of the sample volume that has gone into the superconducting state.

For the measurements we chose one crystal of each type. The type β-1.5 crystal, obtained by an electrochemical method, had dimensions of $\sim 1 \times 0.7 \times 0.3$ mm. The $R(T)$ curve for this crystal exhibited a step in the interval between 7 and 9 K at which its resistance decreased by a factor of 2.5, indicating a partial superconducting transition. The type β-7.5 crystal, obtained by the conversion $\epsilon \rightarrow \beta$, had dimensions of $\sim 3 \times 0.9 \times 0.07$ mm. The superconducting transition according to the resistance began at 8.5 K, and the center of the transition lay at $T_c = 7.2$ K. The resistance measurements in both cases were done by a dc four-point-probe method in the direction of the high-conductivity axis a. The low-temperature parts of the $R(T)$ curves are shown in Fig. 1.

The change in the dynamic susceptibility of the samples upon their transition to the superconducting state was detected from the out-of-balance voltages induced in two measuring coils connected in opposition, one of which contained the crystal under study and the other a Nb–Ti reference sample of similar shape and volume, with $T_c = 9.25$ K. The signal observed in this way was due to the reaction of the sample to a change in the external magnetic field and, consequently, represented the screening signal.

The coils were 3 mm long, had an inside diameter of 1 mm, and contained 1500 turns each. They were placed in an alternating magnetic field $H_\sim$ created by a common magnetizing coil. The amplitude of the field could be chosen between 5 and 500 mOe and the frequency between 10^3 and 10^4 Hz.

For cooling the samples below 1.5 K we used the adiabatic demagnetization of ferric ammonium sulfate. For this purpose the system of coils was mounted on one end of a copper cold finger, the other end of which was pressed into a salt pellet. The samples were cemented to the cold stage with BF-2 adhesive. The samples and coils were shielded from changes in the external magnetic field by a superconducting shield. For the temperature measurements we used two

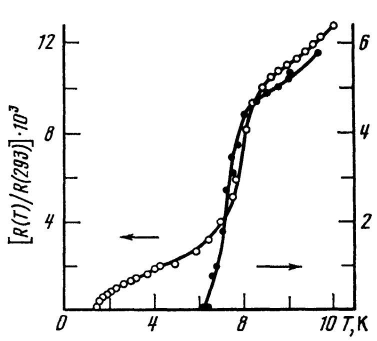

FIG. 1. Temperature dependence of the resistance of samples of two modifications of β-$(\mathrm{BEDT{-}TTF})_2I_3$. The open points are for a β-1.5 type crystal (electrochemically grown); the filled-in points are for a β-7.5 crystal (obtained by $\varepsilon \rightarrow \beta$ conversion).

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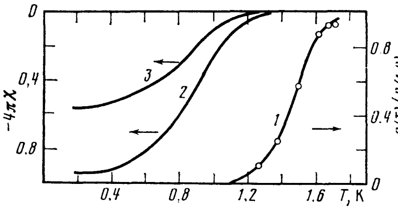

FIG. 2. Superconducting transition in a β-1.5 type crystal: 1) temperature dependence of the resistance in the transition region; 2,3) change in the diamagnetic susceptibility $4\pi\chi$ during the transition for two different directions of the measuring field, $H_\sim \| c^*$ and $H_\sim \| a$, respectively.

semiconducting resistance thermometers,[10] cemented to the cold finger. The accuracy of their calibration and the agreement of their temperature with that of the samples were checked against the superconducting transition of the reference sample ($T_c = 9.25$ K) and a Cd sample ($T_c = 0.518$ K) placed next to the crystal under study. The error in the temperature measurement was less than 0.01 K in the interval from 0.1 to 4 K and less than 0.1 K at temperatures above liquid-helium temperature.

The results of the measurements for the β-1.5 crystal are shown in Fig. 2. Curve 1 shows the temperature dependence of the resistance in units of its value at 1.8 K. Curves 2 and 3 show the quantity $4\pi\chi$, defined as the ratio of the signals from the test and reference samples, divided by the ratio of their volumes. Curve 2 refers to the case $H_\sim \| c^*$, curve 3 to $H_\sim \| a$. The strength of the measuring field $H_\sim = 15$ mOe was chosen such that a further decrease in it did not change the results. No dependence of the susceptibility on frequency was observed within the measurement error.

For $H_\sim \| c^*$ the value of $4\pi\chi$ below 0.3–0.4 K corresonds to a practically complete screening of the entire sample. For $H_\sim \| a$ it reaches ~55% of its maximum value. In both cases the appreciable growth of the diamagnetic susceptibility begins at $T \approx 1.2$ K, where the sample has practically no resistance. The end of the transition occurs at temperature much lower than the temperature $T_c = 1.45$ K defined as the center of the resistive transition.

We observed absolutely no screening effect corresponding in temperature to the eight-kelvin step on the $R(T)$ curve.

Figure 3 shows the analogous data for the β-7.5 type crystal. In this case for the $H_\sim \| c^*$ measurements, which were done after $H_\sim \| a$ measurements, the crystal was cut into several parts which were then cemented into a packet of dimensions $\sim 0.4 \times 0.4 \times 1$ mm, with the long axis along c^*. The value of $H_\sim$ was 0.5 Oe.

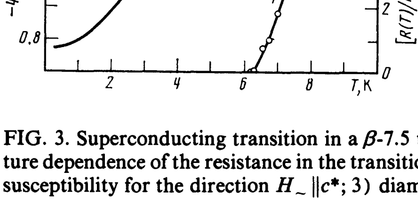

FIG. 3. Superconducting transition in a β-7.5 type crystal: 1) temperature dependence of the resistance in the transition region; 2) diamagnetic susceptibility for the direction $H_\sim \| c^*$; 3) diamagnetic susceptibility for the direction $H_\sim \| a$.

The appreciable growth of the diamagnetic susceptibility for this crystal also begins after the resistive transition is practically complete. For $H_\sim \| c^*$ the maximum value of $4\pi\chi$ corresponds to a screening of ~85% of the sample volume, while for $H_\sim \| a$ it is 25%. With allowance for the error in determining the volumes of the samples and the difference in their shapes, it can be assumed that in this case the screening for $H_\sim \| c^*$ is practically complete below 0.6–0.7 K.

The behavior of the samples exhibits several features that should be discussed. First of all, there is a noticeable shift of the transition toward lower temperatures from that of the resistive transition. In Ref. 11 the diamagnetic transition in β-1.5 crystals was observed in approximately the same temperature interval, but unfortunately there were no data on the resistive transition in that study. Analogous behavior, though less pronounced, is characteristic of the Bechgaard-type superconductors $(\mathrm{TMTSeF})_2\mathrm{X}$ (Ref. 12).

It is clear that, generally speaking, the observed shift of the transition is due to the fact that the diamagnetic susceptibility is proportional to the volume of the screened part of the sample, whereas the resistance can be due to parts of the sample with very small volumes. Therefore, any inhomogeneity of the sample with respect to T_c will shift the diamagnetic transition toward lower temperatures from those of the resistive transition. This evidently explains why there is no screening signal corresponding to the partial transition at ~8 K in the β-1.5 crystal. A temperature shift can also be caused by an anomalously large magnetic-field penetration depth, exceeding the linear dimensions of the superconducting regions which are formed. Which of these two causes is decisive is hard to say right now. We shall merely point out that the appreciable width of the transitions, especially in the case of the β-7.5 crystal, argues more in favor of an inhomogeneity of the samples.

The different degree of screening in different directions is evidently due to features of the β-$(\mathrm{BEDT{-}TTF})_2\mathrm{I}_3$ structure, which is characterized[8] by an alternation, along the c^* direction, of layers of BEDT–TTF molecules separated by layers of the anions I_3^-. Under such conditions, the passage of flow-through screening currents in the direction of the c^* axis can be inhibited by various causes.

In conclusion we note that the results of our study of superconducting transitions in crystals of two modifications of β-$(\mathrm{BEDT{-}TTF})_2\mathrm{I}_3$ on the basis of the diamagnetic-screening signal indicate that these transitions have a bulk character. It might be assumed that such a large screening signal is due to surface superconductivity, but then it would become difficult to explain the smooth, wide (especially for the β-7.5 crystal) superconducting transition. A distinctive characteristic of these crystals is a shift of the diamagnetic transition toward lower temperatures from those of the resistive transition. This is most likely indicative of a strong nonuniformity of the samples over their volume.

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Translated by Steve Torstveit