Coexistence of different superconducting phases with transition temperatures between 1.5 and 7 K in the (BEDT-TTF)-I_3^- system

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Two superconducting phases can be identified in the (BEDT-TTF)-I_3^- system; the transition temperature for the first phase is $T_c = 1.5$ K, while T_c varies between 2 and 3.3 K for the second phase, depending on the crystal. Appreciable variations in composition are typical for crystals of both phases. The small amount of the second phase present in crystals in the first phase causes the resistance to drop for $T \approx 4$ K, i.e., prior to the start of the transition itself. In addition, pretransition phenomena beginning at $T = 7$–8 K are observed for crystals of both phases. These may be attributed to the existence of another superconducting phase in (BEDT-TTF)-I_3^- with $T_c \approx 7$ K.

The superconducting properties of the triclinic β-phase of the (BEDT-TTF)-I_3^- system with composition $(BEDT\text{-}TTF)_2I_3$ and transition temperature $T_c = 1.5$ K were studied in Ref. 1, where it was noted that the resistance fell by 50% as T dropped in the pretransition range from 4 to 1.8 K for "pure" crystals (i.e., crystals for which the ratio $R_{300}/R_{4.2}$ was $\approx 5 \cdot 10^{12}$), although no such decrease was found for less perfect crystals. Investigation of numerous crystals of varying degrees of perfection grown under different conditions revealed that the pretransition drop is not uniquely determined by $R_{300}/R_{4.2}$.

As an example, Fig. 1 shows the behavior for two crystals with virtually identical $R_{300}/R_{4.2} \approx 600$ but markedly different temperature dependence $R(T)$. The resistance of one of the samples (presumably the more perfect crystal) clearly saturates for $T = 5$–6 K and remains almost constant down to 2.8 K; there is almost no pretransition drop in this case. On the other hand, R for the other crystal starts to fall quite rapidly when T drops below 4–4.5 K, and the rate of decrease increases only slightly for $T < 2$ K, i.e., during the superconducting transition itself.

We can attribute this behavior to the existence of a second superconducting phase in crystals with a higher transition temperature. The existence of such a phase (the γ-phase) with $T_c = 2.5$ K was reported in Ref. 1, and some experimental results were presented in Ref. 2.

Like the β-phase crystals, the γ-phase crystals were produced by electrochemical methods; however, trichloroethane was used as the solvent in the latter case, and the current density during growth was ~ 10 times higher.

Studies of different γ-phase crystals grown under various conditions revealed that their compositions were generally quite irregular. First and foremost, the "hump" in the curves $R(T)$ for $T = 100$–130 K (Ref. 2) is probably not directly related to the γ-phase itself. Some of the crystals which appeared outwardly to be single crystals were found to actually consist of pieces with appreciably different properties. Measurements under the conditions indicated in Fig. 2 revealed that in some cases the material near the contacts 2, 3 had an $R(T)$ curve with a large hump and did not become superconducting, whereas there was almost no hump between the contacts 6, 7, where the superconducting transition was complete.

According to Ref. 2, there is no correlation between the size of the humps and the temperature of the superconducting transition; this is another indication that the humps are

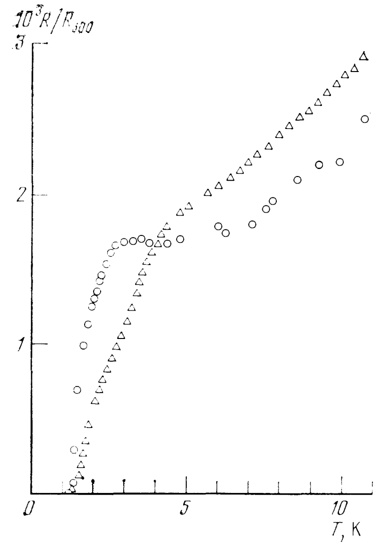

FIG. 1. Temperature dependences of the resistance for two crystals with equal $R_{300}/R_{4.2}$ but different pretransition behaviors.

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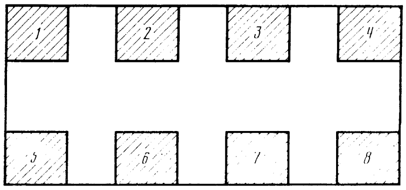

FIG. 2. Sketch showing the arrangement of the contacts used to study the homogeneity of the crystals.

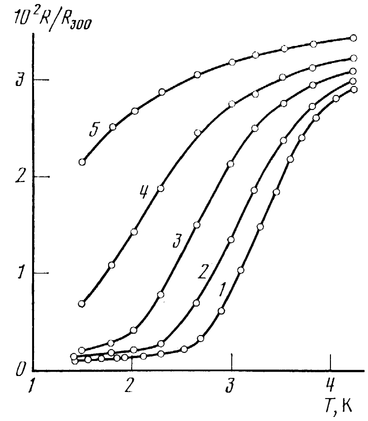

FIG. 4. Example of an incomplete superconducting transition with $T_c = 3.3$ K: 1) $H = 0$; 2) $H = 6$ kOe; 3) $H = 16$ kOe; 4) $H = 30$ kOe; 5) $H = 50$ kOe.

not associated with the superconducting phase. Figure 3 shows a striking example. Because of the almost 14-fold increase in the resistance for $T \approx 100$ K, the sample resistance $R_{4.2}$ at $T = 4.2$ K exceeded the resistance R_{300} at room temperature by 150%. Nevertheless, the superconducting transition was essentially complete at the same temperature $T = 2.5$ K.

At the same time, it was found that T_c for the γ-phase can vary widely from 2–2.2 K to 3–3.3 K for some samples, depending on the growth conditions. As before, however, no correlation was found between the size of the hump and the value of T_c.

To be sure, we should note that the transitions in some of the samples were not complete, which again can probably be attributed to variations in their composition. Figure 4 shows an example of an incomplete transition with $T_c = 3.3$ K; the influence of the magnetic field on this transition is also shown. These curves indicate that a superconducting transition is almost certainly involved.

It is difficult to account for the variations in the samples and the broad temperature spectrum T_c for the superconducting transition to the γ-phase. The humps in the curves might possibly be caused by the existence of an additional phase of the (BEDT-TTF)-I_3^- system which undergoes a metal-insulator or a metal-semimetal transition in this temperature range.

We note that in addition to the superconducting phases, two metallic phases have been identified in (BEDT-TTF)-I_3^- which lose their conductivity (become dielectrics) for $T = 135$–140 K. One of these, the α-phase (Ref. 3), has a triclinic lattice and the same composition $(BEDT\text{-}TTF)_2I_3$ as the β-phase; the other the δ-phase, is monoclinic and has the composition $(BEDT\text{-}TTF)I_3$.[1)] At present, however, there are no grounds for believing that these phases are responsible for the humps.

If there were an entire interval of iodine concentrations for which the γ-phase were stable, this could explain the spread in T_c for the γ-phase crystals grown by different methods. Such a phase of variable composition was observed

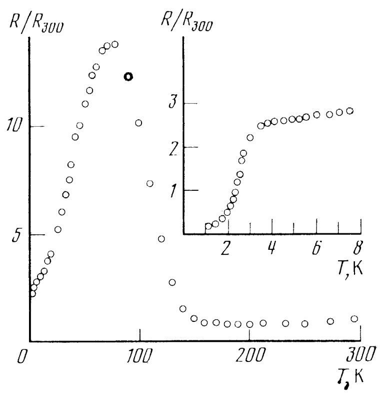

FIG. 3. Temperature dependence of the resistance of a γ-phase crystal with a 14-fold peak near $T \sim 100$ K. The insert shows the low-temperature part of the curve in greater detail.

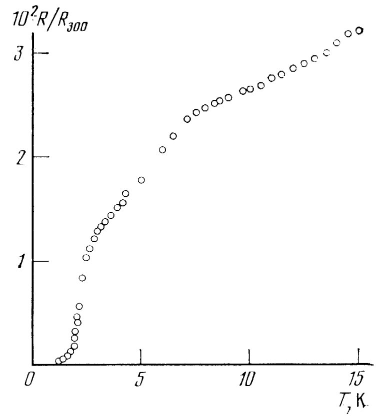

FIG. 5. Pretransition drop of the resistance for a γ-phase crystal for T between 8 and 3 K.

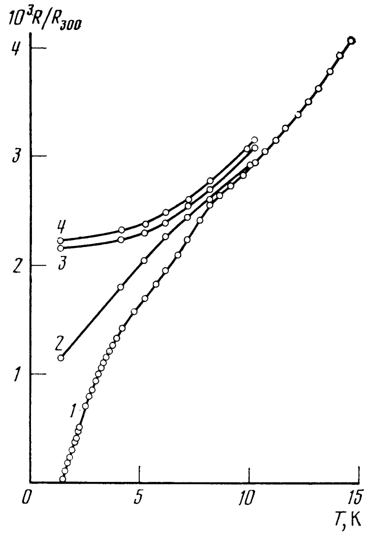

FIG. 6. Pretransition drops in the resistance for a β-phase crystal and its suppression by a magnetic field: 1) $H = 0$; 2) $H = 6$ kOe; 3) $H = 34$ kOe; 4) $H = 50$ kOe.

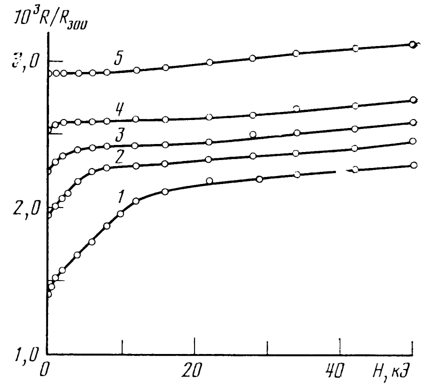

FIG. 7. Field dependences of the resistance for the same crystals as in Fig. 6: 1) $T = 4.2$ K; 2) $T = 6.2$ K; 3) $T = 7.2$ K; 4) $T = 8.2$ K; 5) $T = 10.3$ K.

previously in the compound $TTT_2I_{3+\delta}$ (Ref. 4). This might be the reason why x-ray structure analysis of these crystals remains difficult, and it could account for the lack of data on their precise composition.

Finally, pretransition phenomena like those observed for β-phase crystals for $2 \leqslant T \leqslant 4$ K were noted for the α- and δ-phases in many crystals for temperatures between ~ 3 and ~ 8 K. Figure 5 shows an example for a γ-phase sample. We see that the decrease in R with T becomes significantly steeper starting with $T = 8$ K; R drops by a factor of 2 when T decreases from 8 to 3 K, after which $R(T)$ starts to fall even more rapidly during the superconducting transition, which is centered at $T = 2.3$ K.

Figure 6 shows the behavior of a β-phase sample for which $R(T)$ drops appreciably for $8 \geqslant T \geqslant 4$ K, in addition to the rapid decrease for $T \leqslant 4$ K (which we attribute to γ-phase impurity). The effects of a magnetic field along the "easy" axis c on $R(T)$ are also shown.[2] For strong fields H the falloff in $R(T)$ with T becomes less rapid for T below 8 K.

Figure 7 shows how the resistance of the same sample depends on the magnetic field for temperatures above 4 K. The initial protions, in which R increases quite rapidly with H, are noteworthy; their slopes decrease as T increases and vanish for $T = 8$ K.

These results suggest that the (BEDT-TTF)-I_3^- system contains an additional superconducting phase with a higher transition temperature near 7 K. It remains unclear how this superconducting phase can spread out the pretransition phenomena noted above for both the β- and the γ-phases. If there is an interval of compositions in one of the crystal phases for which T_c varies continuously, this could explain the blurring of the transition parameters. Such an explanation is supported by the fact that T_c for the γ-phase transition varies by almost 1.5 K. On the other hand, the blurring could also be a consequence of proximity effects associated with macroscopic inclusions of high-temperature phase of various diameters in the nonsuperconducting matrix. Further work is needed here, as well as to identify the superconducting phase with $T_c \approx 7$ K in a pure form.

[1)]The structures of the phases were determined by P. R. Shibaeva and V. F. Kaminskiĭ.

[1]É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].
[2]É. B. Yagubskiĭ, I. F. Shchegolev, S. I. Pesotskiĭ *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 275 (1984) [JETP Lett. **39**, 328 (1984)].
[3]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**, 17 (1984)].
[4]I. F. Shchegolev and E. B. Yagubskii, in: Extended Linear Chain Compounds, Vol. 2 (J. S. Miller, ed.), Plenum, New York (1982), p. 385.

Translated by A. Mason