Metastable state of β-(BEDT-TTF)$_2$I$_3$ with a superconducting transition temperature of 7.5 K

V. B. Ginodman, A. V. Gudenko, I. I. Zasavitskiĭ, and É. B. Yagubskiĭ[1)]
P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

(Submitted 5 October 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **42**, No. 9, 384–386 (10 November 1985)

The high-temperature superconducting phase with $T_c = 7.5$ K, which arises in β-(BEDT-TTF)$_2$I$_3$ crystals when subjected to pressure, is shown to be metastable. The observed value of T_c is apparently the highest value for this high-temperature superconducting phase in β-(BEDT-TTF)$_2$I$_3$ samples synthesized by chemical oxidation.

1. The overwhelming majority of the triclinic (BEDT-TTF)$_2$I$_3$ crystals go superconducting at temperatures of 1.2–1.5 K. It has been suggested in several papers,[1,2] however, that crystals of β-(BEDT-TTF)$_2$I$_3$ may also contain an admixture of another superconducting phase, with a higher critical temperature. It was subsequently shown in Ref. 3 that iodine-rich ϵ-phase crystals of the composition (BEDT-TTF)$_4$(I$_3$)$_2$I$_8$ convert, when heated in a vacuum, into β-(BEDT-TTF)$_2$I$_3$, and at standard pressure they are observed to go superconducting at $T_c \cong 6$ K. Study[4,5] of the effect of pressure on the superconducting properties of β-(BEDT-TTF)$_2$I$_3$ has shown that at pressures above 1 kbar a new superconducting phase with $T_c = 7.5$ K appears in these crystals. Data obtained in Ref. 4 on the $T_c(P)$ dependence of the high-temperature superconducting phase and on the presumed phase boundary between the original low-temperature superconducting phase and the new high-temperature superconducting phase led to the suggestion[4] that if it is possible to preserve the high-pressure phase in a metastable state, then it might be possible to achieve a superconducting transition temperature of 10–11 K at standard pressure. In the present letter we report an effort to resolve this question.

2. We have studied the effect of relatively low pressures, up to 1.5 kbar, on the possibility of the formation of, and on the properties of, the new high-temperature superconducting phase in β-(BEDT-TTF)$_2$I$_3$ crystals synthesized by chemical oxidation of (BEDT-TTF) by tetrabutylammonium triiodide in a trichloroethane solution.[6]

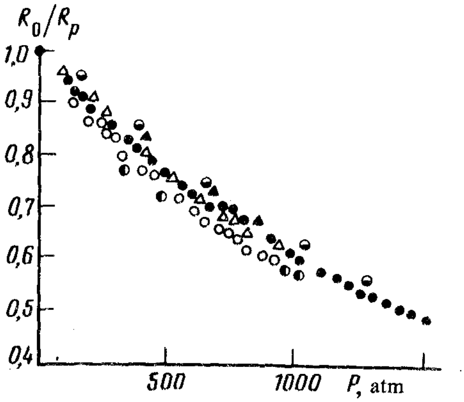

FIG. 1. Electrical resistance versus the pressure at room temperature for several β-(BEDT-TTF)$_2$I$_3$ samples synthesized by chemical oxidation.

It should be noted that at standard pressure the superconducting transition in these samples is observed only at $T_c = 1.2$ K, and the temperature dependence of the resistance is completely identical to that found for the β-(BEDT-TTF)$_2$I$_3$ samples studied by us in Ref. 2.

We use the four-contact technique described in Ref. 2 to measure the electrical resistance of samples through which a current is flowing along the $\bar{a}$ axis. The samples, with a thermometer, are held in a bomb, where a hydrostatic pressure is produced by compressing a gas. The pressure is monitored continuously and can be held constant or varied in any desired way during cooling down to the temperature at which the gas solidifies. For the compression we use helium, hydrogen, or nitrogen. The experimental procedure is as follows: The pressure in the bomb is raised at room temperature to a certain value (varied in different experiments from 0.3 to 1.2 kbar; the behavior of the resistance of the samples with increasing pressure at room temperature is shown in Fig. 1; at $P = 1.5$ kbar, the resistance decreases by a factor of two). The sample is then cooled at a constant pressure to ~ 90 K; at this temperature, the pressure is lowered to standard pressure, and the subsequent cooling is carried at standard pressure. We observe a superconducting transition with $T_c = 7.5 \pm 0.1$ K (T_c is determined from the middle of the transition). It is thus clear that when a pressure is imposed, and there is a further cooling of the β-(BEDT-TTF)$_2$I$_3$ crystals, there is a transition to a new high-temperature superconducting phase, which persists in the crystal even after the pressure is removed.

We then attempted to determine the conditions required for this phase transition. For this purpose, after the procedure described above, the sample is heated to a temperature which was varied in different experiments from 300 to 150 K. The sample is then recooled at standard pressure. If the temperature to which the sample is heated exceeds 175 K, the superconducting transition at 7.5 K is not observed; if, on the other hand, the sample is heated to a temperature below 150 K, the superconducting transition with $T_c = 7.5$ K is observed again. Variation of the initial pressure from 1.2 to 0.5 kbar does not change T_c; after the pressure is removed, we observe in all cases a rather sharp transition, which begins at $T_c = 8$ K, and has a width $\Delta T_c = 0.5$–0.7 K, indicating that the samples are quite homogeneous. If, on the other hand, the initial pressure is below 0.5 kbar, we observe a complex superconducting transition, which begins at 8

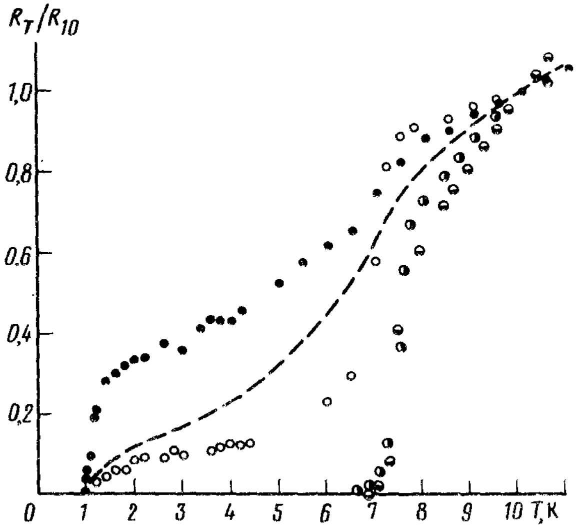

FIG. 2. Superconducting transitions of β-(BEDT-TTF)$_2$I$_3$ samples. Samples synthesized by chemical oxidation: ●—Sample not subjected to pressure; ◑—sample subjected to an initial pressure of 1.1 kbar; ⊖—sample subjected to an initial pressure of 0.5 kbar; - - - - —sample subjected to an initial pressure of 0.3 kbar. ○—Sample synthesized by electrochemical oxidation and not subjected to pressure. All the results were measured at standard pressure.

K and which terminates completely at $T = 1.2$–1.5 K (Fig. 2).

3. It can be concluded from these experiments that a new superconducting phase with $T_c = 7.5$ K forms in β-(BEDT-TTF)$_2$I$_3$ crystals synthesized by the method described above at a pressure of 0.5 kbar. This new superconducting phase is metastable; it persists when the pressure is removed. The temperature at which this new superconducting phase reverts to the original phase at standard pressure is 160 ± 10 K.

The data reported in Ref. 4 on the dependence $T_c(P)$ for β-(BEDT-TTF)$_2$I$_3$ crystals, also synthesized by chemical oxidation, and our results for the same crystals suggest that $T_c = 7.5$ K is apparently the highest critical temperature for the high-temperature superconducting phase in these crystals.

The results obtained in the present experiments make it possible to refine the position of the boundary of the phase transition between the low-temperature and high-temperature superconducting phases; this transition occurs at pressures of 0.4–0.5 kbar, not at 1 kbar, as reported in Ref. 4. One possible reason for the discrepancy might be an error in the determination of the pressure at low temperatures in a chamber in which a liquid is used as the medium to transfer the pressure. Another possible factor would be the differences in the samples used.

It should be noted that in studying the properties of β-(BEDT-TTF)$_2$I$_3$ crystals synthesized by electrochemical oxidation of (BEDT-TTF) in a solution of trichloroethane on a platinum anode at a direct current ($J = 10\ \mu$A/cm^2) at $T = 50$ °C, with (Bu)$_4$NI$_4$ used as an electrolyte, we observed a superconducting transition of complex shape in these samples at standard pressure. This transition also began at 8 K and had two clearly defined steps at $T = 7.5$ K and $T = 1.2$ K. It follows that in the crystals synthesized by this technique the high-temperature superconducting phase is present from the outset and coexists with the high-temperature phase in Fig. 2; similar steps on curves of superconducting transitions in β-(BEDT-TTF)$_2$I$_3$ crystals have been mentioned in Refs. 7 and 8.

Further study is required to resolve the nature of the high-temperature phases which arise in β-(BEDT-TTF)$_2$I$_3$ crystals synthesized in different ways [by heating ϵ-phase crystals of (BEDT-TTF)$_2$(I$_3$)$_2$I$_8$ in a vacuum and by compressing β-(BEDT-TTF)$_2$I$_3$ samples] and which exist at standard pressure in certain β-(BEDT-TTF)$_2$I$_3$ crystals synthesized by electrochemical oxidation. Another question that requires further study is why two superconducting phases with dramatically different superconducting transition temperatures occur in the same substance, with the same crystal structure.

We are deeply indebted to I. F. Shegolev, L. N. Bulaevskiĭ, and V. I. Laukhin for several useful discussions of the results; E. É. Kostyuchenko and A. A. Ignat'ev for assistance in synthesizing the samples; L. N. Zherikhina for assistance in this study; and A. B. Fradkov for constant support.

[1)]Institute of Chemical Physics, Academy of Sciences of the USSR.

[1]É. B. Yagubskiĭ, I. F. Shegolev, V. N. Topnikov, S. I. Pesotskiĭ, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, S. I. Dedik, and L. I. Buravov, Zh. Eksp. Teor. Fiz. **88**, 244 (1985) [Sov. Phys. JETP **61**, 142 (1985)].

[2]V. B. Ginodman, A. V. Gudenko, and L. N. Zherikhina, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 41 (1985) [JETP Lett. **41**, 49 (1985)].

[3]V. A. Merzhanov, E. E. Kostyuchenko, V. N. Laukhin, R. M. Lobkovskaya, M. K. Makova, R. P. Shibaeva, I. F. Shegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 146 (1985) [JETP Lett. **41**, 179 (1985)].

[4]V. I. Laukhin, E. É. Kostyuchenko, Yu. V. Sushko, I. F. Shegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 68 (1985) [JETP Lett. **41**, 81 (1985)].

[5]K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. **54**, 1236 (1985).

[6]E. É. Kostyuchenko, E. B. Yagubskiĭ, O. Ya. Neĭland, and V. Yu. Khodarovskiĭ, Izv. Akad. Nauk SSSR, Ser. Khim. No. 12 (1984).

[7]É. B. Yagubskiĭ, I. F. Shegolev, V. N. Topnikov, S. I. Pesotskiĭ, N. I. Makova, V. N. Laukin, E. É. Kostyuchenko, P. A. Kononovich, N. V. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, 23-e Vsesoyuznoe soveshanie po fizike nizkikh temperatur (Proceedings of the 23rd All-Union Conference on Low Temperature Physics), Part I, Tezisy dokladov, Tallin, 1984, p. 124.

[8]L. I. Buravov, M. V. Kartsovnik, V. F. Kaminski, *et al.*, Synthetic Metals (in press).

Translated by Dave Parsons