Investigation of the *T–P* phase diagram for α-(BEDT-TTF)$_2$I$_3$

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Information is presented on the *T–P* phase diagram of α-(BEDT–TTF)$_2$I$_3$ obtained by investigating the temperature dependence of the resistance in the temperature range 1.3–300 K and at pressures up to ~11 kbar. The results given indicate the existence of at least three different phases of α-(BEDT–TTF)$_2$I$_3$.

INTRODUCTION

It was established earlier[1,2] that the cation-radical salt bis(ethylenedithiolo)tratrafulvalene iodide α-(BEDT–TTF)$_2$I$_3$ exists in two polymorphic modifications (α and β phases) which differ strongly in physical properties. β-(BEDT–TTF)$_2$I$_3$ is an organic superconductor at normal pressure with $T_c \sim 1.5$ K, while the α phase undergoes a sharp metal-dielectric transition at ~137 K ($P = 1$ bar).

Similar sharp dielectric transitions in the temperature region ~100 K are observed in some Bechgaard salts: (TMTSF)$_2$ReO$_4$,[3] (TMTSF)$_2$FSO$_3$,[4] and also (BEDT-TTF)$_4$(REO$_4$)$_2$.[5] In all these cases the application of a hydrostatic pressure of 5 to 10 kbar leads to suppression of the metal-dielectric transitions, as a result of which the compounds remain metals and go into the superconducting state in the region 1–2 K. It is of interest in this connection to study the effect of pressure on the properties of the α phase of (BEDT-TTF)$_2$I$_3$.

In the present work we will present information on the *T–P* phase diagram of α-(BEDT–TTF)$_2$I$_3$, obtained by studying the temperature dependence of the resistance in the pressure range up to ~11 kbar.

EXPERIMENTAL METHOD

The α-phase crystals were in the form of 0.05 mm thick plates with a characteristic dimension 1.5 mm in the plane of the plates. The resistance of the specimens was measured by a four-probe dc method in an arbitrary direction in the *ab* plane which coincided with the plane of the plate. Platinum electrodes 10 to 20 μm in diameter were stuck with silver paste to four gold strips deposited on the crystals. The resistivity of α-(BEDT–TTF)$_2$I$_3$ crystals in the *ab* plane at room temperature and normal pressure is $(3\text{–}5)\times 10^{-2}\Omega\cdot$cm.

The pressure was applied in a "piston-and-cylinder" type chamber made of 40KhNYu steel with a working channel diameter of 4 mm and GKZh-94 silicone fluid as pressure transmitting medium. The loading of the chamber and fixing of the pressure in it was carried out at room temperature. Calibration of the chamber was against the phase transition in the organic metal (TSeT)$_2$Cl which occurs at 5 kbar and 300 K.[6] Monitoring with a superconducting reference showed that on approaching helium temperatures, the pressure in the chamber is reduced by 25–30 %. In constructing the phase diagram it was assumed that this fall takes place linearly in the range from 33 to 40 K, after which the pressure remains constant.

EXPERIMENTAL RESULTS

The effect of hydrostatic pressure on the temperature dependences of resistance of two specimens of α-(BEDT–TTF)$_2$I$_3$ is shown in Fig. 1. It can be seen that at atmospheric pressure the resistance of the specimens grows sharply in the region of ~137 K, which is evidence of the metal-dielectric type of phase transition (curves 1 and 2). The application of pressure shifts the start of the resistance growth noticeably into the lower temperature region. As the pressure is increased the transition becomes more smeared out. However, the growth in resistance still remains appreciable up to 8 kbar (curves 1–5).

Further increase in pressure leads to a sharp suppression of the transition. For example, the resistance of specimen II at 7.9 kbar (curve 5) increases by three orders of magnitude to 1.3 K, while it is only an order of magnitude at a pressure of 8.5 kbar (curve 6). In the same pressure region the variation of the resistance of specimen I (curve 7) becomes nonmonotonic and the characteristic "hump" appears with a maximum in the region of ~15 K. We note that the decrease in resistance below the maximum continues with appreciable speed down to 1.3 K. The size of the "hump" decreases as the pressure grows.

The "hump" disappears for $P > 9.0$ kbar (curves 9 and 10) and the fall in resistance from 300 K changes in the region of 10–15 K to an appreciable increase in it.

A characteristic feature is that in this pressure region the temperature of the start of the increase in resistance is independent of pressure, while the subsequent growth in resistance of the crystals with increasing pressure becomes ever more appreciable. The latter is well seen in Fig. 2 where the temperature dependence of the resistance of specimens I and II in the range 1.3–20 K is shown plotted as $\log(R/R_{300})$ vs $1/T$. All this is evidence that for $P > 9$ kbar a low-temperature phase transition takes place in α-phase specimens, different from the transition observed at lower pressures.

Noticeable hysteresis was not found in the $R(T)$ curves for all specimens studied. We note that the average value of the quantity $[d\sigma(P)/\sigma(1\text{ bar})]/(dP)$ for α-phase specimens at $T = 300$ K is ~40%/kbar, which is typical of the majority of known organic metals.[7]

THE *T–P* PHASE DIAGRAM OF α-(BEDT-TTF)$_2$I$_3$

The experimental results presented above are evidence of the existence of at least three different phases for α-(BEDT-TTF)$_2$I$_3$ and enables the *T–P* phase diagram of this

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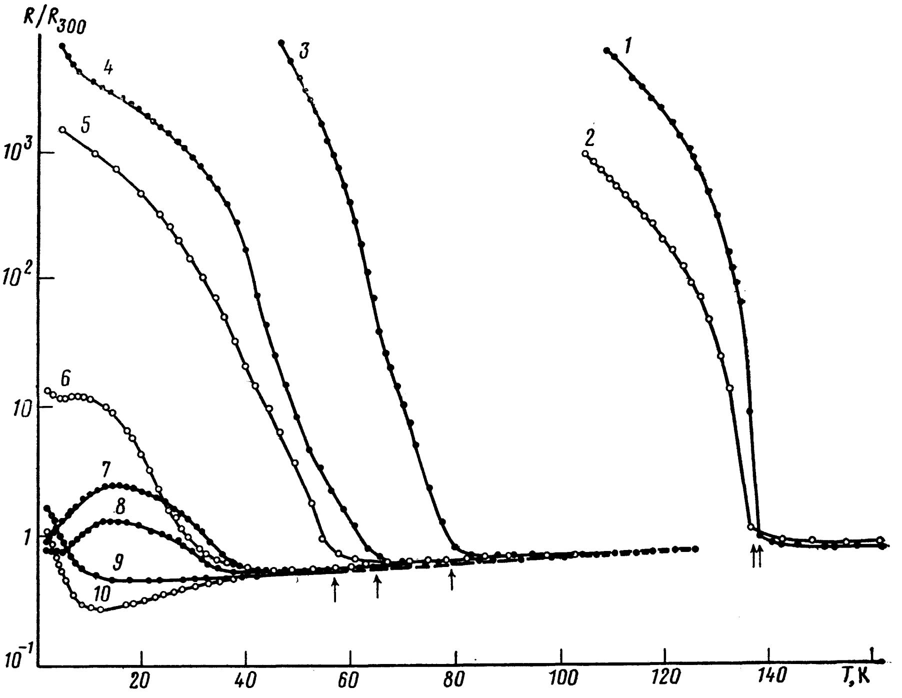

FIG. 1. The temperature dependences of the resistance of specimens I (●) and II (○) of α-(BEDT-TTF)$_2$I$_3$ at pressures of 1), 2) 1 kbar; 3) 6.3 kbar; 4) 7.5 kbar; 5) 7.9 kbar; 6) 8.5 kbar; 7) 8.3 kbar; 8) 9.0 kbar; 9) 9.3 kbar; 10) 9.1 kbar. All values of pressure refer to room temperature.

complex to be constructed (Fig. 3). The different phases in the diagram are indicated by the labels *I, II* and *III*. The dashed part corresponds to the region of existence of the "humps" in the $R(T)$ curves.

The nature of the temperature dependences of the resistance of specimens at $P =$ constant is evidence in favour of α-(BEDT-TTF)$_2$I$_3$ in the regions *I* and *II* behaving as metal and dielectric respectively. The $I \rightarrow II$ transition is most likely purely structural in nature or connected with structural changes, for example of the Peierls type. The absence of hysteresis phenomena favors the latter.

In the dashed region of the *T–P* diagram a sharp suppression of state *II* takes place with increase in pressure and possibly a nucleation of phase *II*, of which the small increase in resistance below 5 K in curves 6 and 8 of Fig. 1 is evidence.

In phase *III*, as has already been noted, the temperature increase of resistance becomes ever more appreciable with increasing pressure. However, at all pressures the slope of the linear sections of the $\log(R/R_{300})$ dependence on $1/T$ in Fig. 2 are about the same and correspond to an activation energy of ~ 2 K, which cannot be connected with the dielectric gap formed in the process of the $I \rightarrow III$ transition, since the temperature of this transition is of the order of ~ 8 K. Phase *III* is evidently a semi-metal, and the number of carri-

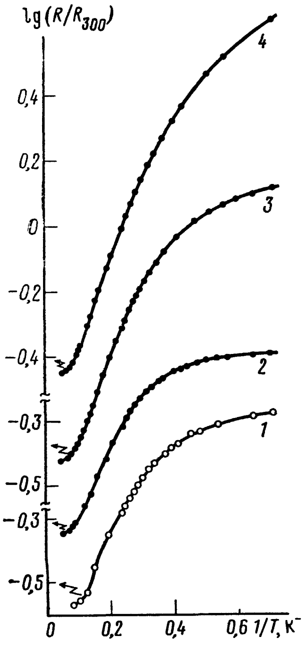

FIG. 2. The dependence of $\log(R/R_{300})$ on $1/T$ for specimens II (curve 1) and I (curves 2, 3, 4) at: 1) 9.1 kbar; 2) 9.3 kbar; 3) 11.1 kbar; 4) 13.9 kbar.

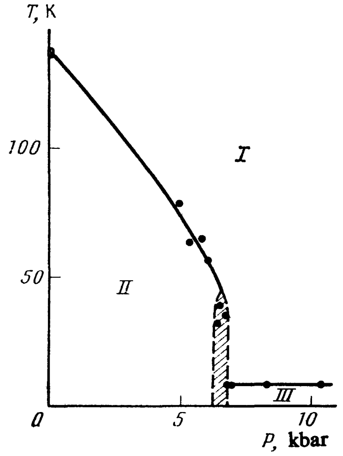

FIG. 3. the *T–P* phase diagram of (BEDT-TTF)$_2$I$_3$. The temperatures of the phase transitions were determined for each pressure from the point of intersection of the linearly extrapolated sections of the $\log R(T)$ curves (marked by arrows in Fig. 1).

ers in it falls all the time with increasing pressure. The low temperature of the $I \rightarrow III$ transition is evidence that this transition is not associated with structural changes in the crystal lattice but is, for example, a transition to a state with a spin-wave density.

In general, the effect of pressure on the $R(T)$ dependences for specimens in phase *II* is unexpected. In organic metals as a rule,[7] an increase in pressure leads to a suppression of dielectric instability at low temperatures. In this sense it is interesting to compare α(BEDT-TTF)$_2$I$_3$ with such complexes as (TMTSF)$_2$ReO$_4$,[3] (TMTSF)$_2$FSO$_3$,[4] and (BEDT-TTF)$_4$(ReO$_4$)$_2$.[5] The *T–P* phase diagrams of these salts are qualitatively similar to that obtained by us, with phases *I* and *III* also showing metallic and dielectric properties. Hydrostatic compression, which suppresses state *II* leads, however, in the complexes mentioned to superconductivity with $T_c \sim 1.5$ K, and not to dielectric instability as in α-(BEDT-TTF)$_2$I$_3$. It would therefore be of considerable interest to elucidate the nature of phase *III* of α-(BEDT-TTF)$_2$I$_3$.

The behavior of those specimens of the α-phase in which a low-temperature fall in resistance with noticeable speed down to 1.3 K is observed (curve 7 in Fig. 1, specimen I) is also of special interest. We note that for specimen I a characteristic "bulge" appears in curves 3 and 4 of Fig. 1 in the region of the rapid growth in resistance (phase *II*), which increases with increasing pressure and precedes the appearance of the "humps." At the same time, the increase in resistance in phase *II* (curve 5) of specimen *II* takes place smoothly and there are no clearly shown "humps" (curve 6).

Such a scatter in the behavior of the specimens is evidently related to their level of purity, namely to the iodine content in the lattice. As has been shown,[2] doping specimens of the α-phase with iodine leads already at $P = 1$ ban to the suppression of the $I \rightarrow II$ transition and the formation of "humps" with a maximum in the region of ~ 100 K. A strong fall in resistance below 100 K then ends in a transition to the superconducting state with $T_c \sim 3.5$ K. It can thus be assumed that there is some excess iodine in specimen I, which reveals itself in the dielectric phase *II* only when this phase is strongly suppressed. The mechanism for the action of iodine is not yet clear.

In conclusion we express our thanks to É. B. Yagubskiĭ for providing the α-(BEDT-TTF)$_2$I$_3$ specimens.

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