

Metal-semiconductor phase transition with a giant hysteresis in the organic metal $(\text{ET})_2\text{IBr}_2$

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Forward and inverse $\beta \rightleftharpoons \alpha$ structural phase transitions in the organic complex $(\text{ET})_2\text{IBr}_2$ have been detected. These transitions have a giant hysteresis, allowing the superconducting β phase or the semiconducting α phase to be retained under normal conditions.

1. Among the organic metals based on ET—bis(ethylenedithio) tetrathiofulvalene—a whole class of superconductors of the composition $(\text{ET})_2\text{X}$, where $\text{X} = \text{I}_3$, IBr_2 , AuI_2 , or $\text{Cu}(\text{NCS})_2$, with the transition temperature T_c ranging from 1.4 K for β_L - $(\text{ET})_2\text{I}_3$ (Ref. 1) to 10.5 K for $(\text{ET})_2\text{Cu}(\text{NCS})_2$ (Ref. 2), have recently been discovered. Nearly every indicated compound can crystallize in various polymorphic modifications. The complex $(\text{ET})_2\text{I}_3$, for example, is present in at least five phase states, four of which undergo a transition to the superconducting state at the following temperatures: $T_c \approx 1.4$ K (the β_L phase), $T_c \sim 7.5$ K (the β_H phase) (Ref. 3), $T_c \sim 3.5$ K (the θ phase) (Ref. 4), and $T_c \sim 3.6$ K (the K phase) (Ref. 5), while the fifth phase (the α phase) undergoes a metal-insulator transition at 137 K (Ref. 6). The superconducting phases with higher T_c sometimes cannot be obtained by direct chemical or electrochemical synthesis. The β_H phase, for example, is synthesized either from the β_L phase under pressure $P \gtrsim 0.5$ kbar (Refs. 3 and 7) or from the α phase upon heating above 80 °C (Ref. 8). In the latter case this phase can remain in the metastable state under normal conditions. This circumstance makes it a matter of vital interest to study the possible phase transitions in the given family of organic metals $(\text{ET})_2\text{X}$ produced as a result of pressure or heating.

In the present letter we report the observation of a direct (crossover) and inverse ($\beta \rightleftharpoons \alpha$) transitions in the compound $(\text{ET})_2\text{IBr}_2$. These phase transitions are accompanied by an anomalously large hysteresis, allowing the β phase or the α phase to remain in the metastable state under normal conditions.

2. A mixture of α - and β - $(\text{ET})_2\text{IBr}_2$ crystals was obtained by chemically oxidizing a concentrated ET solution in nitrobenzene by $(\text{Et})_4\text{NiBr}_2$, which was increased fivefold. The total yield of such a reaction is $\sim 67\%$. The external appearance of these crystals is so perfect in most of the cases that the β modification of $(\text{ET})_2\text{IBr}_2$ can visually be distinguished from its α modification. Because of their internal perfection and high purity, the single crystals have a record-high (for organic metals) ratio of the room-temperature resistance to the residual resistance, $R_{295\text{K}}/R_{3.5\text{K}} \gtrsim 4000$, and a narrow superconducting-transition width, $\Delta T_c \approx 0.1$ K, at $T_c = 2.8$ K (curve 1 in Fig. 1). The room-temperature conductivity of these single crystals is $\sigma_{295\text{K}} \approx 50 \pm 10 \Omega^{-1}\cdot\text{cm}^{-1}$, roughly twice that of β - $(\text{ET})_2\text{I}_3$.

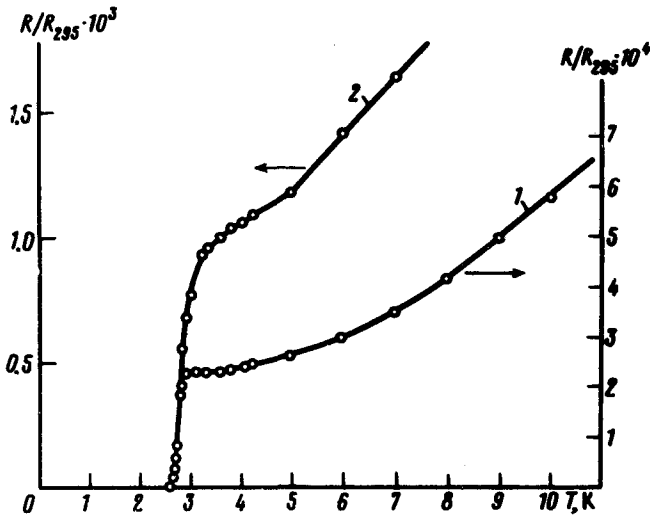


FIG. 1. Temperature dependence of the normalized resistance of β -(ET)₂IBr₂ crystals near the superconducting phase transition. 1—Sample obtained by means of direct chemical synthesis. 2—sample after a $\alpha \rightleftharpoons \beta$ transition (see the text proper).

Figure 2 shows the resistance of one of the single crystals of β -(ET)₂IBr₂, plotted as a function of pressure. We see that the resistance initially decreases smoothly with increasing pressure. At $P \approx 18$ kbar it increases sharply by nearly an order of magnitude and then again begins to decrease monotonically. A decrease in the pressure does not cause the reciprocal resistance jump to occur and the resistance increases mono-

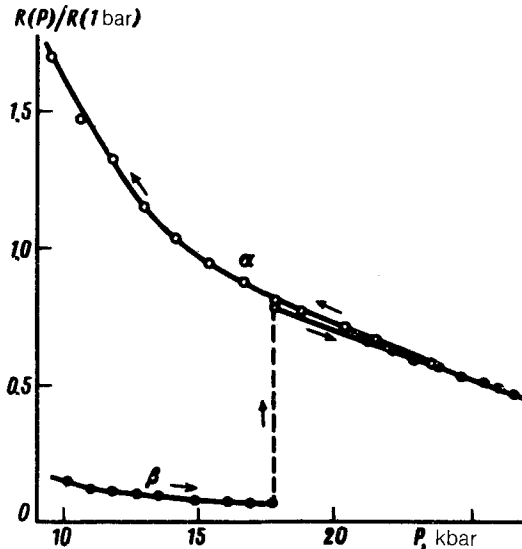


FIG. 2. Resistance versus the pressure near the $\beta \rightleftharpoons \alpha$ phase transition in the (ET)₂IBr₂ crystal.

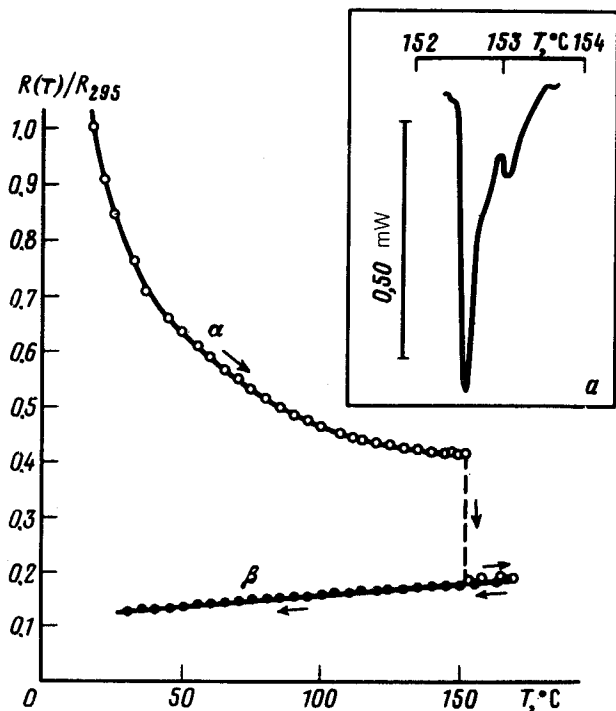


FIG. 3. Resistance versus the temperature near the $\alpha \rightleftharpoons \beta$ phase transition in the $(\text{ET})_2\text{IBr}_2$ crystal; a—thermogram of the $\alpha \rightleftharpoons \beta$ transition.

tonically until the pressure is removed completely. An x-ray diffraction study shows unambiguously that β - $(\text{ET})_2\text{IBr}_2$ crystals undergo a transition to α - $(\text{ET})_2\text{IBr}_2$ crystals as a result of the effect of high pressure. The conductivity of α - $(\text{ET})_2\text{IBr}_2$ single crystals is an order of magnitude lower than that of β - $(\text{ET})_2\text{IBr}_2$ (Refs. 9 and 10). The α phase of the $(\text{ET})_2\text{IBr}_2$ compound which is formed in this manner is retained under normal conditions an unlimited length of time: we have kept crystals of the α phase for more than two years.

To convert the crystals of $(\text{ET})_2\text{IBr}_2$ from the α phase to the β phase, they must be heated to a temperature $T = 153\text{--}155^\circ\text{C}$ at a normal pressure (Fig. 3). As can be seen from Fig. 3, an inverse resistance jump occurs and the semiconductor temperature dependence of the resistance is replaced by a metallic temperature dependence. Cooling these crystals to low temperatures shows that even after such a phase transition the quality of these crystals is acceptable: $R_{295\text{K}}/R_{3.5\text{K}} \approx 1000$, the superconducting-transitions width is $\Delta T_c \approx 0.5$ K, and $T_c \approx 2.8$ K (curve 2 in Fig. 1). These crystals yield x-ray photographs with clearly defined reflections, a feature which the $\alpha \rightarrow \beta$ phase transition of the $(\text{ET})_2\text{I}_3$ complex lacked.⁸

The $\alpha \rightarrow \beta$ phase transition in the $(\text{ET})_2\text{IBr}_2$ compound occurs with an absorption of heat. The thermogram of this transition (Fig. 3a) was obtained with a Mettler DSC-20 differential scanning calorimeter. The latent heat of the transition is $\Delta H \approx 0.5 \pm 0.1$ J/g, an order of magnitude lower than that of the $\alpha \rightarrow \beta$ transition in

the $(\text{ET})_2\text{I}_3$ compound.⁸ We also note that the phase transition $\alpha \rightarrow \beta$ in the $(\text{ET})_2\text{IBr}_2$ compound, in contrast with that of $(\text{ET})_2\text{I}_3$, occurs abruptly and apparently is of a martensitic nature. The inverse $\beta \rightarrow \alpha$ transition, which occurs under pressure, is of the same nature.

The volume effect of the $\beta \rightleftharpoons \alpha$ phase transition of $(\text{ET})_2\text{IBr}_2$, calculated from the data on the x-ray structural analysis, amount to $\Delta V/V_0 \approx 0.5\%$, whereas the volume effect of this transition in $(\text{ET})_2\text{I}_3$ complex is $\Delta V/V_0 \approx 0.8\%$. Since these samples are highly brittle, even such a small volume effect will often cause the single crystals, especially those that are large in size, to break up during the $\alpha \rightarrow \beta$ phase transition. Accordingly, very small samples must be used in order to obtain curves such as those shown in Fig. 3.

3. We have established that the $(\text{ET})_2\text{IBr}_2$ complex can be changed from the superconducting β phase to the semiconducting α phase and back again. The hysteresis of this conversion is anomalously large, allowing both phases to remain, under normal conditions, in the metastable state for an unlimited time. The region in which the α phase is stable is held at high pressure, while the β phase is heated to a temperature $T \gtrsim 155^\circ\text{C}$.

In terms of the structure of the cation and anion layers, the α and β modifications of the $(\text{ET})_2\text{IBr}_2$ compound are closer to each other than the α and β phases of the $(\text{ET})_2\text{I}_3$ complex.⁹⁻¹¹ In the $\beta \rightarrow \alpha$ transition in $(\text{ET})_2\text{IBr}_2$ the lattice constant a roughly doubles, the $[110]$ direction of the cation-radical stacks (the lattice constant in this direction is 8.777 \AA) changes to the $[010]$ direction ($b = 8.898 \text{ \AA}$), and the adjacent stacks are no longer equivalent. In the anion layer all IBr_2^- are parallel in both the α phase and the β phase.^{9,10} Such analogies are not seen in the comparison of the structures of the α and β phases for $(\text{ET})_2\text{I}_3$ (Ref. 11). This circumstance probably accounts for the fact that application of pressure causes β - $(\text{ET})_2\text{IBr}_2$ to change to α - $(\text{ET})_2\text{IBr}_2$ and heating causes α - $(\text{ET})_2\text{IBr}_2$ to change to β - $(\text{ET})_2\text{IBr}_2$, with a latent heat of transition an order of magnitude lower than that of the $\alpha \rightarrow \beta$ transition of $(\text{ET})_2\text{I}_3$ (Ref. 8) and with a smaller volume effect.

For the same reason β - $(\text{ET})_2\text{I}_3$ clearly does not undergo a transition to α - $(\text{ET})_2\text{I}_3$ even at high pressures: Application of pressure to $P \approx 60$ kbar does not lead to the formation of α - $(\text{ET})_2\text{I}_3$ but it stabilizes the β_H phase with $T_c \approx 8 \text{ K}$ (Ref. 12).

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¹É. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].

²H. Urayama, H. Yamochi, G. Saito *et al.*, Chem. Lett. **55**, 115 (1988).

³V. N. Laukhin, E. É. Kostyuchenko, Yu. V. Sushko *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 68 (1985) [JETP Lett. **41**, 81 (1985)].

⁴H. Kobayashi, T. Kato, A. Kobayashi *et al.*, Chem. Lett. **53**, 789 (1986).

⁵R. Kato, H. Kobayashi, A. Kobayashi *et al.*, Chem. Lett. **54**, 507 (1987).

⁶V. F. Kaminskii, T. G. Prokhorova, R. P. Shibaeva, and É. B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 15 (1984) [JETP Lett. **39**, 17 (1984)].

- ⁷V. B. Ginodman, A. V. Gudenko, P. A. Kononovich *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 523 (1986) [*JETP Lett.* **44**, 673 (1986)].
- ⁸G. O. Baram, L. I. Buravov, L. S. Degtyarev *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 293 (1986) [*JETP Lett.* **44**, 376 (1986)].
- ⁹J. M. Williams, H. H. Wang, M. A. Beno *et al.*, *Inorg. Chem.* **23**, 3839 (1984).
- ¹⁰R. P. Shibaeva, R. M. Lobkovskaya, M. A. Simonov *et al.*, *Kristallografiya* **31**, 1105 (1986) [*Sov. Phys. Crystallogr.* **31**, 654 (1986)].
- ¹¹V. F. Kaminskiĭ, V. N. Laukhin, V. A. Merzhanov *et al.*, *Izv. Akad Nauk SSSR, Ser. Khim.*, No. 2, 342 (1986).
- ¹²A. V. Zvarykina, M. V. Kartsovnik, V. N. Laukhin *et al.*, *Zh. Eksp. Teor. Fiz.* **94**, 277 (1988) (sic).

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