

An increase in the superconducting-transition temperature of β -(BEDT-TTF) $_2$ I $_3$ to 6–7 K at a normal pressure

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β -(BEDT-TTF) $_2$ I $_3$ crystals can be obtained by heat treating iodine-rich ϵ -phase crystals of the (BEDT-TTF) $_4$ (I $_3$) $_2$ I $_8$ composition in a vacuum. The superconducting-transition temperature of a β -(BEDT-TTF) $_2$ I $_3$ crystal obtained in this manner increases from 1.5 K to 6–7 K at a normal pressure, reaching a record level for organic superconductors.

A BEDT-TTF molecule, when combined with iodine, can form several compounds which differ from each other in their composition and/or structure.¹ The phases containing least iodine are the α - and β -(BEDT-TTF) $_2$ I $_3$ phases, of which the former undergoes a dielectric transformation at 137 K (Ref. 2) and the latter is a superconductor with $T_c = 1.5$ K (Ref. 3). The most iodine-rich phase of all the phases known currently—the ϵ -phase of the composition (BEDT-TTF) $_4$ (I $_3$) $_2$ I $_8$ (Ref. 1)—undergoes a transition to the superconducting state at 2.5 K. In its properties this phase is very close to the orthorhombic γ -phase.⁴

A surprising feature of the BEDT-TTF-I system is that the iodine-poor β -phase crystals can be obtained from the ϵ -phase crystals by holding the latter in a vacuum at an elevated temperature. In spite of the great difference in the crystal structures of these phases, such a procedure does not cause the crystals to fracture under a mechanical stress. As a result, conventional methods can be used to study these crystals. In the present letter we describe some properties of the β -(BEDT-TTF) $_2$ I $_3$ crystals obtained in this manner.

We have carried out several experiments, in which groups of ϵ -phase crystals were held under a vacuum of 10^{-2} torr for 4–5 h at 100 °C. In one of the experiments, such a heat treatment was carried out on a Faraday's magnetic balance,⁵ allowing us

to continuously monitor the sample's weight and to measure its susceptibility. After a 5-h treatment, the weight of a crystal decreased by nearly 30%. This weight loss is in fairly good agreement with the loss that is expected to occur upon a transition for an ϵ -phase composition to a β -phase composition. The weight-reduction rate falls off appreciably after 5 h of heating.

After a heat treatment in a vacuum, the surface of the crystals usually acquires a rust-colored tint that disappears after the crystals are washed in benzonitrile. An x-ray analysis shows that the crystal lattice of these crystals corresponds to the β -phase (BEDT-TTF)₂I₃. The fact that the $\epsilon \rightarrow \beta$ transformation is nearly total is also indicated by the behavior of the magnetic susceptibility which changes radically after the heat treatment and becomes essentially indistinguishable in magnitude and temperature behavior from the magnetic susceptibility of the β phase that was measured previously.⁶

In Fig. 1 the temperature region below 6–7 K is an exception. We see that the susceptibility in this region has a large diamagnetic component which increases with decreasing temperature and magnetic field. Measurements of the temperature dependence of the resistance of heat-treated crystals show that this diamagnetic component of susceptibility is caused by a transition to the superconducting state.

Figure 2 shows the corresponding data for superconducting transitions of an original ϵ -phase crystal and of a β -phase crystal which was obtained after a heat treatment in a vacuum. All curves are normalized to the corresponding resistance at 15 K. Typical values of the resistance ratio R_{300}/R_{10} are 30–50 for the original crystals and 100–150 for heat-treated crystals.

Heat-treated crystals have a rather diffuse superconducting transition that begins at 7.5–8 K and sometimes ends near 2 K. This behavior is evidently attributable to the fact that the heat-treated crystals are not yet completely homogeneous. The temperature at the midpoint of the transition, which rises as the transition becomes sharper, lies in the temperature range 5–6 K in this case. The temperature at the midpoint of

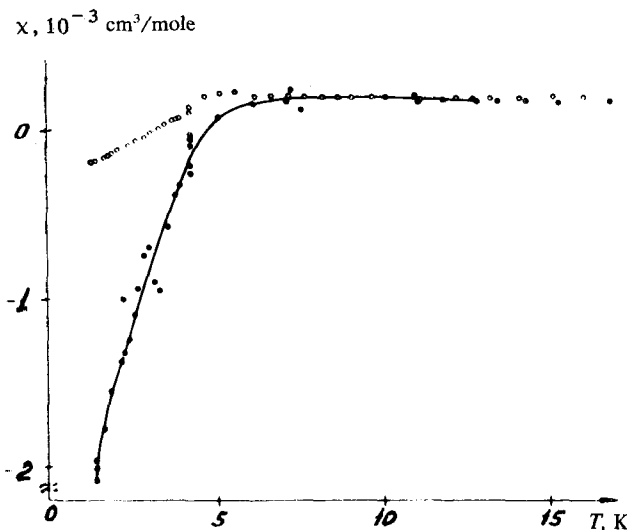


FIG. 1. Temperature dependence of the susceptibility in a 2.8-kOe field (●) and in a 8-kOe field (○). The diamagnetic component of the lattice has been subtracted from the measured values— 5.14×10^{-4} cm³/mole.

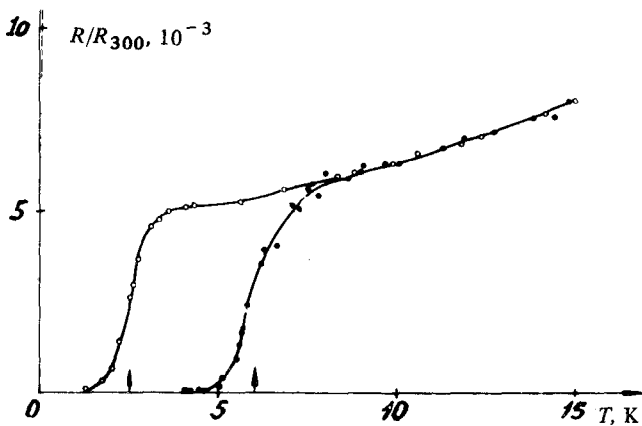


FIG. 2. Superconducting transitions of the original ϵ -phase crystal (\circ) and of the β -phase crystal obtained after a heat treatment in a vacuum (\bullet). The arrows indicate the temperatures at the midpoint of the transitions.

the transition of more refined samples, whose transition width is ~ 0.5 K, must therefore be near 7 K.

The study of β -(BEDT-TTF) $_2$ I $_3$ crystals with such high critical temperatures sheds some light on the origin of the pretransitional effects which occur in the temperature range 7–8 K and which were discussed in Refs. 7–9. The cause of such a sharp increase in the critical temperature, however, has not yet been determined.

It is possible that a sharp increase in T_c is attributable to a slight change in the stoichiometric composition of iodine, which does not lead to a change in the crystal structure and which is accompanied by a slight change in the number of carriers. The first experiments involving direct iodine doping of β -(BEDT-TTF) $_2$ I $_3$ crystals have shown that the transition temperature does indeed increase, although not to the extent indicated. A slight change in the stoichiometric composition of iodine, on the other hand, may be only a factor, rather than a direct cause, that either stimulates or impedes the potential low-temperature phase transformations. Finally, it may turn out that a change in the iodine content is not a factor at all and that the internal strain produced in a crystal as a result of an $\epsilon \rightarrow \beta$ transformation is the answer.

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