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## Homogeneous superconducting state at 8.1 K under ambient pressure in the organic conductor $\beta$ -(BEDT-TTF) $_2$ I $_3$

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**Résumé.** — Nous présentons la première observation d'une transition supraconductrice étroite et complète à 8.1 K dans  $\beta$ -(BEDT-TTF) $_2$ I $_3$  sous pression atmosphérique. Ce résultat est obtenu après l'application d'une pression hydrostatique en hélium gazeux de 1.5 kbar et le relâchement de la pression à basse température. Nous apportons des évidences expérimentales indiquant l'instabilité au-dessus de 250 K de l'état métastable responsable à cette supraconduction homogène sous pression atmosphérique.

**Abstract.** — We report the observation of the first narrow and complete superconducting transition yet obtained in  $\beta$ -(BEDT-TTF) $_2$ I $_3$  at 8.1 K and ambient pressure after pressurization up to 1.5 kbar and a release of the helium gas pressure at low temperature. We show experimental evidences indicating that the metastable state giving rise to homogeneous superconductivity at ambient pressure is not stable above 250 K.

### 1. Introduction.

The series of organic conductors based on the BEDT-TTF (<sup>1</sup>) molecule has provided new organic superconductors with a substantial enhancement of the critical temperature as compared to the (TMTSF) $_2$ X family [1].

Extensive high-pressure work recently performed on the trihalide salts of BEDT-TTF both in the USSR [2] and Japan [3] has shown that  $T_c$  of the  $\beta$ -modification can be raised up to 7.5 K under a pressure of 1.3 kbar. The two groups have also claimed the stabilization of superconductivity around 7 K at ambient pressure either after temperature cycling [4] or after the release of a high pressure at ambient temperature [5]. However, according to reference [5] the onset of

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(<sup>1</sup>) BEDT-TTF = Bis(ethylenedithio)tetrathiofulvalene.

superconductivity observed by 4-probe resistive measurements extends over the broad temperature domain between 8 and 2 K.

The purpose of the present work was a study of the onset of superconductivity in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> using the helium-gas high pressure cycling technique which is available at Orsay. Following a particular high pressure and low temperature operating procedure we have been able to stabilize superconductivity showing a sharp superconducting transition at 8.1 K under ambient pressure with its onset at 8.5 K. Temperature and pressure cycling data suggest that the establishment of an homogeneous superconducting state in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at ambient pressure requires releasing pressure at low temperature.

## 2. Experimental.

Single crystals of  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> have been prepared by electrochemical methods as reported recently [6]. In this preparation using tetrahydrofurane as a solvent,  $\alpha$ -phase and  $\beta$ -phase crystals of (BEDT-TTF)<sub>2</sub>I<sub>3</sub> grow simultaneously at the anode. Both modifications have different shapes ( $\alpha$ -phase : thin plates ;  $\beta$ -phase : canted rhombohedrons) and can be separated easily under a microscope. In addition, the  $\beta$ -phase crystals used in this study were also identified by the EPR technique [7]. The resistivity data have been obtained on small crystals of typical size  $1 \times 0.6 \times 0.2$  (mm)<sup>3</sup>. Four gold contacts have been evaporated at the corners of the samples where thin gold wires have been attached using silver paint. The resistance has been measured with the usual low-frequency lock-in technique passing a current of 0.1 mA through the sample along its *a*-axis. The room temperature conductivity has been estimated to  $50\text{-}70$  ( $\Omega$  cm)<sup>-1</sup>. The high pressure was provided by helium gas hydrostatic medium using a Be-Cu pressure vessel. Therefore, it was possible to monitor the high pressure, even at low temperature, as long as the experimental conditions were kept in the T-P domain where helium remains in its fluid state.

## 3. Results.

Three T-P runs reported in this section have been performed on the same sample using the four-contact arrangement. First, we applied pressure up to 1.5 kbar at room temperature on a virgin sample. The concomitant increase of the conductivity is displayed in figure 1. Then, keeping the

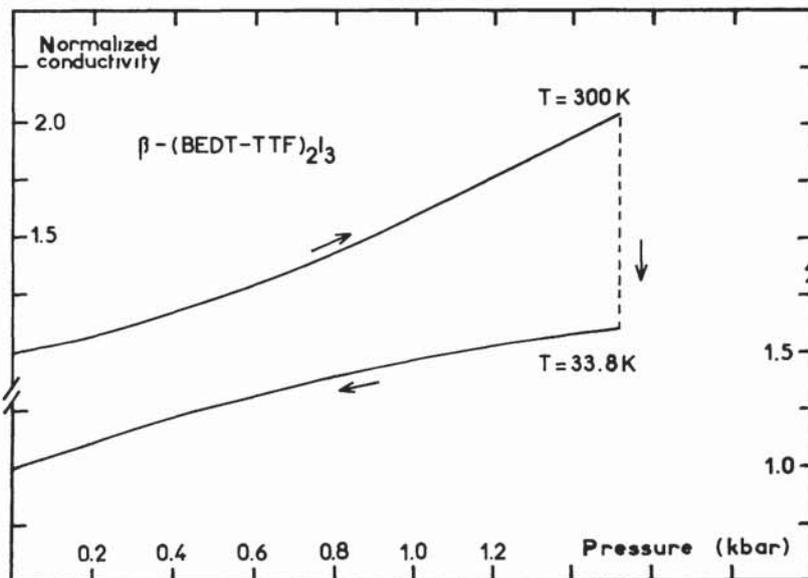


Fig. 1. — Normalized pressure dependence of the conductivity at room temperature and at 33.8 K in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> according to the T-P cycling described in the text (runs 1 and 3).

pressure constant, the sample was cooled down to 33.8 K. During this cooling process the resistance decreased by a factor about 100. At the constant temperature of  $33.8 \pm 0.1$  K, the pressure was released down to the ambient value. The conductivity was found less pressure dependent at low temperature than at room temperature (Fig. 1). With further cooling, we observe a sharp superconducting transition (Fig. 2). The departure of the resistance from its temperature dependence above the transition defines an onset temperature of about 8.5 K. However, the transition temperature evaluated by the centre of the resistive transition amounts to 8.1 K. By 7.4 K the

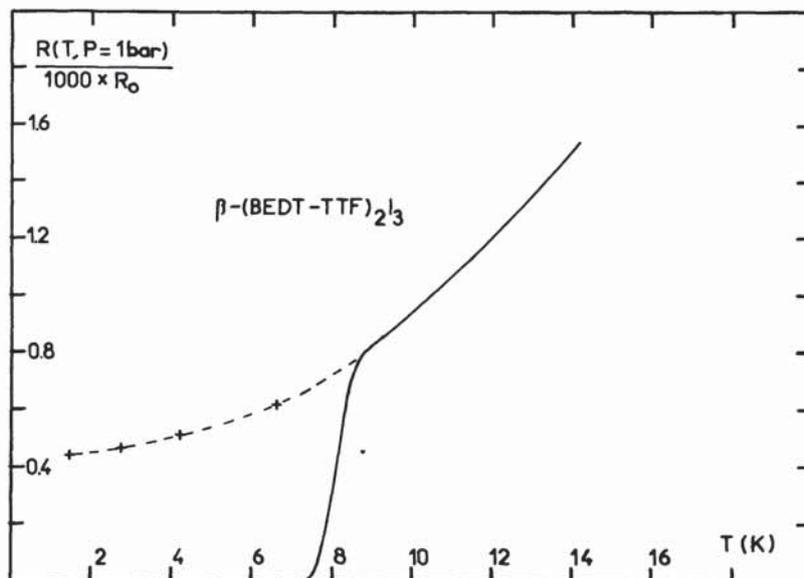


Fig. 2. — Superconducting transition at ambient pressure in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. The resistance is normalized to its room temperature value at 1 bar. The crosses indicate the behaviour of the  $R$  versus  $T$  dependence derived from the zero-field extrapolation of the magnetoresistance in figure 3.

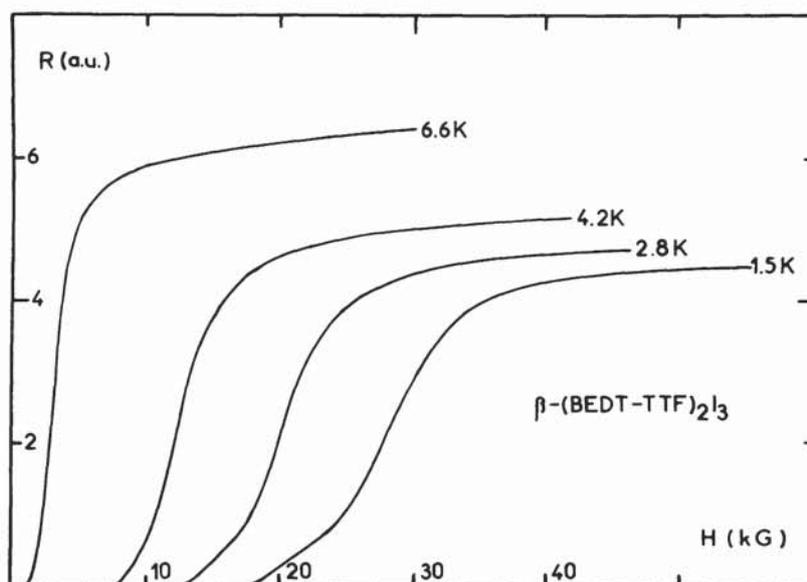


Fig. 3. — Effect of the magnetic field along  $c^*$  on the superconducting transition of  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at various temperatures.

superconducting transition is complete; the resistivity has dropped by more than 99 %. The same procedure was reproduced on two other samples with essentially similar results as those shown in figure 2.

The suppression of the superconducting state by magnetic field along the  $c^*$  axis at various temperatures is shown in figure 3. The upper critical fields  $H_{c_2}$  evaluated by the mid-transition are reported in figure 4. We may notice that the slope of  $H_{c_2}$  versus temperature is about twice larger than the one reported at 1.3 kbar [3] in spite of fairly similar transition temperatures. Subsequently, the sample was kept at low temperature for three days and no change in the superconductivity phenomenon could be noticed when looking at the transition *via* magnetic field scanning or temperature cycling between 1.5 and 30 K.

In the second run, the same sample was warmed from 4.2 K up to 250 K at ambient pressure and kept at this temperature for 30 minutes. The sample was then cooled again down to helium temperature with no pressure application. As shown in figure 5, an upturn of the resistivity is

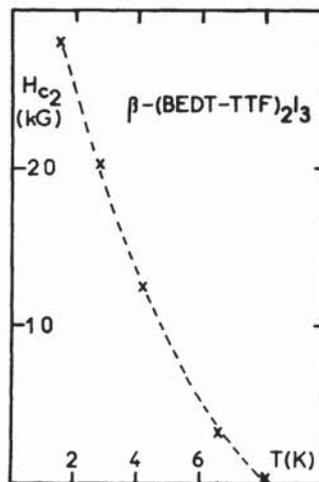


Fig. 4. — Upper critical field in the high- $T_c$  phase of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  versus temperature. The line is a guide for the eyes.

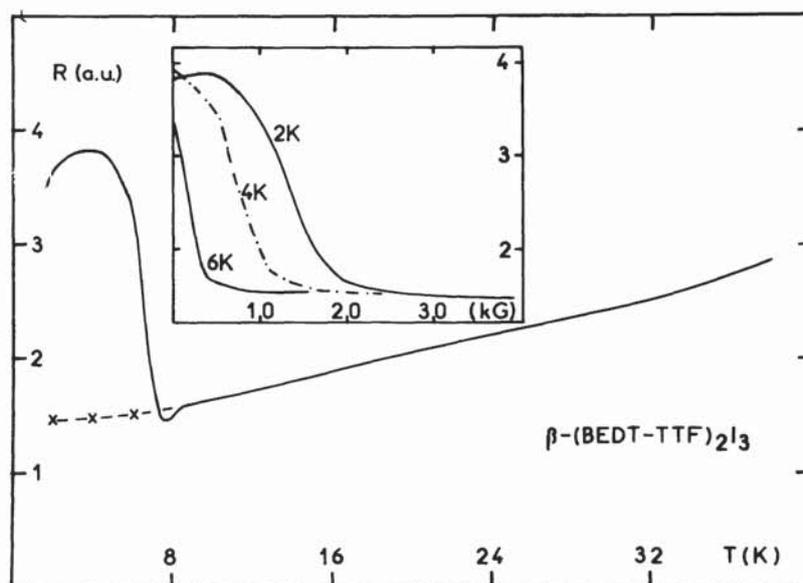


Fig. 5. — Resistive anomaly in the mixed state of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  in the second run (see text). Insert shows the suppression of the anomaly by magnetic field along  $c^*$ . The crosses indicate the behaviour of the  $R$  versus  $T$  dependence derived from the zero-field extrapolation of the magnetoresistance.

observed at the same temperature where superconductivity was achieved in the first run. The drop of resistivity observed on further cooling could be an indication of the transition to a superconducting state around 1.2 K already reported at ambient pressure [8]. The effect of the magnetic field on this resistivity upturn was remarkable in as much as the field along the  $c^*$  axis suppressed this anomaly in about the same manner as superconductivity in the first run. In the second run the temperature dependence of the resistivity above 8 K is much smaller than in the first run. This seems to be a genuine intrinsic effect in the sample resulting from the cooling procedure and cannot be attributed to the occurrence of microcracks as shown by the behaviour of the resistance in the following run.

After warming up to room temperature, the third run was performed on the same sample with a T-P cycling procedure identical to the first run. The sharp and complete superconducting phenomenon reappeared exactly as observed from the data in the first run : showing similar values of  $T_c$ , critical fields and resistivity *versus* temperature above  $T_c$ .

Finally, we have checked on a fresh sample that no anomaly is observed around 8 K when it is cooled under ambient pressure without any prior pressurization. This implies that the effect reported in the second run had some connection with the temperature and pressure treatment of the sample. A similar although smaller upturn of the resistivity has been also reported by Kwak *et al.* [9] in the same compound around 7 K at 0.5 kbar.

#### 4. Discussion.

To try and understand the new data presented in this work, it is useful to survey the behaviour of superconductivity previously reported in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. Superconductivity at a low  $T_c$  of 1.3 K at ambient pressure (we call it  $\beta$ -L phase) was first reported by Yagubskii *et al.* [8]. Then Laukhin *et al.* [2] and Murata *et al.* [3] have shown that it is possible to stabilize a high- $T_c$  phase ( $T_c = 7.4$  K) which we call from now on the  $\beta$ -H phase by applying a pressure of  $\approx 1.3$  kbar. There has been several claims for superconductivity around 8 K at ambient pressure following a special temperature or pressure treatment of the sample. In reference [4] the sample was cycled between room and helium temperature and Tokumoto *et al.* [5] have released the pressure at room temperature. Both report a broad transition which extends well below 8 K and superconductivity obtained with two steps of the resistivity. Rather similar behaviour has been observed by Merzhanov *et al.* [10] starting from the  $\epsilon$ -phase.

In the present work, we have prepared for the first time the sample in the state exhibiting complete superconductivity above 8 K at ambient pressure (runs 1 and 3). Furthermore, the upturn of the resistance occurring at the temperature where superconductivity is observed in the  $\beta$ -H phase (run 2) can be accounted for by a perturbation of the current distribution in the sample due to the coexistence of superconducting and non-superconducting domains. It is possible to imagine that, given the particular square-geometry of the contacts, the formation of superconducting domains below 8 K induces a disturbance of the current paths in the non-superconducting regions, with a resulting change and possibly increase of the measured voltage drop [11]. When the magnetic field is applied, the superconducting domains disappear and the regular behaviour of the resistivity is recovered (Fig. 5). The weak temperature dependence of the resistance above 8 K in run 2 may thus be related to some additional electron-scattering process provided by the coexistence of two phases with different structural features.

The comparison between the three runs performed on the same sample suggests that the  $\beta$ -H phase of  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> which is stabilized at ambient pressure and low temperature by our pressure cycling procedure becomes no longer stable when the sample is warmed up to 250 K. The homogeneous character of the  $\beta$ -H phase is lost above a temperature which is situated between 35 and 250 K. Therefore, at the present state of our investigations, we assume that the  $\beta$ -H and  $\beta$ -L phases of  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> correspond respectively to the structure stable at room temperature and either to the modulated structure [12] or to the superstructure observed at

100 K [13]. In the superstructure [space group P1 :  $a = 18.27 \text{ \AA}$ ,  $b = 21.04 \text{ \AA}$ ,  $c = 6.543 \text{ \AA}$ ,  $\alpha = 93.56^\circ$ ,  $\beta = 94.84^\circ$ ,  $\gamma = 99.86^\circ$ , at 100 K [13, 14]] — with a volume of the unit cell of about three times that of the room temperature phase — a pronounced distortion of the triiodide chain but only minor changes in the position of the BEDT-TTF molecules exist with respect to the room temperature phase [13, 14]. This superstructure is different from the incommensurate phase detected by neutron scattering below 220 K [12]. The neutron scattering data [12] and the X-ray data at 100 K [13, 14] seem to imply that the phase transition is not driven by the divergence of the Peierls/SDW channel in the low-dimensional electron gas. However, this structural phase transition is likely to affect the intermolecular contacts (consequently  $N(E_F)$  and/or the electron-electron coupling constant responsible for superconductivity). The moderate pressure (1.3 kbar) which is needed to make the  $\beta$ -H phase stable and uniform at low temperature and the possibility to mix  $\beta$ -L and  $\beta$ -H phases by thermal cycling [4] show that both phases are energetically close to each other. Consequently, the procedure we have utilized in this work (run 1) freezes the  $\beta$ -H state at low temperature (and ambient pressure) with no traces of  $\beta$ -L phase which could be detected by resistivity measurement.

## 5. Conclusion.

We have presented new results on the stabilization of superconductivity at high temperature in the  $\beta$ -phase of  $(\text{BEDT-TTF})_2\text{I}_3$  at ambient pressure. We have given some indication that a depressurization below 1.3 kbar must be performed at low temperature in order to obtain homogeneous superconductivity with a  $T_c$  of 8.1 K under ambient pressure. Furthermore, we suggest that all superconducting anomalies reported at ambient pressure by previous workers could be related to the coexistence of two crystallographically different states of the compound. This study has emphasized once more that the superconductivity of organic conductors is extremely sensitive to slight changes of physical parameters. In this respect, the organic superconductivity cannot be considered as a « poor imitation » of the superconductivity in metals. More work is presently under completion to establish the stability of the  $\beta$ -H phase in the T-P plane and the nature of the  $\beta$ -L to  $\beta$ -H transition.

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