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The High-T_c Superconducting State of β-(BEDT-TTF)$_2$I$_3$ at Atmospheric Pressure: Bulk Superconductivity and Metastability.

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Abstract. – The AC susceptibility study of β-(BEDT-TTF)$_2$I$_3$ reveals that the high-T_c metastable superconducting state which can be stabilized at atmospheric pressure after a particular pressure-temperature cycling procedure, exhibits bulk superconductivity resembling very closely that of the high-T_c state, which is stabilized above 1 kbar. Annealing experiments show that the high-T_c state remains stable at low temperature as long as the annealing temperature does not exceed 125 K.

1. Introduction.

The new series of organic conductors based on the (BEDT-TTF) ([1]) molecule has been the subject of great interest over the past few years [1]. The interest arose from the existence of relatively high T_c for superconducting transitions as compared to compounds of the (TMTSF)$_2$X series (Bechgaard salts). In particular, the β modification of the trihalide salt exhibits the highest ever reported T_c in an organic conductor. In a recent paper [2], we have shown that the high-T_c superconducting phase observed under pressure [3, 4] can be stabilized at ambient pressure, provided a well-defined process is followed: an increase of the pressure up to 1.5 kbar at room temperature, followed by a decrease of the temperature down to 33.8 K at constant pressure, and finally the release of the pressure down to the

([1]) BEDT-TTF = Bis(ethylenedithio)tetrathiofulvalene.

atmospheric value at fixed temperature. Using resistivity techniques and the previous particular cooling procedure, we have been able to stabilize superconductivity with a sharp and complete superconducting transition at 8.1 K under ambient pressure. We have also given other experimental results suggesting that superconducting anomalies reported by other groups at ambient pressure around 7 K, either after temperature cycling [5] or after a high-pressure release at room temperature [6], are possibly due to the mixture of two structurally different phases. We have called β-H the phase which is isostructural to the room temperature phase, and β-L the phase which corresponds either to the distorted state observed at 100 K [7] or to the modulated structure below 200 K [8]. From our point of view, the β-H phase, which is stabilized at ambient pressure and low temperature by our pressure cycling process, is the only phase exhibiting homogeneous superconductivity above 7 K. Furthermore, we gave some hints as to the instability of this phase when the sample is warmed up to 250 K.

In this work, we have carried on the study of the β-H phase stability using an AC detection technique for superconductivity. First, we show that the high-T_c superconducting transition stabilized at ambient pressure exhibits a response similar to the one observed at 1.3 kbar. Secondly, we present additional temperature-pressure cycling processes, which strongly suggest that the stability of the β-H phase at ambient pressure is related to structural transitions above 100 K and that the superconducting state at 8 K remains stable as long as the sample is not warmed above 125 K.

2. Experimental.

Small single crystals of β-(BEDT-TTF)$_2$I$_3$ have been prepared by the electrochemical method [9]. For superconductivity detection, we put the powdered sample of total weight ~ 30 mg in the tank circuit of a Robinson oscillator [10]. As the frequency of the resonant circuit is around 9.5 MHz, small drifts in resonance frequency observed above T_c can be attributed to the temperature dependence of the skin depth. From resistivity measurements at low temperature, the smallest penetration depth in the normal state is of the order of 100 μm at this frequency, a value much higher than the particle size of the powdered sample (a few microns). However, a rapid increase of the resonance frequency is expected when a bulk superconducting transition occurs. High pressure was provided by a helium-gas hydrostatic medium in a Be-Cu pressure vessel. That way, it was possible to monitor the temperature-pressure cycling in the domain where helium remains fluid.

3. Results.

The first run (fig. 1*a*)) was achieved under a pressure of 1.6 kbar. At this pressure, the superconducting transition has been observed by resistivity measurements [3, 4] and corresponds to a true bulk effect according to the detection of Meissner expulsion [11]. With the present detection method, the signature of the transition is a sharp increase of the resonance frequency starting at 8 K as shown in fig. 2*a*). Furthermore, this frequency increase is sensitive to a magnetic field of the order of 10 kG, but no quantitative information can be derived from these data because of the anisotropy of the critical fields in these materials [12].

In the second run (fig. 1*b*)), the sample has been cooled following the Orsay process. A drop of the susceptibility (fig. 2*b*)) is observed at ambient pressure at about the same temperature where superconductivity was previously observed by resistivity

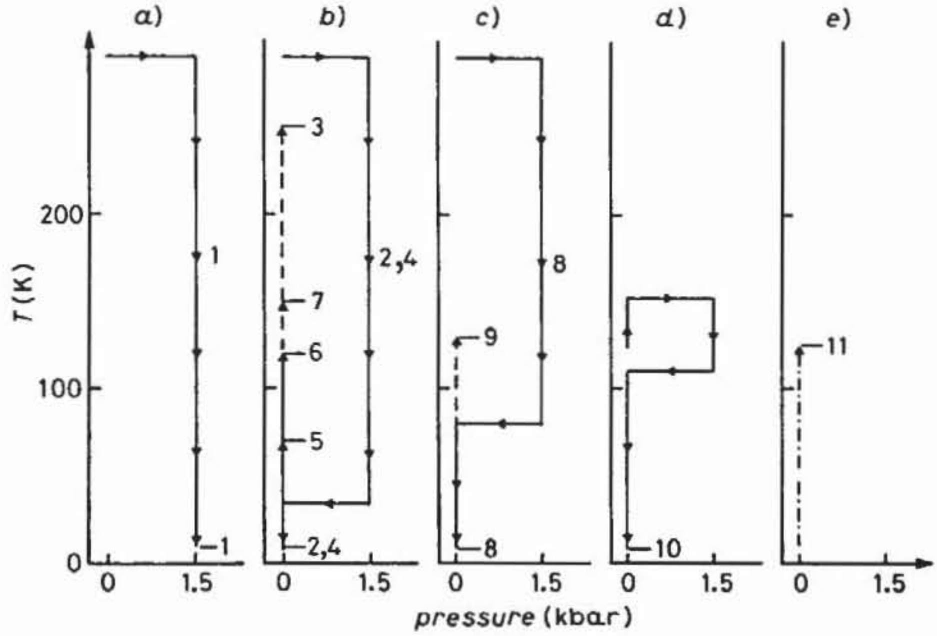

Fig. 1. – Display of the different temperature-pressure routes used in this work.

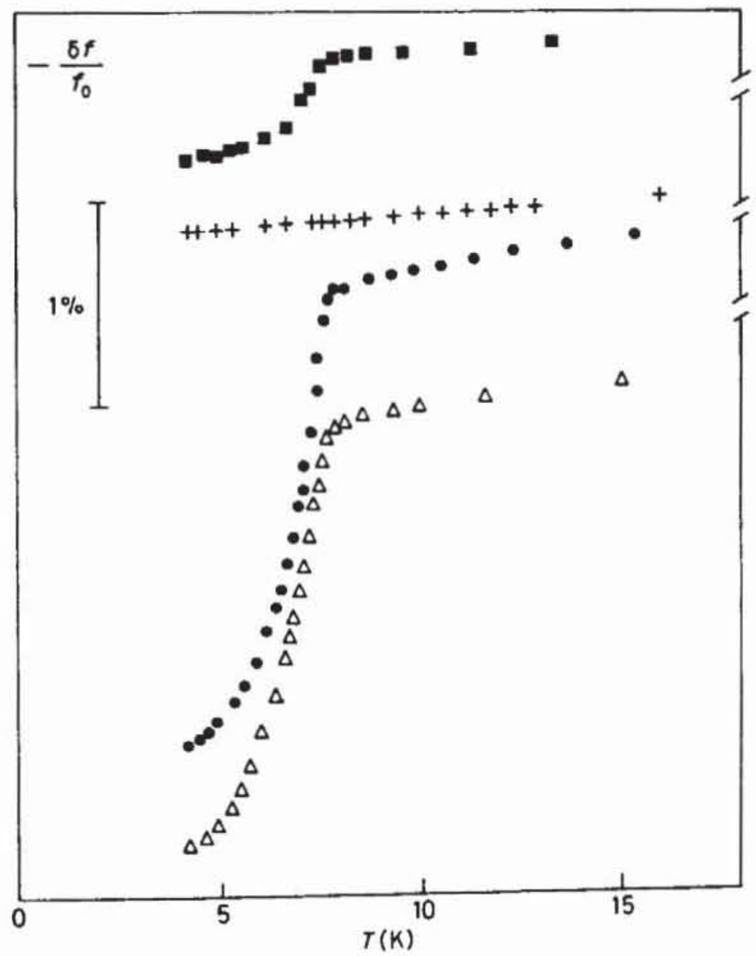

Fig. 2. – AC susceptibility signal in β-(BEDT-TTF)$_2$I$_3$: △ under pressure (1.6 kbar), ● at ambient pressure after release of pressure at low temperature, + at ambient pressure after annealing above 131 K, ■ at ambient pressure after annealing at 125 K.

measurements [2]. We have noticed a small increase of about 6% in comparison to the one performed at 1.6 kbar for the susceptibility change between 8 K and 4.2 K. This can probably be attributed to a difference in skin depth penetration, since the conductivity has fallen by a factor 1.7 between 1.6 kbar and ambient pressure [2]. Anyway, referring to the similarity between the data at 1.6 kbar and ambient pressure, we infer that superconductivity is a bulk effect even at ambient pressure.

In the third run (fig. 1*b*)) we warmed the sample up to 250 K and kept it at this temperature for 30 minutes, before further cooling down to 4.2 K. Hence, no signal could be detected around 7 K using the AC susceptibility technique as shown in fig. 2*c*), in spite of the observation of an anomaly observed by resistivity techniques and attributed to traces of superconductivity [2].

In run 4, using the Orsay process, bulk superconductivity has been recovered identical to that of run 2. In runs 5, 6 and 7, we tried to anneal the sample: starting from the superconducting state, we warmed the sample up to 71 K, 121 K and 152 K, respectively and kept the sample at this temperature for about 5 minutes. The first two runs lead to the same complete superconducting phenomenon, but the last (annealing at 152 K) destroys completely superconductivity.

Run 8 (fig. 1*c*)) was similar to the Orsay process (runs 2 and 4), with the only difference that the high pressure was released at 80 K. Consequently, the bulk superconducting behaviour reappeared exactly as observed in runs 2 and 4. Run 9 shows another 5 minutes' annealing process up to 131 K which suppressed completely the superconducting transition as for runs 3 and 7.

Run 10 (fig. 1*d*)) is quite interesting. Starting at low temperature from a β-L state, we warmed the sample up to 153 K. Then, at this temperature, we applied a pressure of 1.5 kbar. The sample was subsequently cooled down to 110 K at constant pressure. At this temperature, we released the pressure down to its atmospheric value and cooled the sample down to 4.2 K. We thus observed exactly the same superconducting transition as for runs 2, 4 and 8.

In run 11 (fig. 1*e*)) the sample was annealed up to 125 K, and kept at this temperature for about 5 minutes. A much weaker decrease of the AC susceptibility was thus observed at approximatively the same temperature (fig. 2*d*)), the overall shift of the frequency being only 25% of the other superconducting signals (runs 2, 4, 8, 10).

Finally, we attempted to cool the sample very quickly (less than 5 seconds between 300 K and helium temperature). No sign of superconductivity above 4.2 K could be detected after this fast-cooling process.

3. Discussion and conclusion.

First, we comment on the nature of the superconducting state which is stabilized using our particular temperature-pressure cycling process. Although the present experimental method (AC susceptibility) does not provide a bulk response as compared to SQUID magnetization measurements, we feel that the data in the first run ($P = 1.6$ kbar) together with the SQUID magnetization data of ref. [11] give a signal which is characteristic of bulk superconductivity with a lower limit of 24% for the superconducting volume. Thus, it seems clear that the superconducting phase at 1 bar prepared by releasing the high pressure at low temperature (fig. 1*b*); runs 2, 4) presents the bulk character. Furthermore, after annealing the sample above 131 K, no bulk superconductivity exists in the sample above 7 K. This feature is in agreement with the absence of the Meissner signal under ambient pressure [11] without Orsay process.

Secondly, we consider the stability in temperature of the β-H phase which can be obtained under ambient pressure by the pressure-temperature cycling. The ambient pressure β-H state appears to be metastable. At very low temperature, say below 40 K, no conversion of the β-H phase into the thermodynamically stable phase can be observed over periods of days or so [2]. However, as shown by the present AC susceptibility data, around 125 K the metastable β-H phase converts rather quickly into the β-L phase. At this temperature, already a break in the slope of the thermopower data [13] has been observed and, therefore, it was assumed that a phase transition might exist. Furthermore, we have shown that, by proper annealing of the metastable β-H phase, it is possible to obtain β-(BEDT-TTF)$_2$I$_3$ in a mixed phase at low temperature showing inhomogeneous superconductivity. Thus, we feel that the assumption made after our previous resistivity study [2] is still justified: the β-L and the metastable β-H phases are structurally different. They correspond to the phase thermodynamically stable at low temperature and ambient temperature, respectively. The crystallographic structure of the β-L phase is still somewhat controversial. An incommensurate distortion detected by neutron scattering below 220 K [8] and also by X-ray diffuse scattering below ~ 175 K [14] may be the crystallographic signature of the β-L phase. However, a pronounced distortion of the triiodide chain giving rise to a commensurate superstructure has also been reported at 100 K [7]. The origin for the apparent discrepancy between the different crystallographic studies is not clear yet. Nevertheless, the moderate pressure which is required to stabilize the β-H phase at low temperature ~ 1 kbar) and the existence of mixed (β-L, β-H) states obtained after adequate annealing show that the β-L and β-H phases are energetically close to each other.

In addition, these experiments have demonstrated that it is possible to prepare the high-T_c metastable state of β-(BEDT-TTF)$_2$I$_3$ via depressurization even above liquid-nitrogen temperature.

Finally, the accuracy of our AC susceptibility experiments allows us to suggest that the resistivity anomaly which is detected around 7 K after temperature cycling [5], or pressure cycling at room temperature [6] does not involve more than about 3% of the sample volume becoming superconducting. The Orsay pressure-temperature cycling procedure seems to be a prerequisite for the stabilization of a homogeneous superconducting state around 8 K at ambient pressure in β-(BEDT-TTF)$_2$I$_3$.

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