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# α- AND β-(BEDT-TTF)$_2$I$_3$ - TWO MODIFICATIONS WITH CONTRASTING GROUNDSTATE PROPERTIES: INSULATOR AND VOLUME SUPERCONDUCTOR

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## Abstract

The α-modification of (BEDT-TTF)$_2$I$_3$ undergoes a metal-to-insulator transition at T = 135 K. Application of hydrostatic pressure shifts the transition temperature to lower values. Above 12 kbar semimetallic behavior is observed, but no superconductivity is detected up to a pressure of 17 kbar and temperatures down to 100 mK. The β-modifcation, on the other hand, exhibits ambient pressure volume superconductivity below $T_c$ = 1.05 K. Measurements of the anisotropy of the diamagnetic shielding- as well as the Meissner-magnetization are presented.

## INTRODUCTION

The first discovery of organic superconductivity (SC) in the family of Bechgaard salts (TMTSF)$_2$X /1,2/ has successfully stimulated the search for new organic materials that exhibit this still fascinating solid state phenomenon at low temperatures. Parkin et al. found the sulfur based compound (BEDT-TTF)$_2$ReO$_4$ (bis-(ethylenedithiolylenetetrathiafulvalene)-perrhenate) to be superconducting below $T_c \sim 2$ K and above a pressure of ∿4 kbar /3,4/. Recently, the interest has focussed strongly on compounds based on the same donor (BEDT-TTF) with the triiodide ($I_3$) molecule as counter ion. Very recently, Yagubskii et al. have reported three of its stoichiometries to be zero pressure SC's with $T_c$ = 1.4 - 1.5 K /5/ and $T_c$ = 2.5 K /6,7/. So far ambient pressure SC has been observed only in (TMTSF)$_2$ClO$_4$ and it could be demonstrated there that SC is

a bulk property which means that all conduction electrons condense into the SC state /8,9/.

The measurement of the electrical resistivity is a common tool in the search for SC, but a drop to a state with zero resistivity is not necessarily an indication of volume SC, as only one complete SC path through the sample can yield zero resistance and thus mask the information about the state of the remaining sample volume. On the other hand, the diamagnetic response of a SC to small magnetic fields (especially the Meissner effect, i.e. the flux expulsion from the SC) yields information about the volume that is superconducting. The compound $(TMTSF)_2FSO_3$ may serve as an example of such a case. Superconductivity has been detected by means of resistivity measurements above a pressure of $\sim 5$ kbar and below $T_c \sim 2$ K /10,11/. The diamagnetic measurements yield an upper limit of only 2 % of the volume that is SC below a transition temperature of 1.0 K /12/.

The main purpose of this paper is to demonstrate by low field magnetization experiments that the zero resistance state of β-$(BEDT\text{-}TTF)_2I_3$ (found by Yagubskii et al. below $\sim 1$ K with a start of the resistive transition at 1.5 K) is in fact a state of bulk volume superconductivity.

Crystals of the triiodide compound in the 2:1 stoichiometry grow in two different structural modifications. The one that we have investigated first, hereafter denoted as the α-modification: α-$(BEDT\text{-}TTF)_2I_3$, undergoes a metal - to-insulator transition at $T_{MI} \sim 135$ K /13,14/. In this paper we report on resistivity measurements of this modification under pressure in order to look for the reduction of $T_{MI}$ and the possible occurence of SC. Ambient pressure SC -as mentioned before- is observed in the other modification - hereafter denoted by β-$(BEDT\text{-}TTF)_2I_3$. The higher $T_c$ phases are of different stoichiometries, e.g. $(BEDT\text{-}TTF)_3(I_3)_2(I_3)_{0.5}$ with $T_c = 2.5$ K and $p_c = 0$ /7/.

## EXPERIMENTAL

Crystals of the α- and β-modification of $(BEDT\text{-}TTF)_2I_3$ were prepared using standard electrochemical techniques, details of which are described in /14,15/. Both modifications grew simultaneously at the anode. In the phase diagram of (BEDT-TTF) and ($I_3$) the minima of the thermodynamical potentials of the various stoichiometries and modifications /7,15/ seem to be very close to each other. Actually at the present state of the art of electrochemistry it is almost impossible to control the parameters of the electrocrystallization in a way to reproducibly grow only one or the other particular stoichiometry in a particular structural modification.

The crystals of α-$(BEDT\text{-}TTF)_2I_3$ that we used for the resistivity measurements were black thin plates of typical dimensions (3x3x0.02 $mm^3$), where the plane of the plates is the a-b plane. Crystals of the β-modifications, grown simultaneously, could be separated from the α-phase under a microscope, since they grow as black canted rhombohedrons with distorted hexagonal cross section

(=the a-b plane). They are somewhat smaller than α-phase-crystals. A typical crystal that has been used in the low field magnetization experiment is shown in the insert of fig. 3 (dimensions: 0.74 mm $\parallel a$, 0.58 mm $\perp a$, 0.22 mm $\parallel c^*$). For the calculation of the demagnetization coefficients /16/ the shape of the sample was assumed to be ellipsoidal (with the sample dimensions as axes of the ellipsoid).

The electrical resistivity of α-crystals was measured by the usual 4 probe ac-method (30 Hz). Copper leads (0.017 mm Ø) were attached to the sample with silver paint on previously evaporated gold pads, yielding contact resistances of a few ohms. The electrical current was always flowing in the a-b plane. Pressure measurements were made in a BeCu-pressure clamp using a 50 : 50 mixture of pentane and isobutane as pressure transmitting medium. The pressure was measured at low temperatures by observing the shift of the SC transition of a Sn-sample.

Our first observation of superconductivity in β-(BEDT-TTF)$_2$I$_3$ crystals came from a measurement of the ac-susceptibility. This was done in a tunnel diode (GE BD-4) oscillator circuit operated at 42 kc in a $^3$He cryostat. The principal experimental set up for the low field dc-magnetization measurements in a dilution cryostat is described in /17/ and the improved version of the apparatus that enabled us to rotate the sample in the magnetic field while it remains at low temperature is discussed in ref. /18/.

## RESULTS AND DISCUSSION

1) α-(BEDT-TTF)$_2$I$_3$

The results of the temperature dependence of the electrical resistance at various pressures are shown in fig. 1. The cooling speed between roomtemperature and 4.2 K was 30 - 60 K/h. The temperature of the metal-to-insulator transition $T_{MI}$, as defined by the maximum of -dlnR/dT, is plotted vs. pressure in fig. 2. At zero pressure $T_{MI}$ = 135 K, as has been observed before /13,14/. Increasing hydrostatic pressure shifts $T_{MI}$ to lower values (at an almost linear rate: $dT_{MI}/d_p \sim -11$ K/kbar). For p > 12 kbar and T > 1.3 K a phase transition temperature can no longer be inferred from the data. The resistivity then does not show activated behavior any more below the temperature of the minimum (which is indicated by the squares in fig. 2). We have cooled one sample in the pressure bomb at 13 kbar in a dilution refrigerator down to 100 mK and did not detect any indications of an onset of superconductivity.

The crucial question as to what causes the metal-insulator transition in the α-phase, remains so far unanswered. We have some indications that it is a structural transition, which however does not take place at the sites of the (BEDT-TTF) molecules. One might speculate that the ($I_3$) molecules distort and thereby loose their inversion symmetry thus opening the possibility of orientational ordering. Detailed structural investigations to clarify the nature of this transition are in progress.

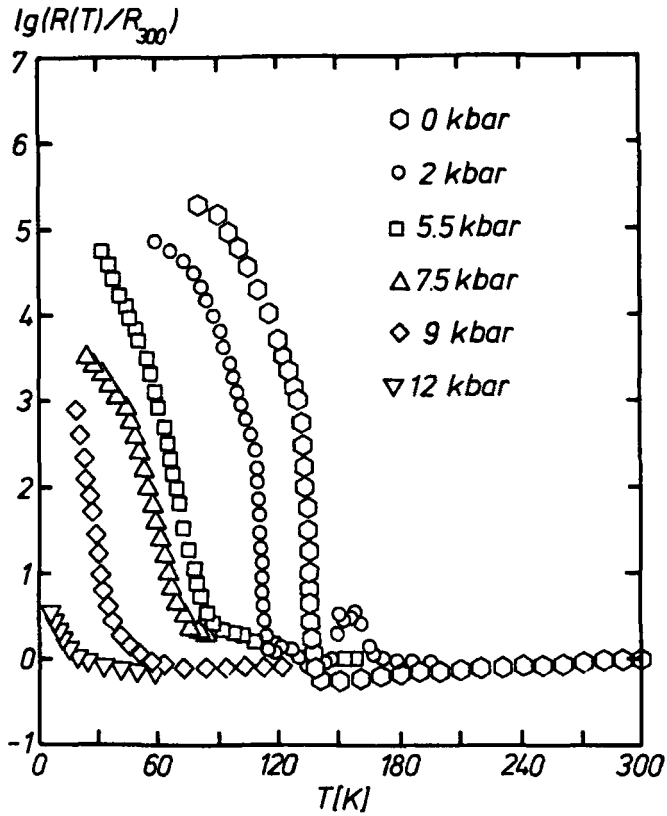


Fig. 1 a-b plane resistivity vs. temperature of α-(BEDT-TTF)$_2$I$_3$ at different pressures.

2) β-(BEDT-TTF)$_2$I$_3$

Samples of this compound have been cooled from roomtemperature to 80 K in 5 - 6 h, and further on to 4.2 K in 1 - 1.5 h. Measurements of the ac-susceptibility clearly show evidence of an onset of diamagnetic shielding currents below 1.05 K /19/. In the dc-magnetization experiment one has to distinguish between two kind of transition curves (fig. 3). When the sample is cooled in zero field well below $T_c$ and the dc-field is then applied, supercurrents on the sample surface (within a layer of the thickness of the penetration depth) are induced that screen the magnetic field from the inside of the sample. Upon warming it up, the decay of the SC screening currents is monitored by the magnetization change: the diamagnetic shielding signal. Leaving the magnetic field on and cooling back the sample leads to the formation of quantized flux

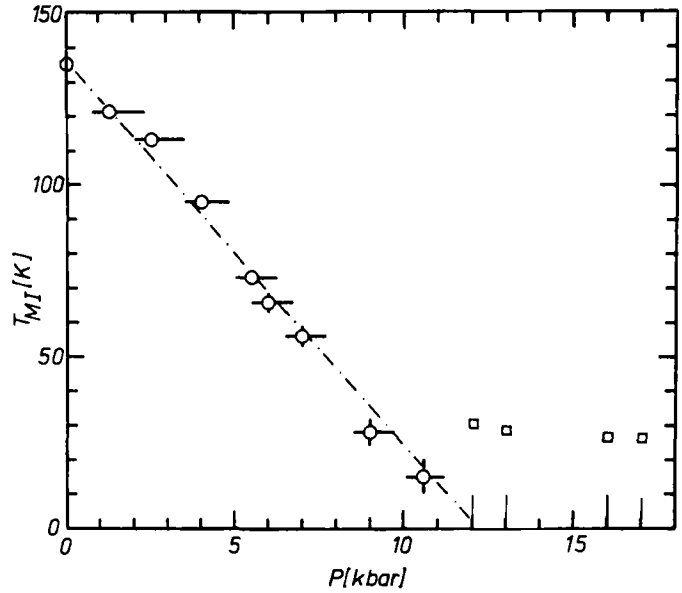


Fig. 2 Phase diagram of α-(BEDT-TTF)$_2$I$_3$. The dash-dotted line corresponds to $dT_{MI}/dp$ = -11 K/kbar. The squares indicate the temperature of the resistance minima in the pressure region above 12 kbar where semimetallic behavior is predomiant.

lines in the sample - that is a departure from the uniform flux distribution in the normal state - and their subsequent expulsion out of the sample: the Meissner effect. Pinning of flux lines at impurity sites or crystal defects leads to a smaller Meissner magnetization than the diamagnetic shielding magnetization. The largest diamagnetic shielding- and Meissner signals (62 resp 18 % of that of a perfect SC, at T = 0.115 K) are observed when the field is oriented normal to the highly conducting a-b plane ($H \parallel c^*$), fig. 3. The transition is broad and not saturated at lowest temperatures, an indication of a considerable spread of $T_c$ over different regions in the sample. A linear extrapolation of the magnetization to zero yields $T_c$ = 1.05 K. From the magnetization curve one can deduce the field when the first flux starts penetrating into the sample: $H_{c1}$. This field is biggest in the orientation $H \perp$ a-b plane: $H_{c1c^*}$ is equal to 0.36 Oe and becomes even smaller when the field is turned into the a-b plane: $H_{c1a}$ = 0.05 Oe and $H_{c1a}$=0.09 Oe. The anisotropy in the a-b plane is not very pronounced, corroborating the two dimensional character of this compound.

Our main finding, in conclusion, is the existence of rather complete dc-shielding supercurrents that demonstrate the existence of closed supercurrent paths on the sample surface which are able

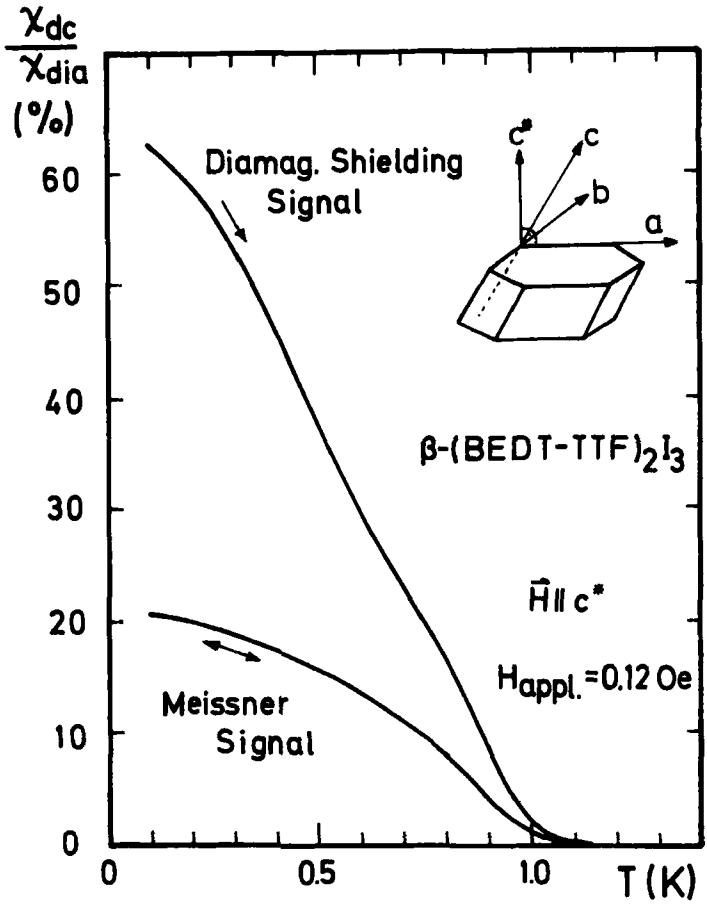


Fig. 3 Diamagnetic shielding and Meissner susceptibility vs. temperature of β-(BEDT-TTF)$_2$I$_3$ in a field applied perpendicular to the a-b plane. The insert relates the morphology of the investigated crystal to its axes.

to keep the bulk of the sample field free. The proof for bulk SC is the ability of the crystal to expell the magnetic flux when cooled in a field. Taking into account flux pinning effects - that are usually observed in bulk type II SC, like (TMTSF)$_2$ClO$_4$ /20/ - the existence of a considerable Meissner effect in β-(BEDT-TTF)$_2$I$_3$ shows that SC in this compound, though anisotropic, is a bulk property.

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