corner-sharing AlO_4 tetrahedra; according to Table 1 its contribution is much weaker with neutrons. The angle Al(4)-O(2)-Al(4) of 132° in the isolated dimeric tetrahedral anion $[Al_2O(OH)_6]^{\ominus}$[12] corresponds with a respective distance Al ··· Al of 3.18 Å. Larger Al-O as well as O-O distances give rise to the peak X 6 around 4.3 Å. Whether the fine structure in $G^N(R)$ in this region is real or is caused by Fourier-ripples cannot be decided presently. It is expected that the broad peaks X 5 and X 6 are also contributed by non-bonding interactions which reflect the partial substitution of aluminum by sulfur in the amorphous structure.

It should be noted that the short range order in amorphous anodic oxide coatings on aluminum shows close similarities to the short range order reported for vitreous silica.[13-17]

Standardization of the chemical composition $(5\,Al_2O_3 \cdot SO_3 \cdot 0.66\,H_2O) \cdot 1.33\,H_2O$ of the porous anodic oxide coatings to a structural formula $(A)^n[X_{n/2}]$, which in the case of $n = 4$ represents the idealized structure of vitreous silica, leads to $(Al_{0.91}\,S_{0.09})^{[3.39]}\,[O_{3.15/2}\,(OH)_{0.24/2}]$ with the water outside the brackets of the oxide formula not taken into consideration. The coordination number of oxygen atoms around aluminum ($4 \le Z_{AlO} \le 5$) which is derived from the $RDF^{X,N}$ shows that the oxygen and hydroxyl-groups are not exclusively bound to only two adjacent cations, an observation which is also valid for the structure of vitreous silica.[17]

A final remark should be made concerning the morphology of the almost hexagonally shaped cells (each containing a pore) which has been discussed as an indication of crystallinity of the anodic oxide layers. The isotropic (circular) growth of cells starts at nuclei which are homogeneously distributed over the surface of the aluminum metal. In the course of growth the cells come into contact and develop a homogeneous nearly hexagonal array of cell boundaries which covers the complete coating surface. A pore size near 150 Å and a distance between the pores of about 370 Å was determined from small angle neutron scattering (SANS)[18] studies on a deuterated sample which was prepared under the same anodizing conditions as applied for the materials for the structural investigations.

Experimental

The X-ray diffraction experiments were performed in transmission mode using two different techniques: Angular dispersive X-ray diffraction (ADXD) with a conventional D 500-Siemens diffractometer and energy dispersive X-ray diffraction (EDXD) with a laboratory-built set up.[19] The sample material was powdered and filled into a flat container with Kapton-foil windows mounted in a vacuum chamber. With ADXD (EDXD) the scattering could be recorded up to the scattering vectors $Q = 13.5\ \text{Å}^{-1}$ ($23.5\ \text{Å}^{-1}$), where $Q = 4\pi \sin \theta / \lambda$. Correction methods and normalization to absolute units were applied as described elsewhere.[20, 21] The structure factors $S(Q)$ were calculated according to the Faber-Ziman definition.[22]

The neutron diffraction experiments were performed at the Institute-Laue-Langevin using the instrument D4B up to $Q = 23.3\ \text{Å}^{-1}$. The evaluation of the structure factor $S(Q)$ was done essentially as reported elsewhere.[23] However, in the present case the incoherent scattering contribution of the hydrogen in the sample had to be corrected for. This was achieved by fitting a smooth function through the absorption corrected intensity curve in such a way that after the subtraction of the smooth H-contribution the resulting structure factor oscillated properly around one. This smooth function agreed very well with a previously reported[24] hydrogen scattering function. Furthermore, from its intensity an H-content of 10.6 at-% was calculated which corresponds well to the analytical value of 11.4 at-%.

Received April 13, 1989

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Superconductivity at 7.5 K and Ambient Pressure in Polycrystalline Pressed Samples of β_p-(BEDT-TTF)$_2$I$_3$**

By *Dieter Schweitzer**, *Emil Gogu*, *Hans Grimm*,
Siegfried Kahlich and *Heimo J. Keller*

Recently, bulk superconductivity at ambient pressure in polycrystalline pressed samples of an organic metal—α_t-(BEDT-TTF)$_2$I$_3$—was observed.[1] This is a remarkable fact because this finding shows that organic superconductors can in principle be used for the production of electronic devices, such as squids, and might even be suitable for the preparation of superconducting cables similar to the high temperature superconductors of the copper oxides.

The polycrystalline pressed samples of α_t-(BEDT-TTF)$_2$I$_3$ were prepared from pulverized single crystals of α-(BEDT-TTF)$_2$I$_3$ and the pressed samples had to be anealed at 75 °C

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[**] We gratefully acknowledge financial support of this work by the Deutsche Forschungsgemeinschaft.

for one or two days in order to obtain the α_t-phase and to observe bulk superconductivity with an onset temperature of about 9 K.[1] Nevertheless, the superconducting transition was rather broad with respect to single crystals of α_t-(BEDT-TTF)$_2$I$_3$ and zero resistivity was found at 2.2 K. On the other hand, single crystals of (BEDT-TTF)$_2$Cu(NCS)$_2$ show the highest transition temperature known so far among the organic superconductors of 10.4 K,[2] although no bulk superconductivity could be found.[1] The reason for the loss of the bulk superconductivity in the polycrystalline pressed sample compared to the single crystals of (BEDT-TTF)$_2$Cu(NCS)$_2$ is not quite clear, but is probably due to a phase transition of the material during the preparation of the sample under pressure.

Here we report the surprising fact that polycrystalline pressed samples of β-(BEDT-TTF)$_2$I$_3$ show bulk superconductivity with an onset temperature to superconductivity of 9 K, zero resistivity at 3.2 K and the middle of the resistive transition at 7.5 K. In contrast to the polycrystalline samples, single crystals of β-(BEDT-TTF)$_2$I$_3$ show a rather sharp superconducting transition but only at 1.4 K (onset temperature 1.6 K).[3] Under an isotropic pressure of about 1 kbar the single crystals of β-(BEDT-TTF)$_2$I$_3$ show a superconducting transition at 7.5 K.[4, 5] After a pressure-temperature cycling procedure, pressurizing the crystal up to 1 kbar at room temperature and then releasing the helium gas pressure at temperatures below 125 K, superconductivity at 8 K and ambient pressure in β-(BEDT-TTF)$_2$I$_3$ was found.[6, 7] However, this specially prepared superconducting state at 8 K and ambient pressure is metastable because superconductivity at 8 K can only be obtained as long as the temperature of the single crystals does not exceed 125 K. It is therefore very surprising that in the polycrystalline pressed samples of β-(BEDT-TTF)$_2$I$_3$ a stable superconducting state with an onset temperature of 9 K at ambient pressure exists. For this reason we term the polycrystalline pressed samples of the β-phase β_p-(BEDT-TTF)$_2$I$_3$, where the index p indicates the polycrystalline *pressed* material.

Samples of the size $4 \times 1 \times 0.5$ mm^3 were prepared from pulverized single crystals of β-(BEDT-TTF)$_2$I$_3$ (the resulting crystallites from the graining process had typical diameters of 0.1–10 µm) by applying a pressure of about $1.5 \cdot 10^4$ kg/cm^2 to the powder. The β_p-(BEDT-TTF)$_2$I$_3$ samples prepared in this way are mechanically very stable and were not tempered as in the case of the previously reported pressed samples of α_t-(BEDT-TTF)$_2$I$_3$. The conductivity was measured with the usual four point method. Typical room temperature conductivities σ_{300} lie between 5 and 10 $(\Omega\,\mathrm{cm})^{-1}$ and are about a factor of 2 lower than in the polycrystalline pressed samples of α_t-(BEDT-TTF)$_2$I$_3$. Figure 1 shows the typical temperature dependence of the resistivity of polycrystalline pressed samples of β_p-(BEDT-TTF)$_2$I$_3$ as well as of α_t-(BEDT-TTF)$_2$I$_3$. It can clearly be seen that the resistivity characteristics of the samples of β_p-(BEDT-TTF)$_2$I$_3$ differ remarkably from those of α_t-(BEDT-TTF)$_2$I$_3$ samples (and in fact also from the resistivity characteristics of single crystals of β-(BEDT-TTF)$_2$I$_3$).[8] While in the α_t-samples the resistivity decreases as it does in a metal as the sample is cooled from room temperature, in the case of the β_p-(BEDT-TTF)$_2$I$_3$ samples the resistivity first increases slowly on lowering the temperature. At around 220 K, the temperature at which an incommensurate structural modulation in single crystals of β-(BEDT-TTF)$_2$I$_3$ occurs,[9] a maximum in resistivity is observed, and below 220 K again as in a metal the resistivity decreases.

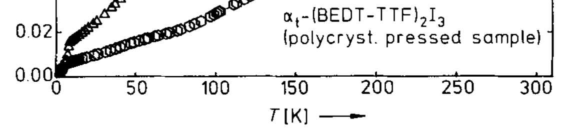

Fig. 1. Temperature dependence of the resistivity of polycrystalline pressed samples of β_p-(BEDT-TTF)$_2$I$_3$ and α_t-(BEDT-TTF)$_2$I$_3$.

Figure 2 shows the resistivity of β_p-(BEDT-TTF)$_2$I$_3$ samples in the temperature range below 16 K. As can be seen the onset of superconductivity lies at around 9 K and zero resistivity is found below 3.2 K indicating a rather broad transition. Nevertheless, the middle of the resistive transition is at around 7.5 K. The onset temperature for superconductivity here in β_p-(BEDT-TTF)$_2$I$_3$ is much higher than that in the single crystals of β-(BEDT-TTF)$_2$I$_3$. The reason for this is not yet clear, but the material probably undergoes a phase transition during the preparation of the polycrystalline samples under pressure. On the other hand, it is clear that the new β_p-phase is not identical with the known α_t-phase indicated by their different resistivity characteristics. In addition, first measurements of the upper critical fields H$_{c2}$ have shown that the polycrystalline pressed samples of the β_p- and α_t-phases have different upper critical fields H$_{c2}$,[10] but these are in both cases much higher than the upper critical field H$_{c2}$ in crystals of α_t-(BEDT-TTF)$_2$I$_3$.[11]

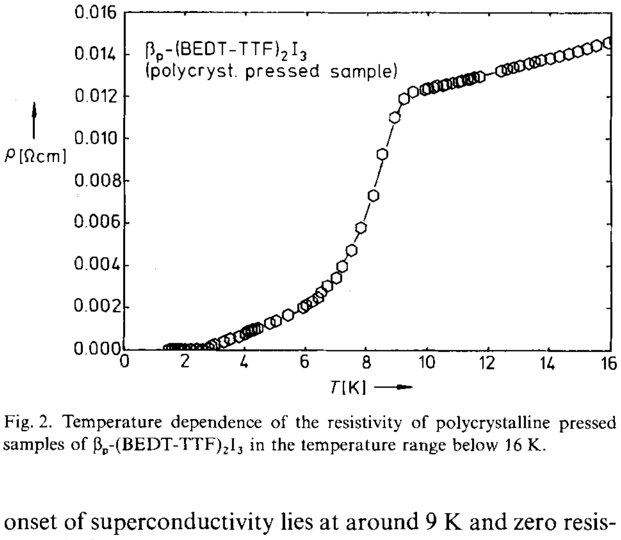

Fig. 2. Temperature dependence of the resistivity of polycrystalline pressed samples of β_p-(BEDT-TTF)$_2$I$_3$ in the temperature range below 16 K.

In order to obtain information on whether the observed superconductivity is a bulk effect of the sample or not, the

AC susceptibility was measured at a frequency of 3 MHz with a field of about 0.2 Gauss. Figure 3 shows the increase in the resonance frequency of the LC-circuit due to exclusion of the RF-field by diamagnetic shielding currents in the polycrystalline pressed sample of β_p-(BEDT-TTF)$_2$I$_3$. There is clear evidence of an onset of diamagnetic shielding below 6 K (in samples of α_t-(BEDT-TTF)$_2$I$_3$ below 7 K). Here in the polycrystalline sample the onset for the diamagnetic shielding is far above the temperature where the resistivity becomes zero as is usually observed in single crystals of organic superconductors. The signal in Figure 3 which still increases on cooling down to 2 K, corresponds to about 50% that expected for a perfect superconductor, indicating a clear bulk effect on the superconductivity in the polycrystalline pressed β_p-(BEDT-TTF)$_2$I$_3$ samples. Nevertheless, the large temperature range in which the frequency shift of the resonance frequency is observed shows that an inhomogeneous distribution of superconducting transitions exists in the sample. A similar broad distribution was already observed in the case of the polycrystalline pressed samples of α_t-(BEDT-TTF)$_2$I$_3$.

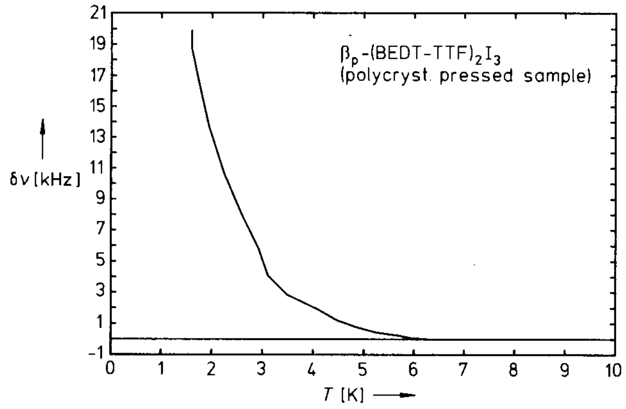

Fig. 3. Increase of the resonance frequency of an LC-circuit (3 MHz) due to exclusion of the RF-field by diamagnetic shielding currents (AC susceptibility) in a polycrystalline pressed sample of β_p-(BEDT-TTF)$_2$I$_3$ caused by cooling the sample from 10 K down to 2 K.

It should be mentioned that tempering of the polycrystalline pressed samples of β_p-(BEDT-TTF)$_2$I$_3$ for one or two days at 75 to 90 °C (as in the case of the samples of α_t-(BEDT-TTF)$_2$I$_3$) does not change the physical properties of the samples.

In conclusion, superconductivity at ambient pressure and 7.5 K exists in samples of β_p-(BEDT-TTF)$_2$I$_3$. The superconducting state is stable and the superconductivity is a bulk effect of the sample. Similar to the polycrystalline samples of α_t-(BEDT-TTF)$_2$I$_3$ here again structural phase transitions during the preparation of the samples under pressure seem to play an important role.

As a consequence of the structural phase transition, here in β_p-(BEDT-TTF)$_2$I$_3$, the transition temperature into the superconducting state is increased. This behavior reemphasizes that organic superconductors might also be of interest for industrial applications, as in the preparation of electronic devices polycrystalline materials are easier to use than single crystals. In addition, the discovery of bulk superconductivity in large pressed samples of crystallites of an organic metal of the typical diameter of 1 μm indicates that the observation of superconductivity in conducting polymers should also be possible.

Received: March 13, 1989

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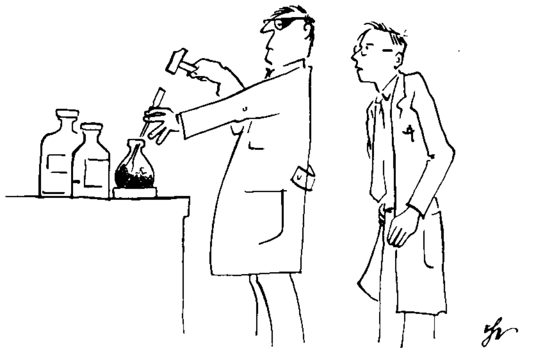

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