SUPERCONDUCTIVITY IN POLYCRYSTALLINE PRESSED PELLETS OF κ -(BEDT-TTF)₂I₃

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ABSTRACT

Investigations of the transport properties of single crystals and polycrystalline pressed samples of κ -(BEDT-TTF)₂I₃ are presented. In contrast to polycrystalline pressed samples of κ -(BEDT-TTF)₂Cu(NCS)₂ and κ -(BEDT-TTF)₂Cu[N(CN)₂]Br those of κ -(BEDT-TTF)₂I₃ show bulk superconductivity indicating that the loss of superconductivity in the first two types of samples is not due to the special structure of the κ -phase, but probably due to a disproportionation of Cu¹⁺ under the anisotropic pressure during the preparation of the samples. Annealing the single crystals as well as the polycrystalline pressed samples of κ -(BEDT-TTF)₂I₃ at 75°C for a few days results in a structural transformation with an increase in the transition temperature for superconductivity (about 8 K for the crystals). IR-spectra indicate a transformation into a structure which is identical with α_t -(BEDT-TTF)₂I₃, which seems to be the thermodynamically most stable phase of the several (BEDT-TTF)₂I₃ phases.

INTRODUCTION

The observation of bulk superconductivity at ambient pressure in polycrystalline pressed samples of organic metals [1,2] is remarkable, because it shows that in principle organic superconductors could be used for applications, especially when the transition temperatures into the superconducting state for this class of materials could be further increased. In polycrystalline pressed samples of β -(BEDT-TTF)₂I₃ and α_t -(BEDT-TTF)₂I₃ bulk superconductivity was observed with an onset at around 9 K and a rather broad superconducting transition. In contrast to these results polycrystalline pressed samples of κ -(BEDT-TTF)₂Cu(NCS)₂ [1] and κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (see fig. 1) do not become superconducting and show partly even a semiconducting behaviour. Since single crystals of the latter two materials have the highest transition temperatures (10.4 K [3] and 11.6 K [4]) at ambient pressure of the organic superconductors it is interesting to learn why the polycrystalline pressed samples do not become superconducting. In order to obtain an answer to the question whether the special structure of the κ -phase or other reasons are responsible for this behaviour we have prepared single crystals of κ -(BEDT-TTF)₂I₃ by electrochemical methods and prepared under the same conditions as described earlier [1] polycrystalline pressed samples of κ -(BEDT-TTF)₂I₃ which are called in the following κ_p -(BEDT-TTF)₂I₃.

Fig. 1. Comparison of the temperature dependence of the resistivity $[\rho(T)/\rho(300)]$ of single crystals and polycrystalline pressed samples of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br.

EXPERIMENTAL

Single crystals of κ -(BEDT-TTF) $_2$ I $_3$ were first prepared and investigated by Kajita et al [5]. In the electrochemical preparation they used in addition to (Bu $_4$ N)I $_3$ also a small amount of (Bu $_4$ N)(AuI $_2$) as electrolyte salt in order to obtain κ -phase crystals. In our preparation we used only (Bu $_4$ N)I $_3$ salt but varied the conditions for the electrochemical process as first described for the preparation of α - and β -(BEDT-TTF) $_2$ I $_3$ [6]. In order to identify the obtained single crystals as κ -phase crystals we reinvestigated the crystal structure by x-ray methods, measured the temperature dependence of the resistivity, the thermopower and the ac-susceptibility. In addition polycrystalline pressed pellets of the size 4×1×0.5 mm 3 were prepared as described earlier [1] and investigated by the same methods. Furthermore we have annealed both types of samples at 75°C in air for 3 days in order to examine whether the κ -(BEDT-TTF) $_2$ I $_3$ crystals undergo a structural phase transition under these conditions, as it was observed for the α -phase.

RESULTS

a: Single crystals of κ -(BEDT-TTF) $_2$ I $_3$.

For the unit cell parameters of the monoclinic (P2 $_1$ /a) single crystals of κ -(BEDT-TTF) $_2$ I $_3$ the following parameters were obtained: a = 12.876 Å, b = 8.504 Å, c = 16.492 Å, β = 108.50°, V = 1705.97 Å 3 . These parameters are slightly different from those obtained by Kajita et al [5] (a = 12.83 Å, b = 8.47 Å, c = 16.39 Å, β = 108.56°). Figure 2 shows the temperature dependence of the resistivity in the a -, b - and c^* - direction of the crystals (measured by the Montgomery method), while fig. 3 shows the low temperature part of the resistivity in a -direction as well as the change in ac-susceptibility when the sample becomes superconducting by lowering the temperature. Figure 4 shows the temperature dependence of the thermopower, again for all three crystal directions. In order to obtain information about the onset

Fig. 2. Temperature dependence of the resistivity in a-, b- and c*-direction of single crystals of κ -(BEDT-TTF) $_2$ I $_3$.

Fig. 3. Resistivity (in a-direction) and ac-susceptibility below 15 K of single crystals of κ -(BEDT-TTF) $_2$ I $_3$.

of superconductivity microwave absorption measurements were performed which are shown in fig. 5. In contrast to the resistivity- and ac-susceptibility data the measurement of the microwave absorption indicates a first onset for superconductivity at about 7.5 K (which is probably a surface state) and a second much stronger onset at about 5.2 K.

b: Polycrystalline pressed samples (κ_p -(BEDT-TTF) $_2$ I $_3$).

Figure 6 shows the low temperature part of the resistivity of polycrystalline pressed samples of κ_p -(BEDT-TTF) $_2$ I $_3$ as well as the change in ac-susceptibility when the sample becomes superconducting. The insert in fig. 6 demonstrates the temperature dependence of the resistivity for the temperature region below 300 K. It can clearly be seen that the samples show a metallic behaviour over the whole temperature range.

Fig. 5. Temperature dependence of the microwave absorption of single crystals of κ -(BEDT-TTF) $_2$ I $_3$.

Fig. 4. Temperature dependence of the thermopower in a-, b- and c*-direction of single crystals of κ -(BEDT-TTF) $_2$ I $_3$.

Fig. 6. Resistivity and ac-susceptibility of polycrystalline pressed samples of κ_p -(BEDT-TTF) $_2$ I $_3$.

Fig. 7. Comparison of the low temperature part of the resistivity of κ -(BEDT-TTF) $_2$ I $_3$ and κ_t -(BEDT-TTF) $_2$ I $_3$ (tempered crystals).

c: Tempered samples of κ -(BEDT-TTF) $_2$ I $_3$ and κ_p -(BEDT-TTF) $_2$ I $_3$.

In figures 7 and 8 the low temperature parts of the resistivity of single crystals and tempered crystals (called κ_t -crystals) as well as of polycrystalline pressed samples (κ_p) and tempered polycrystalline pressed samples (κ_{pt}) of κ -(BEDT-TTF) $_2$ I $_3$ are shown. Finally fig. 9 shows the FT-IR spectra in the range of the CH $_2$ stretching modes of crystals of κ - and κ_t -(BEDT-TTF) $_2$ I $_3$ as well as for comparison of α_t -(BEDT-TTF) $_2$ I $_3$.

Fig. 8. Low temperature part of the resistivity of polycrystalline pressed samples of κ_p - and κ_{pt} -(BEDT-TTF) $_2$ I $_3$.

Fig. 9. FT-IR spectra (CH $_2$ stretching modes) of crystals of κ -, κ_t - and α_t -(BEDT-TTF) $_2$ I $_3$.

DISCUSSION

The resistivity data of the single crystals of κ -(BEDT-TTF)₂I₃ shown in fig. 2 demonstrate the typical two dimensional electronic character of the crystals. In fig. 3 the onset for superconductivity is observed at about 5.2 K and zero resistivity at 4.0 K. The middle of the transition is found at 4.3 K, somewhat higher (3.6 K) with respect to the measurements of Kajita et al [5]. This might be due to the different electrochemical preparation of our crystals. The observed change in ac-susceptibility (see fig. 3) - indicating bulk superconductivity - is rather sharp and the measured onset is found at 3.9 K, a temperature where already zero resistivity is observed. This behaviour is typical for single crystals of organic superconductors. Nevertheless the signal in the change of the ac-susceptibility starts to saturate here already at 3.3 K indicating that a large fraction of the sample ($\approx 70\%$) became superconducting. In order to obtain information about the real onset for superconductivity the temperature dependence of the microwave absorption in a field of 10 Gauß was measured. While in the case of other single crystals of organic superconductors (e.g. κ -(BEDT-TTF)₂Cu(NCS)₂, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and α_t -(BEDT-TTF)₂I₃) the onset observed in resistivity and the microwave absorption signal is more or less identical, here in the case of κ -(BEDT-TTF)₂I₃ we observed as well a strong change in microwave absorption starting at 5.2 K as in the resistivity, but in addition a weaker signal (see fig. 5) starting at 7.5 K with a maximum at 6 K. This weak signal was found as well in freshly prepared crystals as in crystals which were about 1 year old. Since in the resistivity data no sign for superconductivity is observed above 5.2 K we assume at the moment that a superconducting surface state is responsible for this signal in the microwave absorption. The thermopower data in fig. 4 demonstrate the metallic character of the single crystals, but the measurements in all three directions indicate a broad structural transition between 170 K and 210 K as well as another possible phase transition at about 25 K.

In the case of the polycrystalline pressed samples of κ_p -(BEDT-TTF)₂I₃ a clear metallic behaviour in the temperature dependence of the resistivity is found (see insert in fig. 6), but in addition a broad superconducting transition with an onset at 5.2 K and zero resistivity at 2 K is observed, while the middle of the transition lies at 4.0 K. Here in the case of the polycrystalline pressed samples the onset for superconductivity in the ac-susceptibility is found at about 4 K, that means at a much higher temperature than the observed zero resistivity. Nevertheless the change in the signal in the ac-susceptibility is much broader than in the case of the single crystals (see fig. 3). Such a behaviour was already found for the polycrystalline pressed samples of the organic superconductors α_{tp} -(BEDT-TTF)₂I₃ and β_p -(BEDT-TTF)₂I₃ [1,2]. It is important to notice that in contrast to the κ -phases of the organic superconductors (BEDT-TTF)₂Cu(NCS)₂ and (BEDT-TTF)₂Cu[N(CN)₂]Br here in the samples of κ_p -(BEDT-TTF)₂I₃ bulk superconductivity is observed, indicating that not the special structure of the κ -phase is responsible for the loss of superconductivity in the pressed samples of the Cu containing κ -phase but more probably that this finding is due to a disproportionation of the Cu¹⁺ in Cu⁰ and Cu²⁺ under the anisotropic pressure during the preparation of the samples. Since Cu²⁺ ions are paramagnetic the proposed disproportionation would disturb superconductivity in samples containing Cu¹⁺.

Since in the case of single crystals of α -(BEDT-TTF)₂I₃ a structural transformation after tempering at 75°C for 3 days was observed [7] and the new α_t -phase becomes superconducting below 8 K, we have tempered the single crystals of κ -(BEDT-TTF)₂I₃ and the polycrystalline pressed samples of κ_p -(BEDT-TTF)₂I₃ as well under the same conditions. To our surprise we observed a similar behaviour of the annealed samples as in the case of α -(BEDT-TTF)₂I₃. In both cases an increase in the superconducting transition temperature is observed (see figs. 7 and 8) after the annealing process. In the case of the tempered crystals (now called κ_t -phase) the middle of the transition occurs at 8.2 K and

for the tempered polycrystalline pressed samples (now called κ_{pt} -(BEDT-TTF)₂I₃) this value lies at about 6K. In both cases a temperature dependent ac-susceptibility measurement indicated again that the superconductivity is a bulk effect of the samples. The observed IR-spectrum in the range of the CH₂-stretching modes of the tempered crystals is quite different with respect to the one of the crystals of the κ -phase. This fact suggests again that a structural phase transition appears to the crystals under the annealing conditions. In fact, the comparison with the IR-spectrum of crystals of α_t -(BEDT-TTF)₂I₃ (see fig.9; but also ref. 8 where the spectrum in the range between 600 and 1600 cm⁻¹ for both crystals is shown) it has to be concluded that both tempered crystals convert into the same phase (that means α_t - and κ_t -phase are identical). This is surprising since the structures of the α - and the κ -phases are totally different with respect to each other but as well with respect to the tempered phase, which is nearly identical with the β -phase (see references 8 and 9). We conclude that the obtained structures by annealing crystals of κ - or α -(BEDT-TTF)₂I₃ at 75°C are identical and this structure is the thermodynamically most stable phase which can be obtained in the series of (BEDT-TTF)₂I₃ phases.

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