

Electrochemically Prepared Radical Salts of BEDT-TTF: Molecular Metals and Superconductors

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The structural, electronic and superconducting properties of several electrochemically prepared BEDT-TTF radical salts are discussed.

Introduction

Since the observation of superconductivity at temperatures up to 100 K in the metal oxides of the type $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ first discovered by Bednorz and Müller [1] superconductivity has attracted again a lot of interest. Although the theoretical understanding of the mechanism leading to superconductivity in these materials is not quite clear yet the most important point is that this discovery has shown that high temperature superconductivity is experimentally achievable.

The idea of high temperature superconductivity is quite old. In 1964 Little proposed a model of a metalorganic superconductor at room temperature [2]. His idea has stimulated a lot of interesting developments in the field of low-dimensional conductors. Nevertheless, up to now no high temperature organic superconductor exists. It took a lot of work until 1980 before superconductivity at 1.3 K under an isotropic pressure of 12 kbar could be observed in an organic material for the first time [3]. At this moment the highest transition temperature into a stable superconducting state at ambient pressure in an organic metal lies at 8 K [4]. The recent finding of high temperature superconductivity in the metal oxides will certainly strongly stimulate further synthetic efforts in the search for other organic metals with higher superconducting transition temperatures.

On the other hand the understanding of the electronic and superconducting properties of the existing organic metals and especially their relation to the molecular structures of these materials is a prerequisite for further directed developments. The electronic properties of different radical salts obtained from the organic donor bisethylenedithio-tetrathiafulvalene (BEDT-TTF) by electrochemical methods in the presence of I_3^- anions [5] are quite well understood. In addition their crystal structures have been studied over a broad temperature range. The relation of the superconducting properties of these organic metals to their typical crystal structures and especially to small structural changes due to phase transitions is known in detail, therefore. In the following a review of the structural, electronic and superconducting properties of the organic metals α -, β - and α_1 -(BEDT-TTF) $_2I_3$ is given.

Why BEDT-TTFs?

After the first discovery of superconductivity in the radical salts of TMTSF (tetramethyltetraselenafulvalene) under pressure [3] and ambient pressure [6] it became clear that besides the usual intrastack contacts in the quasi one-dimensional metals intermolecular interactions between donor molecules in neighbouring stacks play an important role in such materials. The resulting two-dimensional contributions lead to a stabilization of the metallic character down to very low temperatures. Therefore, Saito et al. [7] introduced the idea that due to the somewhat nonplanar structure of BEDT-TTF even stronger interstack contacts in radical salts of this donor could be achieved. In fact electrochemically prepared crystals of (BEDT-TTF) $_2 \cdot ClO_4(TCE)_{0.5}$ showed the typical electronic behaviour of a quasi two-dimensional organic metal [7, 8] down to low temperatures, but did not become superconducting. In a similar salt (BEDT-TTF) $_4(ReO_4)_2$ the two-dimensionality is somewhat less pronounced but Parkin et al. [9, 10] did find a superconducting state near 3 K under an isotropic pressure of about 4 kbar, whereby the isotropic pressure was necessary to suppress a metal-insulator transition at 80 K and ambient pressure. This was the first observation of superconductivity in an organic sulfur donor system. Nevertheless, the electrochemical preparation of this radical salt is not at all trivial. A large number of radical salts with different stoichiometries and crystal structures might grow simultaneously.

The preparation of radical salts of BEDT-TTF with I_3^- counterions in THF solutions is [5, 11, 12] easier to control. Two radical salts with identical stoichiometries but different structures (see Fig. 1), the so-called α - and β -(BEDT-TTF) $_2I_3$ phases are obtained. Both types of crystals can be easily distinguished by eye. α -phase crystals have usually a plate-like shape while β -phase crystals are canted rhombohedrons. In addition the room temperature ESR line-width of the conduction electrons can be used to discriminate unequivocally between both salts (70 to 110 Gauss for α -phase crystals and 20 to 25 Gauss for β -phase crystals depending on the direction of the crystals with respect to the magnetic field [13, 14]). α -(BEDT-TTF) $_2I_3$ crystals

turned out to be two-dimensional organic metals with a metal insulator transition at 135 K [5, 12]. β -(BEDT-TTF)₂I₃ crystals are two-dimensional metals as well but stay metallic down to low temperature and – as was shown first by the group of Shegolev [15] – become superconducting at 1.3 K and ambient pressure. We will show that under certain conditions both phases become superconducting even at 8 K and ambient pressure. The superconducting state at 8 K is metastable in the β -phase, but stable in α -phase crystals after tempering them at 75°C for several days. The surprising properties of this tempered so-called α -phase are best understood on the basis of the special features of the normal α - and β -phase which are discussed first.

α -(BEDT-TTF)₂I₃

The unit cell of α -(BEDT-TTF)₂I₃ crystals (triclinic: $a = 9.211$, $b = 10.85$, $c = 17.488$ Å, $\alpha = 96.95^\circ$, $\beta = 97.97^\circ$, $\gamma = 90.75^\circ$, $V = 1717$ Å³ [5]), contains two crystallographically different stacks (Fig. 1). There are large dihedral angles (59.4 and 70.7°) between the molecular planes of the BEDT-TTF molecules in neighbouring stacks causing a strong coupling between the different stacks due to short (<3.5 Å) interstack S-S contacts in addition to the contacts within a stack. This results in a nearly isotropic conductivity in the ab -plane of such crystals with typical room temperature values between 60 and 250 S/cm. In the direction perpendicular to this plane at least a 1000 times smaller value is observed [5, 12]. The α -phase crystals contain linear I₃⁻ anions. All CH₂-groups of the BEDT-TTF donor molecules are ordered [5].

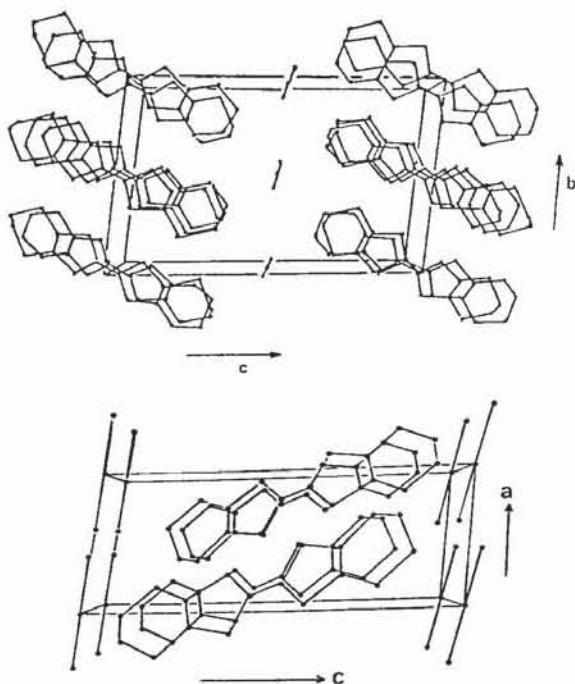


Fig. 1

Stereoscopic projection of the structure of
a) α -(BEDT-TTF)₂I₃ (left) along the stacking axis,
b) β -(BEDT-TTF)₂I₃ (right) along the stacking axis

At ambient pressure α -(BEDT-TTF)₂I₃ undergoes a metal-insulator phase transition at 135 K (see also Fig. 7) which can be suppressed by an isotropic pressure of > 12

Kbar, but no sign of superconductivity could be observed down to 100 mK [16]. This 135 K transition is a first order phase transition as shown by a differential thermal analysis [17]. It can be utilized to demonstrate the validity of the Wiedemann-Franz Law in an organic metal as well [13]. The Wiedemann-Franz Law takes the form $K_c/\sigma = L_0 \cdot T$. K_c represents the thermal conductivity of the charge carriers, σ the electrical conductivity, T the temperature and $L_0 = 2.44 \cdot 10^{-8}$ V²/K², the Lorentz number. Fig. 2 shows the temperature dependence of the total thermal conductivity K of α -(BEDT-TTF)₂I₃. Assuming that the jump of 1.5 mW/(cm·K) in K is due to the loss of charge carriers at the metal insulator phase transition this value gives the approximate contribution K_c of the charge carriers in the metallic range. Taking typical values for the conductivity of $\sigma = 400$ –450 S/cm at 135 K results in a value of (2.5–2.8) $\cdot 10^{-8}$ V²/K² for the ratio $K_c/(\sigma \cdot T)$ which agrees within the experimental error quite well with the Lorentz number. In addition the results of the thermal conductivity investigations plotted in Fig. 2 demonstrate that in this organic metal the contribution to K due to the lattice phonons predominates the contribution of the charge carriers which is in contrast to the usual metals.

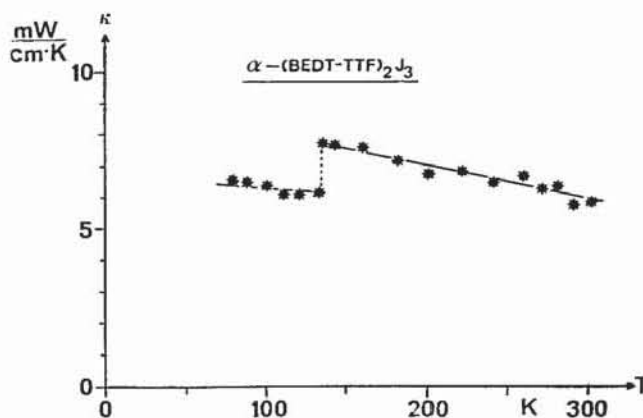


Fig. 2

Thermal conductivity K of α -(BEDT-TTF)₂I₃ versus temperature. The jump of 1.5 mW/(cm·K) at 135 K is due to the loss of the charge carriers caused by a metal insulator phase transition

β -(BEDT-TTF)₂I₃

The discovery of superconductivity in β -(BEDT-TTF)₂I₃ at $T_c = 1.3$ K and ambient pressure by Yagubskii et al. [15] was confirmed by Williams et al. [18]. Meissner effect measurements [19] demonstrated the bulk property of the superconductivity in these crystals. A short time later it was found that under a pressure of 1.3 kbar the superconducting transition in β -phase crystals can be raised to 7.5 K [20, 21]. After a particular pressure-temperature cycling procedure – pressurization up to 1.5 kbar at room temperature and release of the helium gas pressure at temperatures below 125 K – superconductivity at $T_c = 8$ K and ambient pressure was found [22–24]. The observed sharp superconducting transition – as measured by the resistivity of the crystal – as well as the suppression of the superconducting state by a magnetic field of about 6 T along the c^* -axis at various temperatures is shown in Fig. 3. The confirmation of bulk superconductivity at 8 K was obtained also by

Meissner effect [25] and ac susceptibility measurements [23]. 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 crystal temperature did not exceed 125 K. At this temperature a metal metal phase transition was observed by thermopower measurements [13] (see Fig. 4). Recently it was shown that this metastable 8 K superconducting state also can be obtained by an electronic excitation with laser light at temperatures below 125 K [26].

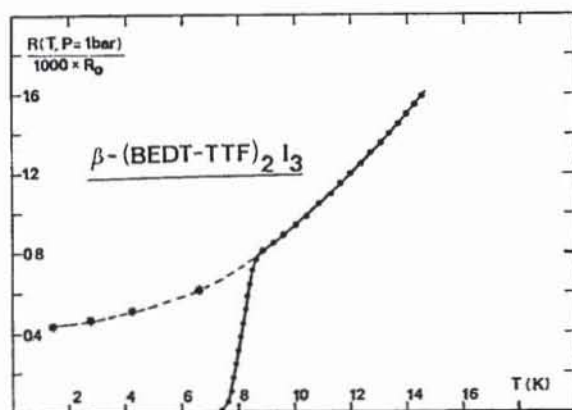


Fig. 3

Superconducting transition at 8 K and ambient pressure in β -(BEDT-TTF) $_2$ I $_3$ after a special pressure temperature cycling procedure [22] as well as its suppression by a magnetic field along the c^* -axis at various temperatures

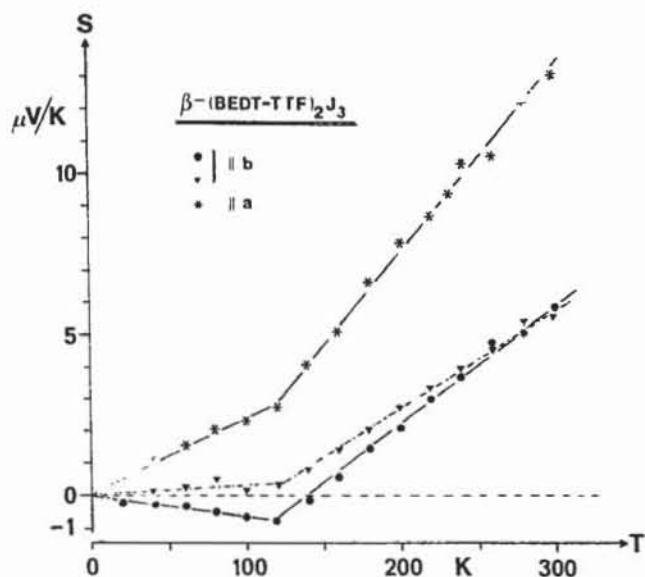


Fig. 4

Thermopower of β -(BEDT-TTF) $_2$ I $_3$ versus temperature for three different crystals, \circ and \blacktriangledown current flow parallel b direction, $*$ current flow parallel a direction. At 125 K a metal metal phase transition is indicated (see also Ref. [13])

In order to understand these somewhat surprising facts, the structural properties of the β -(BEDT-TTF) $_2$ I $_3$ crystals under the different conditions have to be discussed. At room temperature β -crystals are triclinic [27, 28] ($a = 15.243$, $b = 9.070$, $c = 6.597$ Å, $\alpha = 109.73$, $\beta = 95.56$, $\gamma = 94.33^\circ$, $V = 848.9$ Å 3) and the structure is very similar to those of the Bechgaard salts. Only one type of crystallographic

equivalent stacks exists (Fig. 1). Below 195 K at ambient pressure an incommensurate structural modulation was observed [29–31]. The origin of this modulation is connected with an anion cation interaction. Below 125 K a commensurate superstructure with a unit cell volume of about three times the size compared to room temperature was observed [32] ($a = 18.269$, $b = 21.04$, $c = 6.543$ Å, $\alpha = 93.56$, $\beta = 94.84$, $\gamma = 99.86^\circ$, $V = 2461$ Å 3). The basic structural change below 125 K with respect to the room temperature structure lies in a pronounced distortion of the triiodide chains and especially in a change of the linear and symmetric I_3^- anions at room temperature into non-linear and asymmetric anions (see Fig. 5). This finding was confirmed by Resonance Raman investigations [26]. Therefore, it was assumed [32] that the symmetric linear structure of the I_3^- anions at room temperature is stabilized down to low temperatures by the special temperature cycling procedure [22, 23] and this more symmetric structure results in the high T_c superconducting transition at 8 K. In fact, this assumption was confirmed recently by neutron diffraction experiments [33, 34]. It was shown that no incommensurate modulated structure at 4.5 K exists, but furthermore, that all the terminal ethylene groups of the BEDT-TTF molecules are ordered. This is in contrast to the room temperature structure in which the ethylene groups of only one side of the stacks are ordered while the others occupy the two possible conformational sites statistically [33, 34].

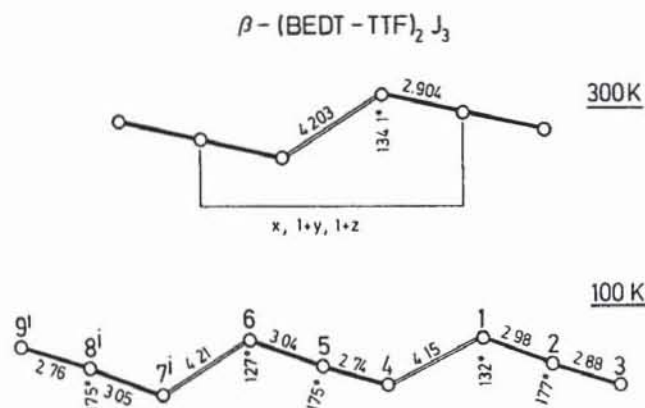


Fig. 5

Comparison of the geometry of the triiodide chains, in β -(BEDT-TTF) $_2$ I $_3$ at room temperature (top) and 100 K (bottom). The unit cell at 100 K contains the three triiodides as shown (see Ref. [32])

It was shown [26] that an electronic excitation of the I_3^- anions in β -phase crystals at temperatures below 125 K by laser light can induce — at least in a thin layer on the surface — the structural transformation from the low temperature $T_c = 1.3$ K structure into the more ordered and symmetric high temperature $T_c = 8$ K structure. This transformation is observed in the Resonance Raman spectrum by a disappearance of the splitting of the symmetric stretching mode of the I_3^- anions with time at constant laser power (see Fig. 6) or immediately at high light intensity (≈ 50 mW) [26]. Therefore, at temperatures between 1.5 and 8 K at least the surface of the crystal — in the moment it is not clear whether IR radiation might even switch the whole volume of the crystal — can be switched optically from the normal

conducting into the superconducting state. But only those parts of the surface are switched which were irradiated by light (optical storage!). However, this transformation is again only stable as long as the crystal temperature does not exceed 125 K [26].

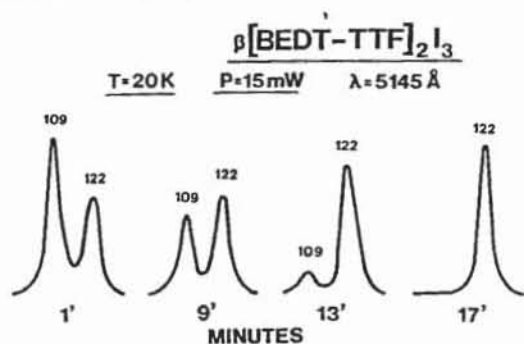


Fig. 6

Structural transformation from the low into the high temperature superconducting phase in β -(BEDT-TTF) $_2$ I $_3$ by irradiation with light [26] as observed by the change of the Resonance Raman spectrum of the symmetric stretching mode (109 and 122 cm^{-1}) of the I $_3^-$ anions with time at constant laser power (15 mW, at 5145 Å)

α_t -(BEDT-TTF) $_2$ I $_3$

Recently, Baram et al. [35] reported a structural transformation of α -(BEDT-TTF) $_2$ I $_3$ into β -phase crystals by tempering the α -phase at a temperature of 70–100°C for about 10 to 20 hours. This is a quite surprising result because of the essential differences in the structures of both phases (see Fig. 1) but the structural transformation was confirmed by Weissenberg pictures [35]. Most surprisingly these crystals show a sharp decrease in resistivity at around 8 K indicating a superconducting transition at this temperature. An additional prove for an eventual superconducting state by applying simultaneously a magnetic field was not reported. Further it was not clear whether or not the indicated superconducting transition is a bulk effect in these tempered crystals.

Another open question is: What are the differences in the structures between the normal grown β -(BEDT-TTF) $_2$ I $_3$ and the tempered α_t -(BEDT-TTF) $_2$ I $_3$ crystals? (In the following tempered α -phase crystals are called α_t -(BEDT-TTF) $_2$ I $_3$). This is an important question since β -(BEDT-TTF) $_2$ I $_3$ becomes superconducting under ambient pressure conditions at 1.3 K while in α_t -(BEDT-TTF) $_2$ I $_3$ this transition seems to be at around 8 K. β -(BEDT-TTF) $_2$ I $_3$ shows superconductivity at 8 K only after special treatment (temperature-pressure cycling).

A systematic study of the temperature dependence of the resistivity (Figs. 7, 8) and ac susceptibility (Fig. 9) both with and without applying a magnetic field as well as ESR (Fig. 10), NMR (Fig. 11), Resonance Raman (Fig. 12) and thermopower investigations on α_t -(BEDT-TTF) $_2$ I $_3$ (Fig. 13) has shown that bulk superconductivity at 8 K and ambient pressure exists in such α_t -crystals [4]. In contrast to the specially prepared 8 K metastable superconducting state in β -crystals the superconducting state in α_t -(BEDT-TTF) $_2$ I $_3$ is stable and entirely reproducible for several temperature cycles up to 380 K [4].

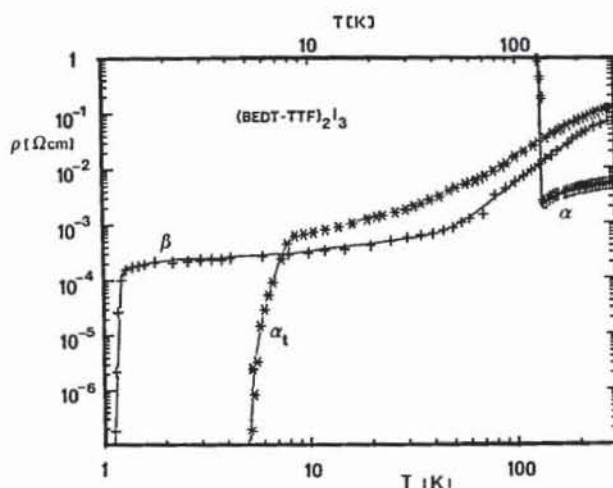


Fig. 7

Resistivity versus temperature (logarithmic scale) for α -(BEDT-TTF) $_2$ I $_3$ (#) (metal insulator phase transition at 135 K), β -(BEDT-TTF) $_2$ I $_3$ (+) and α_t -(BEDT-TTF) $_2$ I $_3$ (*)

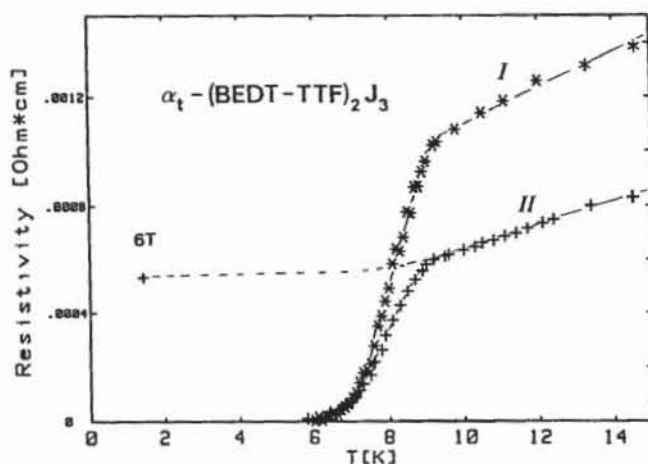


Fig. 8

Resistivity of two α_t -(BEDT-TTF) $_2$ I $_3$ (I and II) in the temperature region between 0 and 15 K. The suppression of superconductivity in sample II by applying a magnetic field of 6 T at 1.3 K parallel to the c^* -axis is shown as well [4]

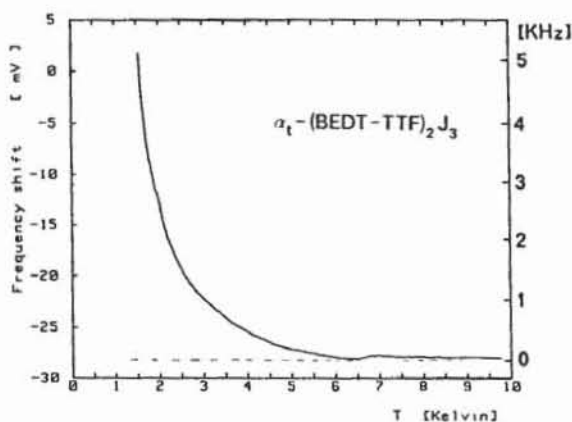


Fig. 9

Increase in resonance frequency of a LC-circuit (3.3 MHz) due to exclusion of the rf-field by diamagnetic shielding currents (ac-susceptibility) in α_t -(BEDT-TTF) $_2$ I $_3$ (sample II of Fig. 2) by lowering the temperature [4]

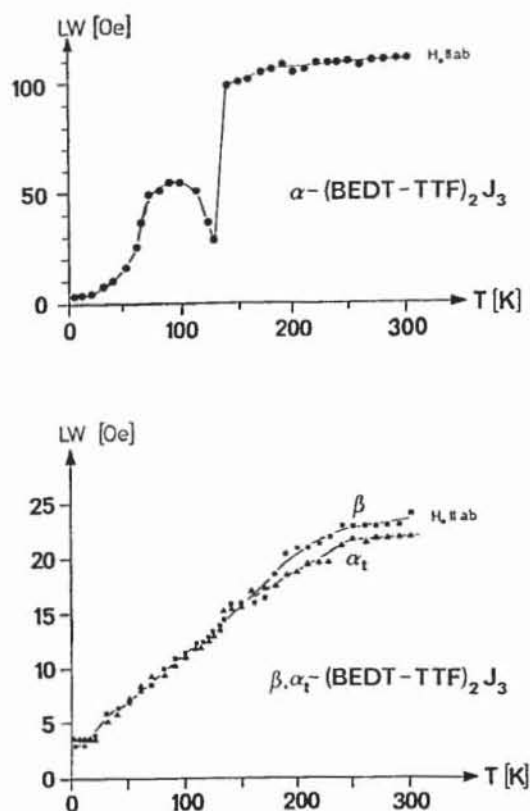


Fig. 10
Temperature dependence of the ESR linewidth for α -(BEDT-TTF) $_2$ I $_3$ (top) as well as for β - (●) and α_1 -(BEDT-TTF) $_2$ I $_3$ (▲) (bottom) crystals [4]

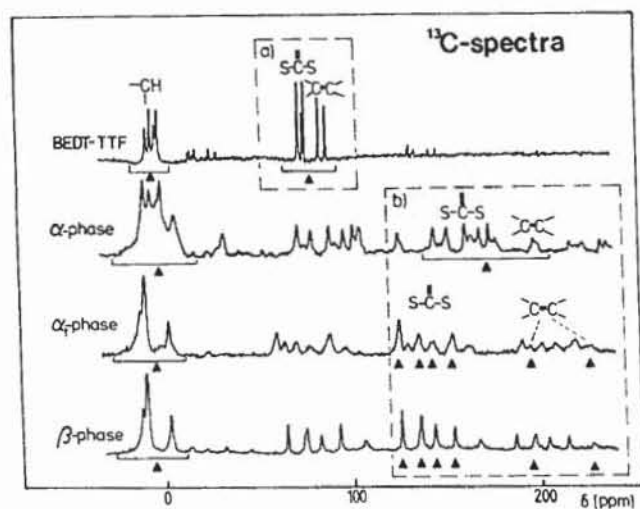


Fig. 11
MAS ^{13}C -NMR spectra at 300 K of the neat donor material BEDT-TTF and of the organic metals α -, β - and α_1 -(BEDT-TTF) $_2$ I $_3$. The center bands are marked by \blacktriangle . Chemical shifts/Knight shifts are referenced to TMS. ($\nu = 68$ MHz, spinning frequency 4–5 KHz [4])

^{13}C -NMR solid state investigations [4] (Fig. 11) have shown that tempering α -crystals above 70°C for several days in air converts *all* crystals used in the experiment (≈ 0.3 g) totally into the new α_1 -(BEDT-TTF) $_2$ I $_3$ -phase.

The ESR linewidth measurements (Fig. 10) as well as the Resonance Raman spectra (Fig. 12) also indicate the phase transition after tempering [4]. The upper critical fields H_{c2}

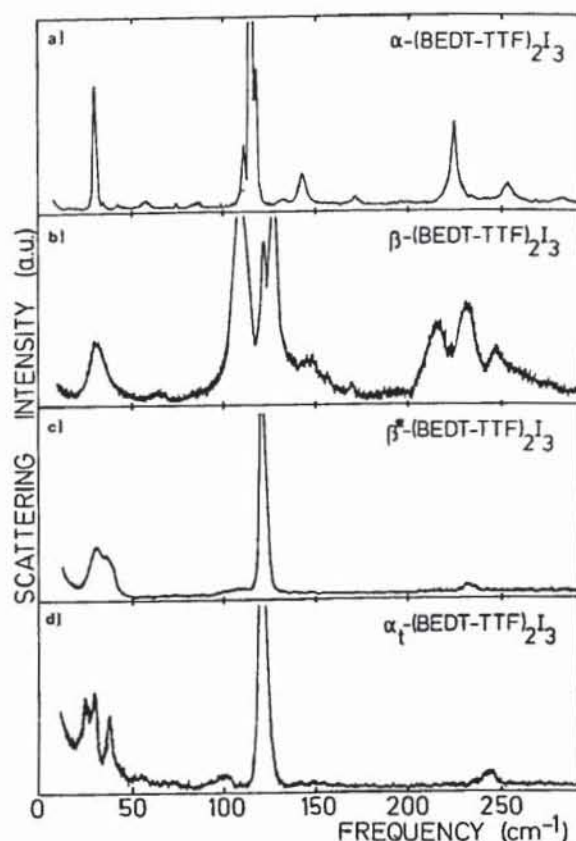


Fig. 12
Low energetic part of the Resonance Raman spectra at 2 K [4] of a) α -(BEDT-TTF) $_2$ I $_3$, b) β -(BEDT-TTF) $_2$ I $_3$ (low temperature superconducting 1.3 K-phase), c) β -(BEDT-TTF) $_2$ I $_3$ (high temperature superconducting 8 K-phase) prepared by optical excitation [26], d) α_1 -(BEDT-TTF) $_2$ I $_3$. (Excitation wave length 4880 Å 10 mW)

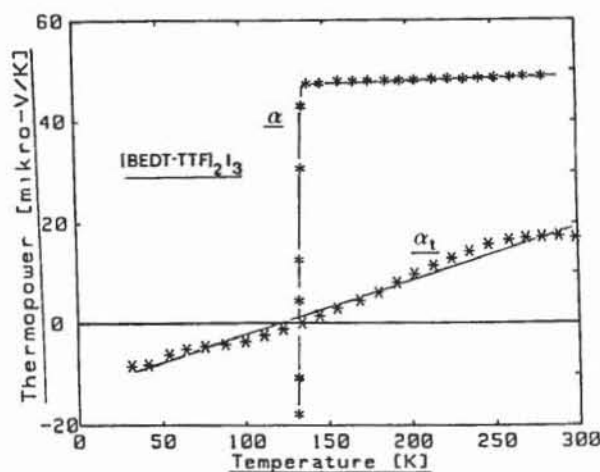


Fig. 13
Thermopower of α - and α_1 -(BEDT-TTF) $_2$ I $_3$ crystals [4]

(Fig. 14) [4] are anisotropic but with 3 to 11 T (depending on the direction of the magnetic field with respect to the crystal axes) relatively high. All the results from Refs. [4] and [35] indicate that the structure of the α_1 -crystal is at room temperature identical with the one of the high- T_c superconducting phase of β -crystals. This is probably due to the fact that in the α -phase crystals at room temperature (and probably at 75 C as well) all terminal ethylene groups

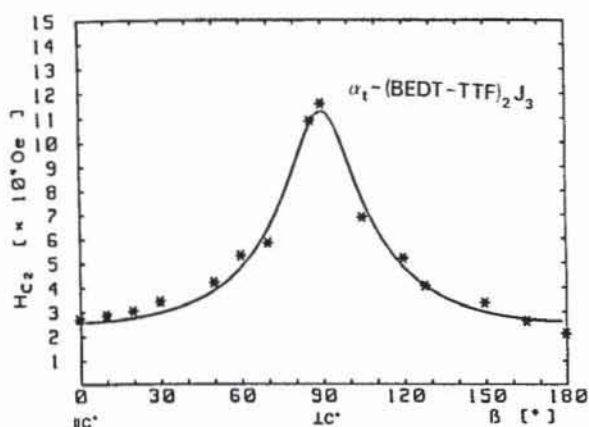


Fig. 14

Upper critical fields H_{c2} at a temperature of 1.3 K for α_1 -(BEDT-TTF) $_2$ I $_3$, as evaluated by the mid-transition of the resistivity curve for several magnetic field directions [4]

of the BEDT-TTF donor molecules are ordered similar to the high- T_c superconducting β -phase. Therefore, it is assumed that the phase transition at 75°C results into an ordered structure. To clarify the situation further X-ray structure investigations are necessary.

BCS Superconductivity

An important question is whether or not the usual electron phonon coupling is responsible for the superconductivity in the radical salts of BEDT-TTF. Tunneling experiments in the normal metallic [36] as well as in the superconducting state [37, 38] were carried out. Tunneling experiments of Hawley et al. [37] on β -(BEDT-TTF) $_2$ (AuI $_2$)-crystals (superconducting transition at ambient pressure at 4.5 K [39, 40]) did show a superconducting gap Δ_T in the ab -plane about 5 times larger than the expected BCS-value. More recent tunneling experiments on β -(BEDT-TTF) $_2$ I $_3$ as well as on β -(BEDT-TTF) $_2$ (AuI $_2$) in the ab -plane [38] show values of Δ_T only about 15% larger than the BCS weak coupling value and are in good accordance with the conventional electron phonon theory of superconductivity. However, the superconducting gap might be quite anisotropic and in fact preliminary band calculations [41] indicate that the Fermi surface has several separate sheets, which obviously may possess different superconducting gaps. In such a situation the average gap may correspond to the BCS-value and the maximum value of the gap may be considerably higher [38]. Therefore, more experimental data for tunneling contacts with different orientations in the ab -plane are needed.

Conclusions

Bulk superconductivity at 8 K and ambient pressure exists in β -(BEDT-TTF) $_2$ I $_3$ and α_1 -(BEDT-TTF) $_2$ I $_3$ crystals. While in the β -crystals the superconducting state has to be prepared under special conditions (temperature-pressure cycling procedure) and is only metastable, in α_1 -(BEDT-TTF) $_2$ I $_3$ this superconducting state at 8 K is stable and entirely reproducible for many temperature cycles up to 380 K.

We would like to thank all our colleagues and co-workers (see references) for the very effective cooperation during all the investigations in the last years. Our special thanks to Professors H. Endres, M. Weger and Dr. Swietlik for many helpful discussions and efficient teamwork in Heidelberg. We gratefully acknowledge financial support of this work through Stiftung Volkswagenwerk, Hannover.

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