

## MOLECULAR METALS AND SUPERCONDUCTORS: BEDT-TTF RADICAL SALTS

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### INTRODUCTION

The first discovery of superconductivity in an organic metal - in the radical salts of TMTSF (tetramethyltetraselenafulvalene) - under pressure /1/ and ambient pressure /2/ has demonstrated that in addition to the usual intrastack contacts between the donor molecules in quasi one dimensional metals intermolecular contacts between molecules in neighbouring stacks are important. These interstack contacts result in a less pronounced one dimensional electronic behaviour leading to a stabilization of the metallic character down to low temperatures.

In 1982, SAITO et al. /3/ showed that due to the somewhat nonplanar structure of BEDT-TTF (bis-ethylenedithiotetrathiafulvalene) the electrocrystallisation of radical salts of this donor results in even stronger interstack contacts. Electrochemically prepared crystals of  $(\text{BEDT-TTF})_2 \cdot \text{ClO}_4(\text{TCE})_{0.5}$  showed in fact the typical electronic behaviour of a quasi two-dimensional organic metal /3, 4/ down to low temperatures, but did not become superconducting. In a similar salt  $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$  PARKIN et al. /5, 6/ did find a superconducting state near 2 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. For the first time in an organic sulphur donor system superconductivity was observed. Nevertheless, the electrochemical preparation of this radical salt is not easy due to the fact that a large number of radical salts with different stoichiometries and crystal structures might grow simultaneously. For that reason radical salts of BEDT-TTF with  $\text{I}_3^-$  counterions in THF solutions were prepared /7-9/ leading to two radical salts with identical stoichiometries but different structures (see fig. 1), the so-called  $\alpha$ - and  $\beta$ - $(\text{BEDT-TTF})_2\text{I}_3$  phases. Both types of crystals can be easily distinguished by eye because  $\alpha$ -phase crystals have usually a plate-like shape while  $\beta$ -phase crystals are canted rhombohedrons. In addition the room temperature ESR linewidth of the conduction electrons can be used to discriminate unequivocally between both salts (70 to 110 Gauss for  $\alpha$ -phase crystals and 20 to 25 Gauss for  $\beta$ -phase crystals depending on the direction of the crystals with respect to the magnetic field /10, 11/.

$\alpha$ - $(\text{BEDT-TTF})_2\text{I}_3$  crystals are two-dimensional organic metals with a nearly

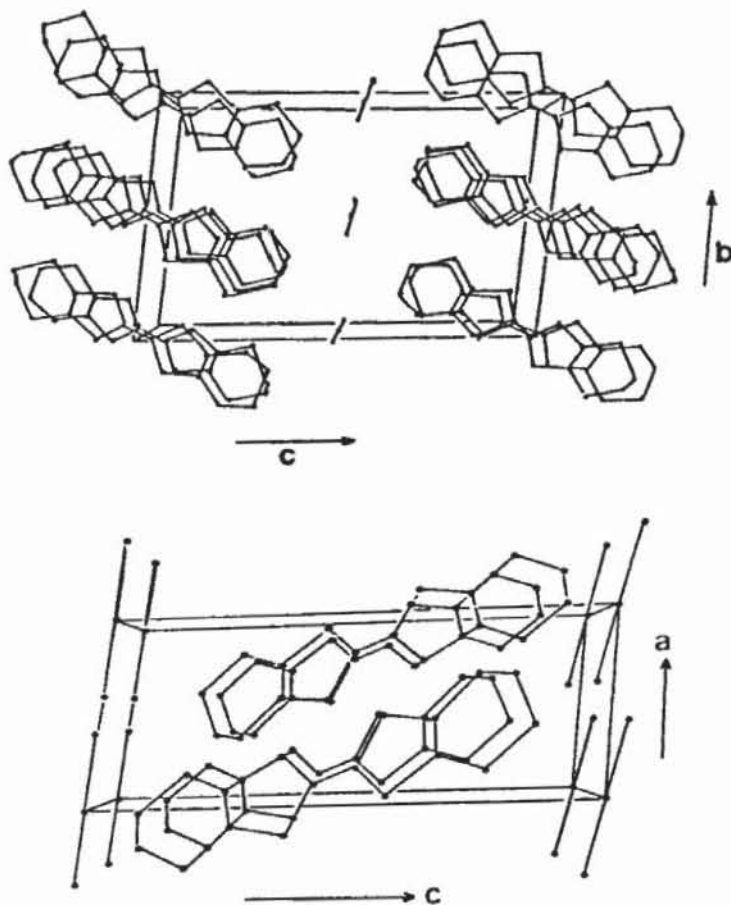


Figure 1. Stereoscopic projections of the structure of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  (top) and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  (bottom) along the stacking axes.

isotropic electrical conductivity ( $\sigma_{300} \approx 60$ -250 S/cm) within the ab-plane, a 1000-times smaller conductivity in the  $c^*$ -direction and a metal insulator transition at 135 K /8, 9/.  $\beta$ -(BEDT-TTF) $_2$ I $_3$  crystals are two-dimensional metals as well ( $\sigma_{300} \approx 10$ -50 S/cm) but stay metallic down to low temperature and - as was shown first by the group of SHEGOLEV /12/ - become superconducting at 1.3 K and ambient pressure.

In the following a review of the structural and physical properties of  $\alpha$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$  shall be given and the conditions will be described under which superconductivity at ambient pressure and 8 K in both types of crystals is observed.

### $\beta$ -(BEDT-TTF) $_2$ I $_3$

The discovery of superconductivity in  $\beta$ -(BEDT-TTF) $_2$ I $_3$  at  $T = 1.3$  K and ambient pressure by YAGUBSKII et al. /12/ was confirmed by WILLIAMS et al. /13/ and Meissner-effect measurements /14/ 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  $\beta$ -phase crystals can be raised to 7.5 K /15, 16/. After a particular pressure-temperature cycling procedure -pressurization up to 1.5 kbar at room temperature and a release of the helium gas pressure at temperatures below 125 K - superconductivity at  $T_c = 8$  K and ambient pressure was found /17-19/. 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 along the  $c^*$ -axis of about 6 T at various temperatures is shown in fig. 2. The confirmation of bulk superconductivity at 8 K as well as was obtained by Meissner-effect /20/ and ac-susceptibility measurements /18/. However, this specially prepared superconducting state at 8 K and ambient

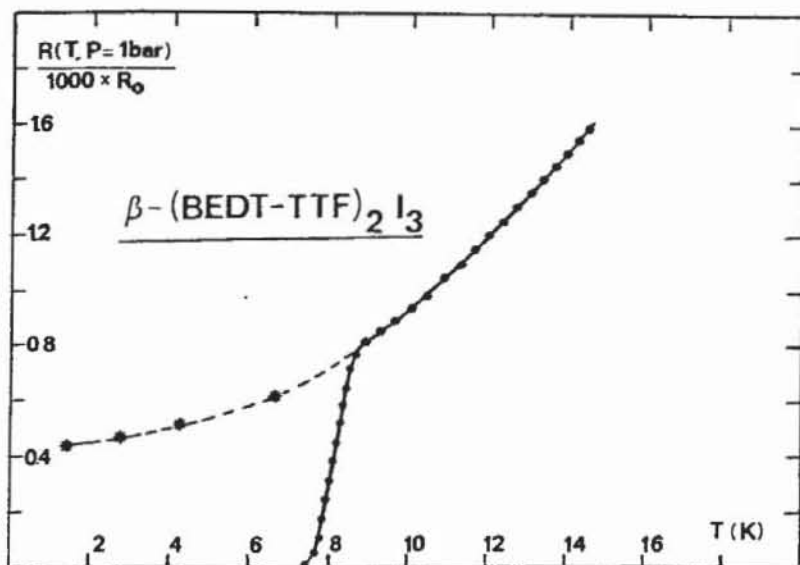


Figure 2. A superconducting transition at 8 K and ambient pressure in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> after a special pressure-temperature cycling procedure /17/ as well as the suppression by a magnetic field along the c\*-axis at various temperatures.

pressure is meta-stable 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 /10/. Recently it was shown that this meta stable 8 K superconducting state can be obtained as well by an electronic excitation with laser light at temperatures below 125 K /21/, but here, due to the fact that the light is absorbed within a few microns only in a thin surface layer.

In order to understand these somewhat surprising facts, the structural properties of the  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> crystals under the different conditions have to be discussed. At room temperature  $\beta$ -crystals are triclinic /22, 23/ ( $a = 15.243$ ,  $b = 9.070$ ,  $c = 6.597$  Å;  $\alpha = 109.73^\circ$ ,  $\beta = 95.56^\circ$ ;  $\gamma = 94.33^\circ$ ;  $V = 848.9$  Å<sup>3</sup>) and the structure is very similar to the Bechgaard-salts. Only one type of crystallographic equivalent stacks exists. Below 195 K at ambient pressure an incommensurate structural modulation exists /24-26/ and the origin of this modulation is connected with an anion cation interaction. Below 125 K a commensurate superstructure with

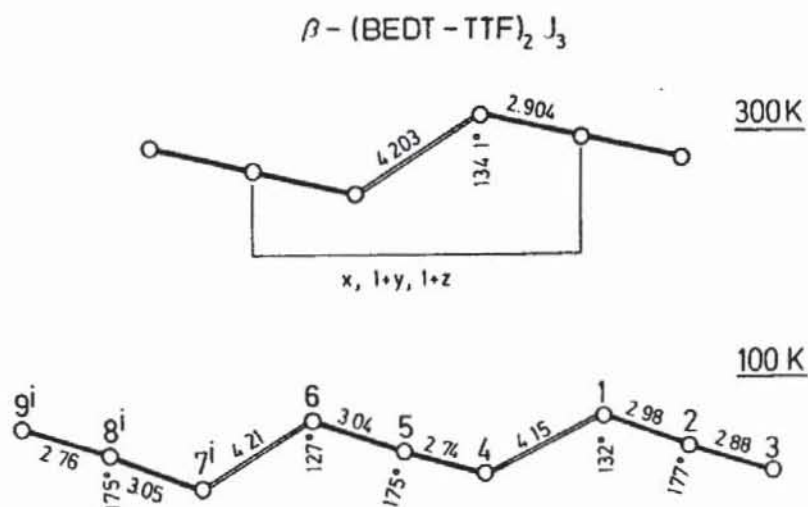


Figure 3. Comparison of the geometry of the triiodide chains in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at room temperature (top) and 100 K (bottom). The unit cell at 100 K contains the three triiodides as shown.



a unit cell of about three times as large as at room temperature was observed [27] ( $a = 18.269$ ,  $b = 21.04$ ,  $c = 6.543$  Å;  $\alpha = 93.56$ ,  $\beta = 94.84$ ,  $\gamma = 99.86^\circ$ ;  $V = 2461$  Å<sup>3</sup>). 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. 3). This finding was confirmed by resonance Raman-investigations [21]. Therefore, it was assumed [27] 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 [17, 18] 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 [28, 29] and it was shown that no incommensurate modulated structure at 4.5 K exists, but furthermore, that the terminal ethylene-groups of the BEDT-TTF-molecules in the stacks are all ordered in contrast to the room temperature structure where only on one side the ethylene groups in the stacks are ordered while on the other side they occupy the two possible conformations statistically [28, 29].

An electronic excitation of the  $I_3^-$  anions in  $\beta$ -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 [21]. 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. 4) or immediately at high light intensity ( $\approx 50$  mW) [21]. 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 [21].

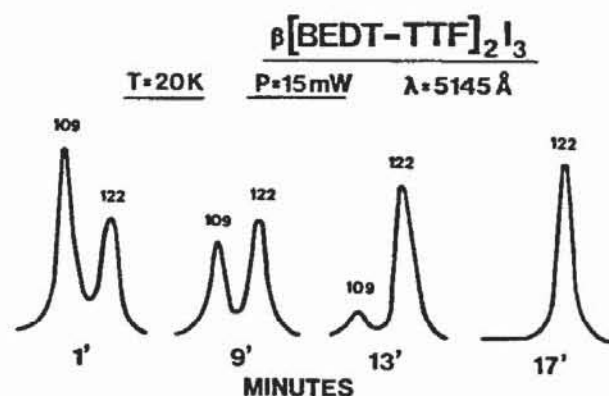


Figure 4. Structural transformation from the low into the high temperature superconducting phase in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> by irradiation with light [21] as observed by the change of the resonance Raman spectrum of the symmetric stretching mode (109 and 122 cm<sup>-1</sup>) of the  $I_3^-$  anions with time at constant laser power (15 mW, at 5145 Å).

#### $\alpha$ - AND $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

The unit cell of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> crystals (triclinic:  $a = 9.211$ ,  $b = 10.85$ ,  $c = 17.488$  Å;  $\alpha = 96.95$ ,  $\beta = 97.97$ ,  $\gamma = 90.75^\circ$ ,  $V = 1717$  Å<sup>3</sup> [9]) at room temperature is twice as large as the unit cell of the  $\beta$ -phase. In contrast to the  $\beta$ -phase crystals in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> two crystallographically different stacks occur and there exist large dihedral angles between the molecular planes (59.4 and 70.4°) of neighbouring donor molecules. The  $I_3^-$  anions are linear and all the terminal ethylene groups of the BEDT-TTF-donor molecules in both crystallographically non-equivalent stacks are ordered. Under ambient pressure the  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> undergoes a metal-insulator phase transition at 135 K [7-9], which can be suppressed by an isotropic pressure of >12 kbar, but no sign of superconductivity could be observed down to 100 mK [30]. It was claimed [31] that doping the  $\alpha$ -phase crystals with iodine at room temperature results in a metallic state below the insulator phase transition at 135 K followed by a transition to superconductivity at around 3.2 K. Similar results

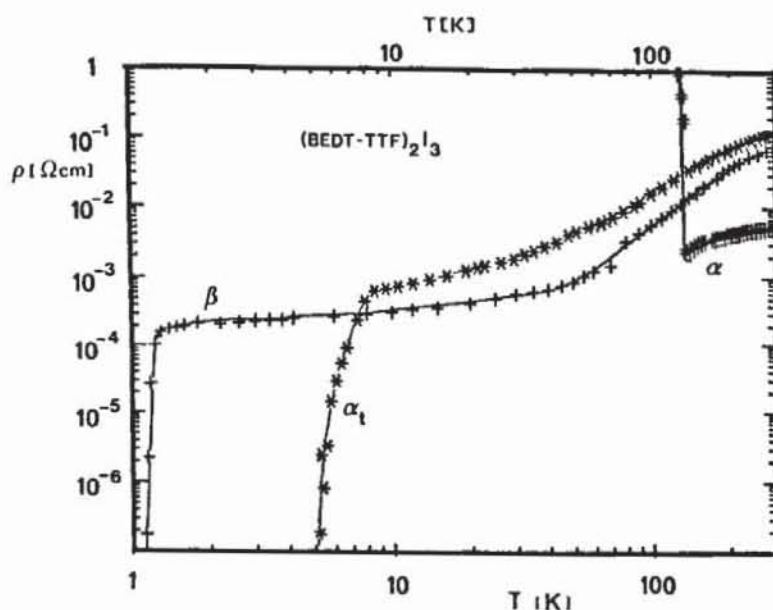


Figure 5. Resistivity versus temperature (logarithmic scales) for  $\alpha$ -,  $\alpha_t$ - and  $\beta$ -(BEDT-TTF) $_2$ I $_3$

as in ref. /31/ for the resistivity for such iodine-doped  $\alpha$ -crystals could be reproduced /32/, but microwave conductivity as well as ac-susceptibility measurements /32, 33/ showed that this metallic state is not a bulk effect in these crystals.

Recently, BARAM et al. /34/ reported a structural transformation of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  into  $\beta$ -phase crystals by tempering the  $\alpha$ -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 but the structural transformation was confirmed by Weissenberg-pictures /34/. The most surprising fact after the structural transformation was that these crystals show a sharp decrease in resistivity at around 8 K indicating a superconducting transition at this temperature, but prove by a simultaneously applied magnetic field was not reported. Further it was not clear whether or not the eventual superconducting transition is a bulk effect in these tempered crystals.

Another open question is what the differences in the structures between the normal grown  $\beta$ -(BEDT-TTF) $_2$ I $_3$  and the tempered  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  crystals are. (In the following tempered  $\alpha$ -phase crystals are called  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$ ). This is an important question since  $\beta$ -(BEDT-TTF) $_2$ I $_3$  becomes superconducting under normal ambient pressure conditions at 1.3 K while in  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  this transition seems to be at around 8 K, whereas the  $\beta$ -(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 (fig. 5, 6) and ac-susceptibility (fig. 7) both with and without applying a magnetic field /35/ as well as ESR (fig. 8), NMR (fig. 9), Resonance Raman (fig. 10) and thermopower investigations on  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  /35/ have shown that bulk superconductivity at 8 K and ambient pressure exist in such  $\alpha_t$ -crystals. In contrast to the specially prepared 8 K meta-stable superconducting state in  $\beta$ -crystals here in  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  the superconducting state is stable and entirely reproducible for several temperature cycles up to 380 K /35/.

$^{13}$ C-NMR solid state investigations /35/ (fig. 9) have shown that by tempering  $\alpha$ -crystals above 70°C for several days in air all crystals used in the experiment ( $\approx 0.3$  g) were totally converted into the new  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$ -phase.

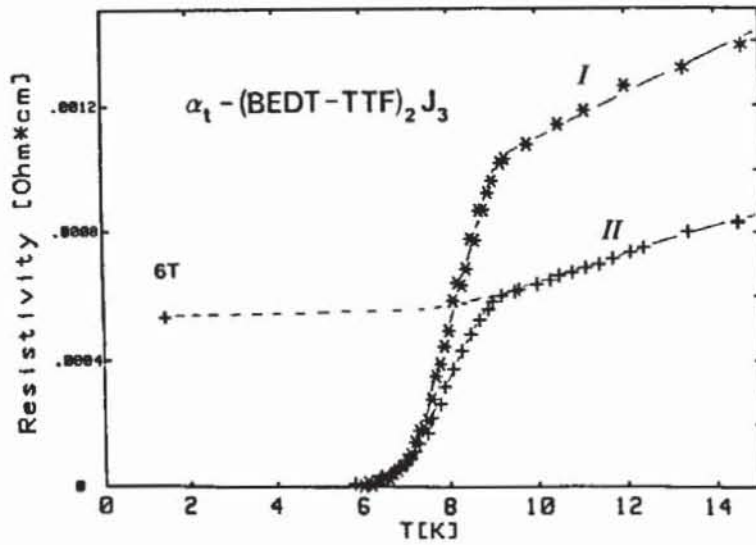


Figure 6. Resistivity of two  $\alpha_1$ -(BEDT-TTF) $_2$ I $_3$  crystals (I and II) in the temperature region between 0 and 15 K /35/. The suppression of superconductivity in sample II by applying a magnetic field of 6 T at 1.3 K parallel to the c\*-axis is shown as well.

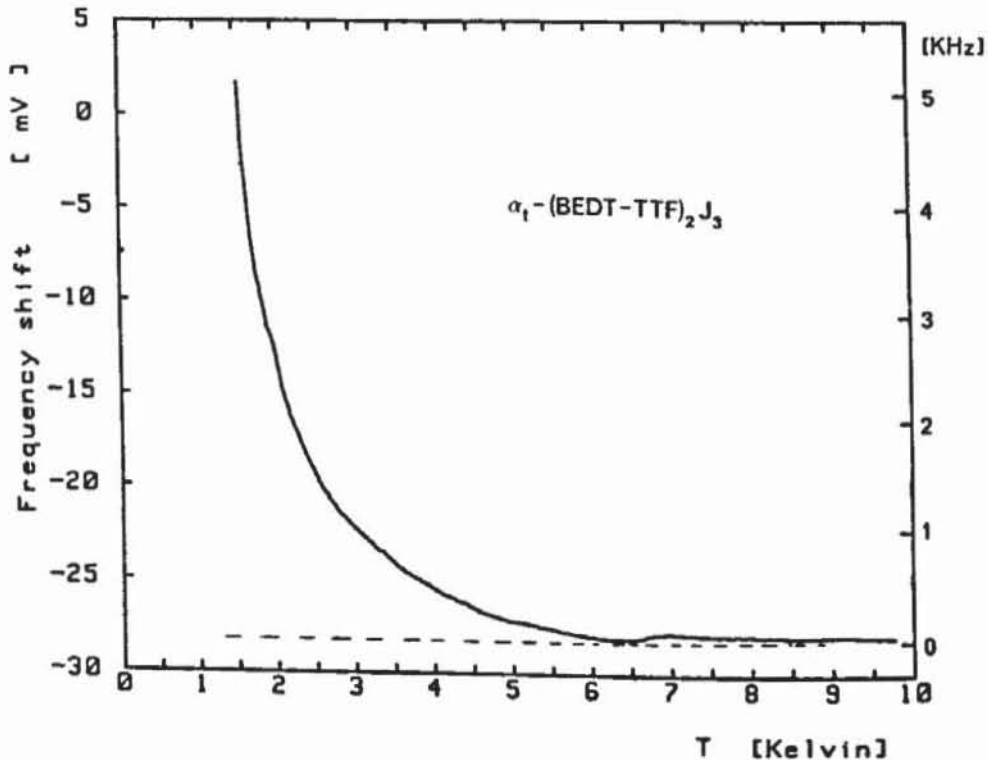


Figure 7. Increase in resonance frequency of a LC circuit due to exclusion of the rf-field by diamagnetic shielding currents (ac susceptibility) in  $\alpha_1$ -(BEDT-TTF) $_2$ I $_3$  (sample II of fig. 5) by lowering the temperature /35/.

The ESR linewidth measurements (fig. 8) as well as the resonance Raman spectra (fig. 10) indicate the phase transition after tempering as well /35/. The upper critical fields  $H_{c2}$  (fig. 11) /35/ are anisotropic but with 2.5 to 11 T (depending on the direction of the magnetic field with respect to the crystal axes) relatively high. All the results from ref. /34, 35/ indicate that the  $\alpha_t$ -crystal structure at room temperature is identical with the one of the high  $T_c$ -superconducting phase of the  $\beta$ -crystals. This is probably due to the fact that in the

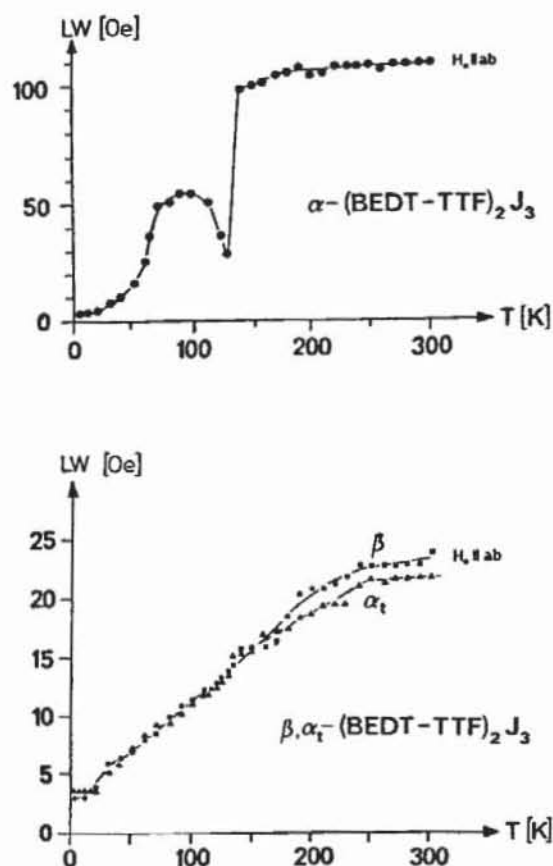


Figure 8. Temperature dependence of the ESR-linewidth for  $\alpha-(BEDT-TTF)_2I_3$  (top) as well as for  $\beta$ - (■) and  $\alpha_t$ - $(BEDT-TTF)_2I_3$  (▲) (bottom) /35/.

$\alpha$ -phase crystals at room temperature (and probably at 75°C the tempering temperature as well) all terminal ethylene-groups of the BEDT-TTF donor molecules are ordered similar as in the high  $T_c$ -superconducting  $\beta$ -phase and therefore 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  $\beta$ -(BEDT-TTF) $_2$ ·[AuI $_2$ ] crystals (superconducting transition at ambient pressure at 4.5 K /39, 40/) did show a superconducting gap  $\Delta_T$  in the ab-plane about 5 times larger than the expected BCS-value. More recent tunneling experiments on  $\beta$ -(BEDT-TTF) $_2$ I $_3$  and on  $\beta$ -(BEDT-TTF) $_2$ [AuI $_2$ ] in the ab-plane as well /38/ show values of  $\Delta_T$  only about 15% larger than the BCS weak coupling value and are in good accordance

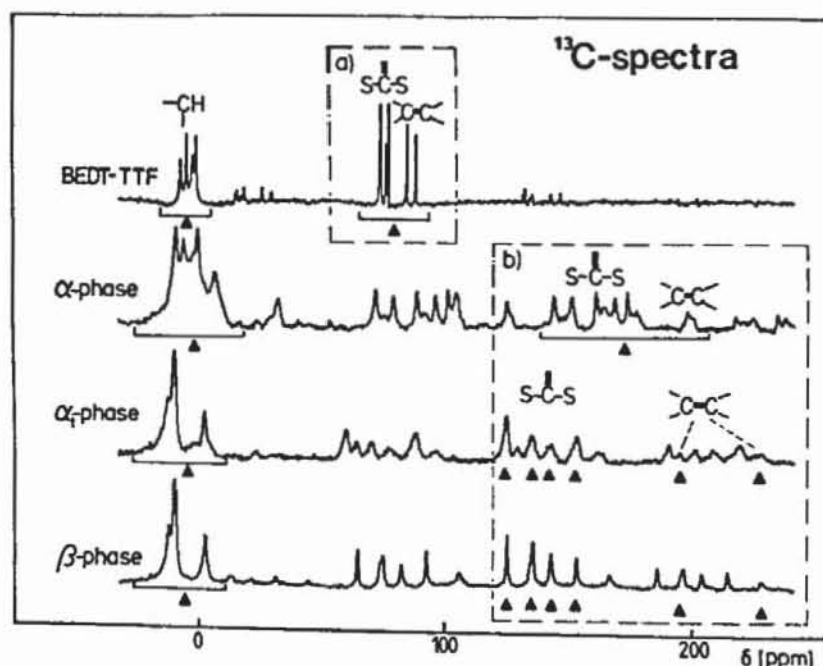


Figure 9. Magic angle spinning (MAS)  $^{13}\text{C}$ -NMR spectra at 300 K of BEDT-TTF and of the organic metals  $\alpha$ -,  $\beta$ - and  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$ . The center bands are marked by  $\blacktriangle$  in the framed parts as well as in the region of the ethylene groups ( $\nu = 68$  MHz, spinning frequency between 4-5 KHz) /35/.

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.



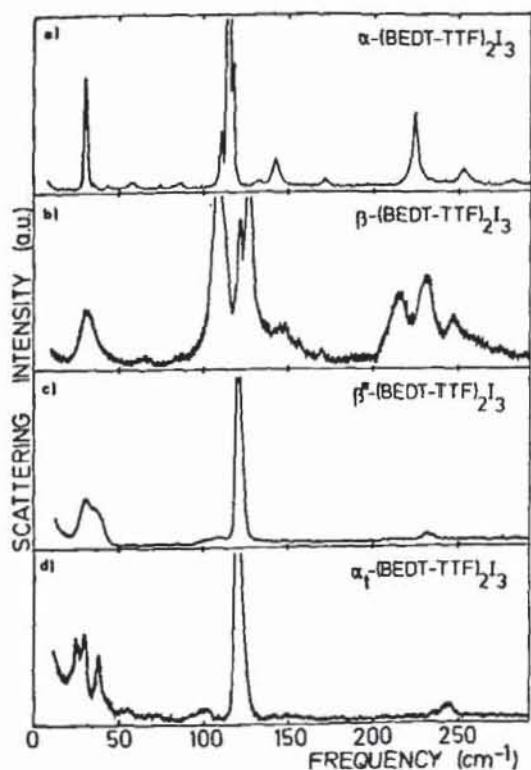


Figure 10. Low energetic parts of the resonance Raman-spectra at 2 K of  
 a)  $\alpha$ -(BEDT-TTF) $_2$ I $_3$   
 b)  $\beta$ -(BEDT-TTF) $_2$ I $_3$  (low temperature superconducting (1.3 K) phase  
 c)  $\beta$ -(BEDT-TTF) $_2$ I $_3$  (high temperature superconducting (8 K) phase, as prepared by optical excitation /21/).  
 d)  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  (excitation wave length 4880 A, 10 mW) /35/.

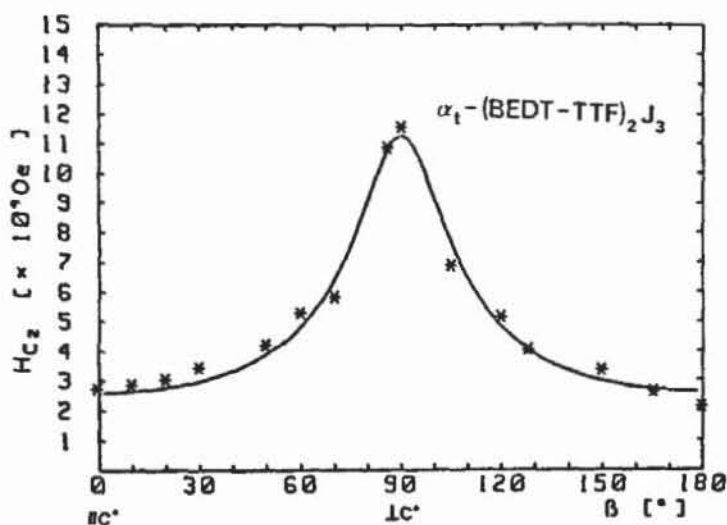


Figure 11. Upper critical fields  $H_{c2}$  at a temperature of 1.3 K for  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  as evaluated by the mid-transition of the resistivity curve for several magnetic field directions /35/.

## CONCLUSIONS

Bulk superconductivity at 8 K and ambient pressure exists in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and  $\alpha$ <sub>t</sub>-(BEDT-TTF)<sub>2</sub>I<sub>3</sub> crystals. While in the  $\beta$ -crystals the superconducting state has to be prepared under special conditions (temperature pressure cycling procedure) and is only meta stable, in  $\alpha$ <sub>t</sub>-(BEDT-TTF)<sub>2</sub>I<sub>3</sub> this superconducting state at 8 K is stable and entirely reproducible for many temperature cycles up to 380 K.

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