

## BULK SUPERCONDUCTIVITY IN POLYCRYSTALLINE PRESSED SAMPLES OF $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$ AND $\beta_p$ -(BEDT-TTF) $_2$ I $_3$ .

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**Abstract** Bulk superconductivity at ambient pressure in pressed samples of polycrystalline  $\alpha_t$ -(BEDT-TTF) $_2$ I $_3$  and  $\beta_p$ -(BEDT-TTF) $_2$ I $_3$  is reported. This finding is remarkable because it demonstrates that organic superconductors can be used in principal for applications such as the preparation of electronic devices and superconducting cables. In addition the observation of bulk superconductivity in large pressed samples of crystallites of a typical diameter of 1  $\mu$ m of organic metals indicates that superconductivity in organic polymers should be observable as well.

### INTRODUCTION

Ten years ago for the first time superconductivity in an organic metal was observed.<sup>1</sup> Today about 30 different organic metals are known which become superconducting under pressure or ambient pressure.

Usually organic metals and superconductors grow as single crystals at an electrode in an electrochemical cell. Therefore physical investigations of organic metals and superconductors are performed on single crystals. This is certainly an important fact for the understanding of the electronic properties of such materials. On the other hand, in the case of possible applications of such organic metals certainly very rarely single crystals could be used. Since up to now superconducting organic polymers are also not available, the only possible way to use organic superconductors at least in principle for applications would be as polycrystalline powders, which might be pressed to larger samples.

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From a physical point of view superconductivity in polycrystalline pressed samples of organic metals should be observable because it was shown that the coherence length in such quasi two dimensional organic superconductors are typically of the order of 10–100 Å, that means of the order of the dimensions of the unit cell. A problem for the observation of superconductivity in polycrystalline pressed samples might arise from the fact that organic metals are usually relatively soft compared to anorganic superconductors. Therefore the organic materials might undergo phase transitions by applying a pressure to the powder in order to obtain mechanically stable samples and the development of annealing processes might be necessary for observing bulk superconductivity.

Here we report the preparation of such polycrystalline pressed samples of  $\alpha_t$ - and  $\beta_p$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> which show bulk superconductivity.

### EXPERIMENTAL AND RESULTS

Mechanically stable samples of the size of 4x1x0.5 mm<sup>3</sup> were prepared from carefully pulverized single crystals of the organic metals  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>,  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> (the resulting crystallites from the pulverisation process had typical diameters of 0.5–10 μm) by applying a pressure of about 1 kbar to the powder. The resistivity of the samples was measured by the usual four point method.

In the polycrystalline pressed samples of  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, which were prepared from a powder of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and the pressed samples than annealed at 75°C for at least 3 days directly after the preparation, bulk superconductivity was observed (at 2 K about 50 % volume superconductivity with respect to an ideal superconductor<sup>2</sup>). Nevertheless the superconducting transition is relatively broad as can be seen from fig. 1. While the onset for superconductivity in the resistivity curve is found near 9 K, zero resistivity is observed at 2.2 K. In the case of crystals of  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub><sup>3</sup> zero resistivity appears already at 6 K (see fig. 1).

A question which arised was whether it is possible to obtain bulk superconductivity in samples of  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> when the preparation of the samples is started already with  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> powder. Curve a in fig. 2 shows the resistivity versus temperature for such a polycrystalline pressed sample of  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. A metal like behaviour was found over the whole temperature range between 300 and 1.3 K but no bulk superconductivity could be found. In contrast after annealing the sample at 75°C for 3 days again a broad superconducting transition could be observed (curve b in fig.2) and ac susceptibility measurements indicate at 2 K a 50 % volume superconductivity with respect to an

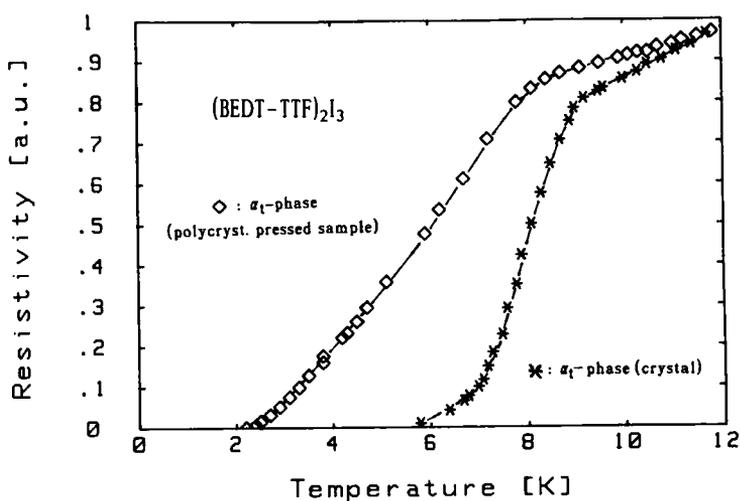


FIGURE 1 Resistivity versus temperature below 12 K (normalized at 12 K) for a polycrystalline pressed sample of  $\alpha_t\text{-(BEDT-TTF)}_2\text{I}_3$  (prepared from  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ , see text) as well as for a crystal of  $\alpha_t\text{-(BEDT-TTF)}_2\text{I}_3$ .

ideal superconductor. In fact the behaviour of such prepared pressed samples of  $\alpha_t\text{-(BEDT-TTF)}_2\text{I}_3$  were more or less identical with those samples prepared from  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  powder.

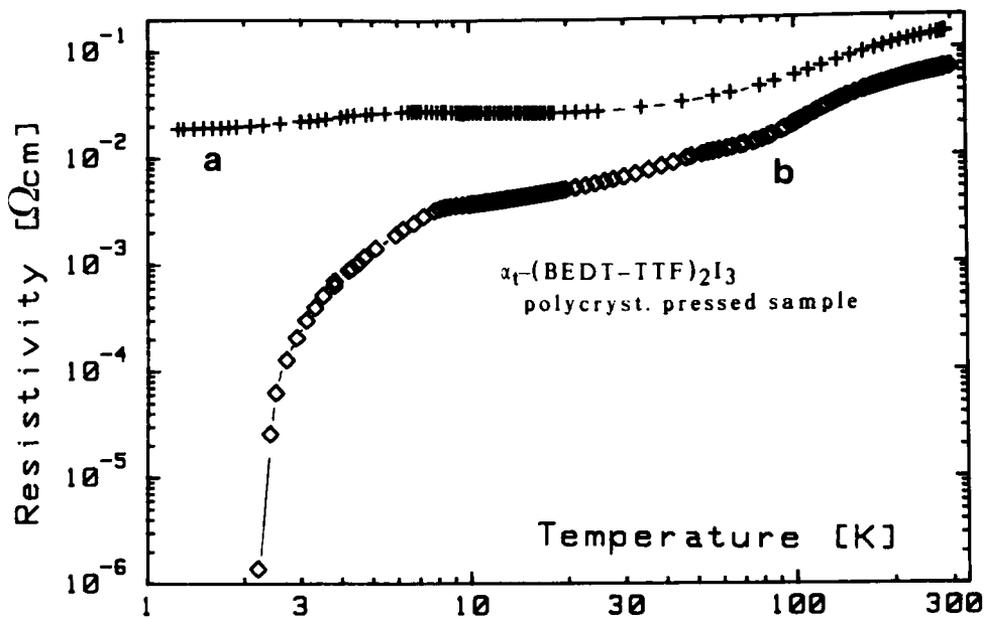


FIGURE 2 Resistivity versus temperature of a polycrystalline pressed sample of  $\alpha_t\text{-(BEDT-TTF)}_2\text{I}_3$  (prepared directly from  $\alpha_t\text{-(BEDT-TTF)}_2\text{I}_3$  powder) (curve a) and of the same sample after annealing at  $75^\circ\text{C}$  (curve b).

In order to obtain some more information about such phase transitions which occur under pressure during the preparation of the polycrystalline pressed samples resonance Raman investigations, in particular on the most intensive vibrational symmetric stretching mode of the  $I_3^-$  anions, were carried out. Earlier measurements on single crystals of  $\alpha$ -,  $\alpha_t$ - and  $\beta$ -(BEDT-TTF) $_2I_3$ <sup>4</sup> had shown that the resonance Raman-spectra are very sensitive to the symmetry of the  $I_3^-$  anions. The symmetric stretching mode of the linear symmetric  $I_3^-$  anions usually is found about 10  $cm^{-1}$  at higher energy compared to the asymmetric and non-linear  $I_3^-$  anions.<sup>4</sup> In the resonance Raman spectra of the polycrystalline pressed sample of  $\alpha$ -(BEDT-TTF) $_2I_3$  symmetric and linear as well as asymmetric and nonlinear  $I_3^-$  anions are observed (see fig. 3a). This indicates that the pressure during the preparation of the samples deforms the  $I_3^-$  anions partially. A similar result can be observed for the polycrystalline pressed samples which were prepared directly from powdered  $\alpha_t$ -crystals<sup>5</sup> and not annealed after the preparation. In contrast to this finding the resonance Raman spectra of the annealed polycrystalline pressed samples of  $\alpha_t$ -(BEDT-TTF) $_2I_3$  (which become superconducting) show only the stretching mode of the linear and symmetric  $I_3^-$  anions (see fig. 3b) indicating again the higher symmetry and higher order of the structure.

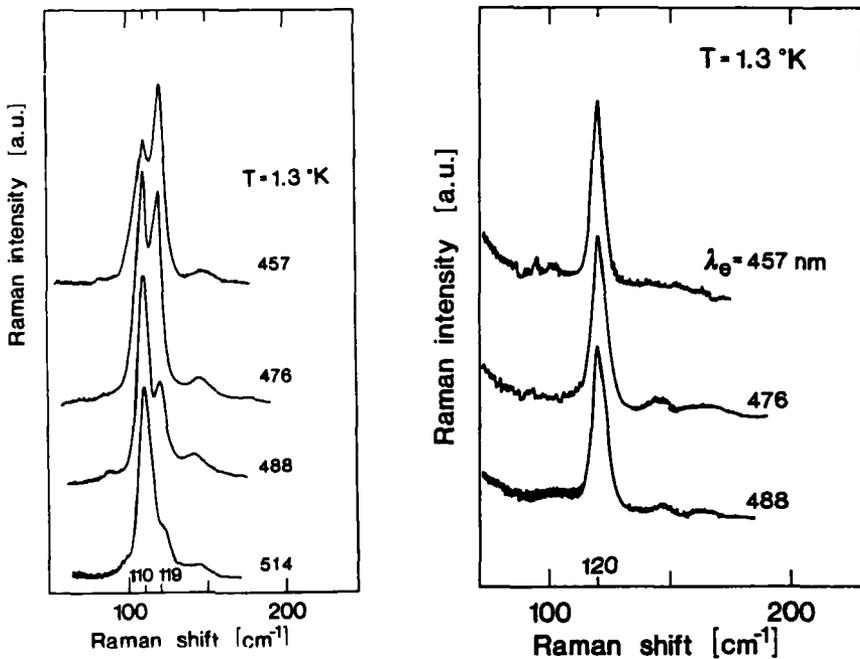


FIGURE 3 Resonance Raman scattering at 1.3 K and several excitation wavelengths of a polycrystalline pressed sample of  $\alpha$ -(BEDT-TTF) $_2I_3$  (left) and a polycrystalline pressed sample of  $\alpha_t$ -(BEDT-TTF) $_2I_3$  after annealing (right).

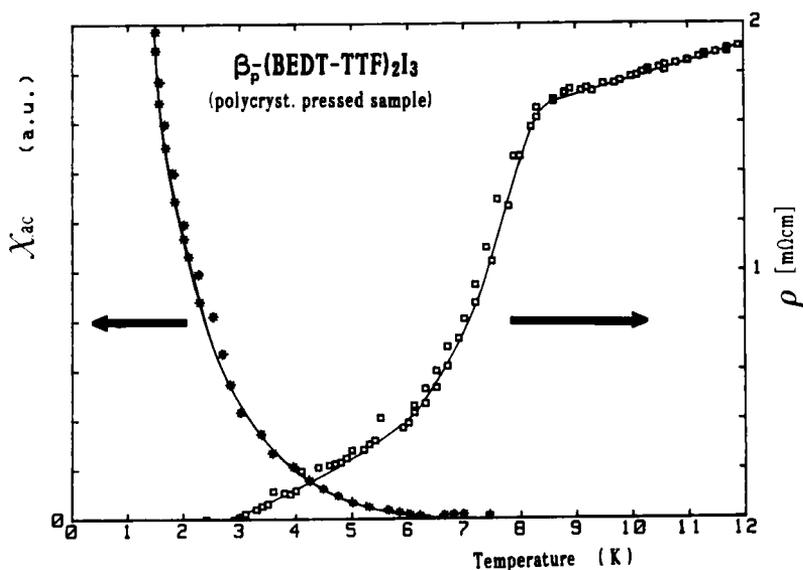


FIGURE 4 Resistivity (right part) and change in ac-susceptibility (left part) versus temperature of a polycrystalline sample of  $\beta_p\text{-(BEDT-TTF)}_2\text{I}_3$  in the temperature range below 12K.

The most surprising observation was made by measuring the temperature dependence of the resistivity of polycrystalline pressed samples of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  (in the following called  $\beta_p\text{-(BEDT-TTF)}_2\text{I}_3$ <sup>6</sup>). Without annealing the samples at 75°C an onset to superconductivity at 9K was found (see fig. 4). Zero resistivity was observed at 3.2K and the middle of the resistive transition at 7.5K (see fig. 4). This observation is surprising because single crystals of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  show a rather sharp superconducting transition at 1.2K<sup>7</sup> and a metastable superconducting state at 8K and ambient pressure, which can be prepared by a special pressure temperature cycle.<sup>8</sup> Here in the polycrystalline samples of  $\beta_p\text{-(BEDT-TTF)}_2\text{I}_3$  the superconducting state at 7.5K is stable and a bulk effect of the sample, as can be seen from the change of the ac susceptibility (see fig. 4) which corresponds at 2K to about 50% of that expected for a perfect superconductor.

The observation of a stable superconducting state at 7.5K in the samples of  $\beta_p\text{-(BEDT-TTF)}_2\text{I}_3$  shows that a structural phase transition occurring under pressure plays again a role. As a consequence of the phase transition here the transition temperature into the superconducting state is increased. This behaviour reemphasizes that organic superconductors might also be of interest for industrial applications.

### ACKNOWLEDGEMENT

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### REFERENCES

1. D. Jérôme, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. Lett. **4**, L 95 (1980).
2. D. Schweitzer, S. Gärtner, H. Grimm, E. Gogu and H.J. Keller, Solid State Comm. **69**, 843 (1989).
3. D. Schweitzer, P. Bele, H. Brunner, E. Gogu, U. Haeberlen, I. Hennig, T. Klutz, R. Swietlik and H. J. Keller, Z. Phys. B. - Condensed Matter, **67**, 489 (1987).
4. R. Swietlik, D. Schweitzer and H. J. Keller, Phys. Rev. B. **36**, 6881 (1987).
5. R. Zamboni, D. Schweitzer and H.J. Keller, in "Lower Dimensional Systems and Molecular Electronics", ed. by R.M. Metzger, P. Day and G. Papavasiliou, Plenum Press, in print.
6. D. Schweitzer, E. Gogu, H. Grimm, S. Kahlich and H. J. Keller, Angew. Chemie Adv. Mater. **101**, 977 (1989).
7. E. B. Yagubskii, I. F. Shegolev, V. N. Laukhin, P. A. Kononovich, M. W. Kartsonovnik, A. V. Zwarykina, L. I. Biwawov, Sov. Phys., JETP Lett. **39**, 12 (1984).
8. F. Creuzet, G. Creuzet, D. Jérôme, D. Schweitzer and H.J. Keller, J. Physique Lett. **46**, L 1079 (1985).