

MICROWAVE CONDUCTIVITY IN POLYCRYSTALLINE (BEDT-TTF)₂I₃ MATERIAL

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ABSTRACT

Polycrystalline material of the α -phase of (BEDT-TTF)₂I₃ was compressed to small samples (4 mm x 1 mm, thickness 0.3 mm typically) at a pressure of 10 kbar. Annealing at 70°C yields the superconducting α_c -phase.

Microwaves (10.2 GHz) enable the measurements of the conductivity for stepwise annealing after every annealing step in always the same sample. For annealing times ≥ 10 min all conductivity versus temperature curves are intersecting in an isosbestic point at 190 K. This behaviour can be described by a conductivity relation for a two component system, from which was determined the volume fraction of the new grown α_c -phase in dependence of the annealing time.

Starting annealing (annealing times < 10 min) shows another unexpected phase transformation. After 2 min annealing the conductivity at 200 K increases by more than one order of magnitude, but then decreases of further annealing (5-10 min) down to the value for the unannealed sample.

INTRODUCTION

Crystals of α -(BEDT-TTF)₂I₃ are quasi two-dimensional organic metals [1]. The crystals undergo a phase transition at 135 K. Cooling down, the dc conductivity increases slightly and then decreases sharply by about six orders of magnitude at 135 K. Cooling down, the microwave conductivity follows the dc conductivity. But the drop at 135 K is only three orders of magnitude. Then, in contrast to the dc measurements between 120 K and 40 K a plateau is reached [2], obviously due to CDW. Tempering the crystals of the α -phase above 70°C for several days yields a structural phase transition. The new phase (α_c -phase) is a quasi two-dimensional organic metal as well which has a stable superconducting state at 8 K and ambient pressure. This process can directly be observed in very small crystals by polarizing microscope techniques [3]. The structure of the α_c -phase is not known yet. Spectroscopic methods lead to the speculation that

the structure of α_c is very similar to the one of crystals of β -(BEDT-TTF) $_2$ I $_3$ [3-5]. A transformation by tempering like the transformation of the α -phase into the α_c -phase is also found in polycrystalline pressed samples [5-6]. An overview is given in [5].

EXPERIMENTAL

A grinding process of α -(BEDT-TTF) $_2$ I $_3$ single crystals yields a powder of crystallites with typical diameters of 0.5 - 10 μ m. Applying pressure of 10 kbar to the powder produces mechanically very stable samples (named α_p -phase). The sample size is 4 mm x 1 mm with thicknesses 0.2 - 0.5 mm typically. The contactless microwave measurements were carried out in a cylindrical cavity, working in the TM $_{010}$ mode at 10.2 GHz by usual cavity perturbation technique [7]. This technique enables the measurements of the conductivity for stepwise annealing after every annealing step in always the same sample. Annealing is done in a preheated drying cupboard at 70°C. Its large volume (about 5 dm 3) allows treatment of the samples also for short times. The samples are left in the styrofoam sample holder so that the position in the cavity is always exactly the same for the different measurements.

RESULTS AND DISCUSSION

For three pressed samples without annealing the relative microwave conductivity is plotted versus temperature in Fig. 1. The behaviour is the same for all three samples. In contrast to the sharp decrease of the microwave conductivity at 135 K found in single crystals [2], the transition is broadened and shifted to higher temperatures. Also the decrease to the plateau is only one order of magnitude in contrast to three orders of magnitude in the case of single crystals. Repeated running through the temperature cycle has no influence on the conductivity behaviour.

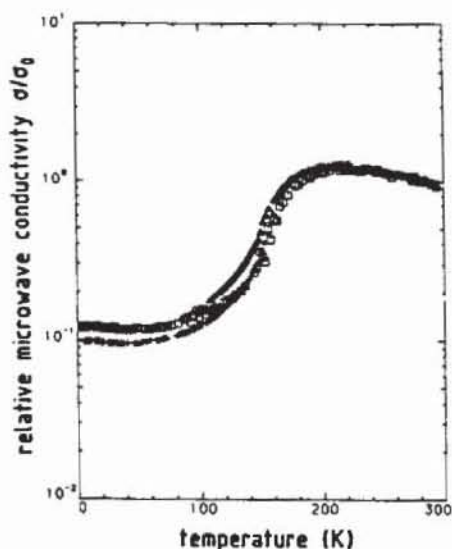


Fig. 1. Microwave conductivity of pressed samples of α_p -(BEDT-TTF) $_2$ I $_3$ without annealing related to the room temperature values $\sigma_{RT} = 10$ -15 (Ω cm) $^{-1}$. Frequency 10.2 GHz. Samples A +, B Δ , C \square .

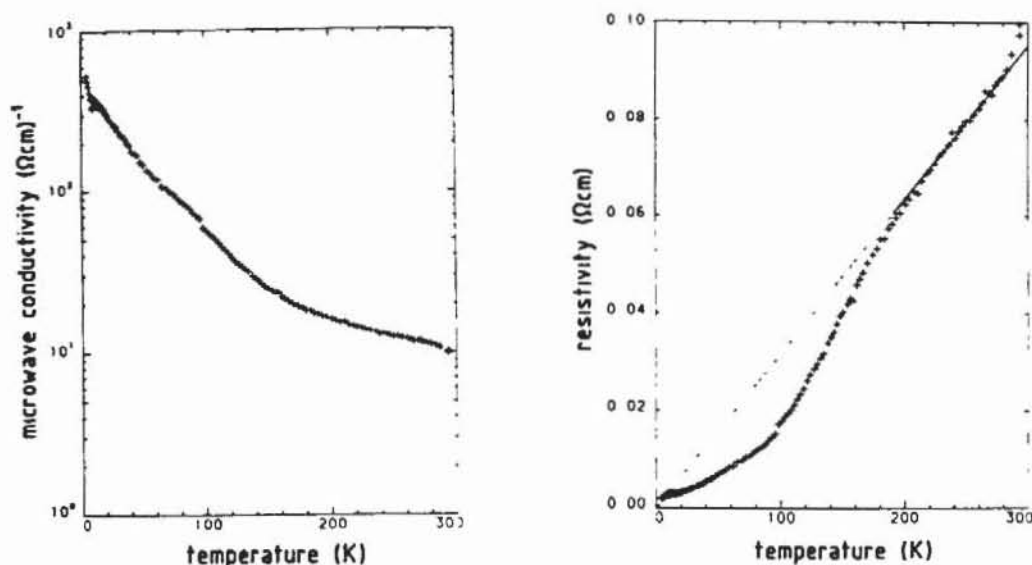


Fig. 2. a) Microwave conductivity of the pressed sample B of $\alpha_{\text{pt}}\text{-(BEDT-TTF)}_2\text{I}_3$ after annealing for 3.5 days at 70°C without interruption. Frequency 10.2 GHz. b) Resistivity versus temperature corresponding to a).

Annealing was applied to sample B without interruption for 3.5 days at 70°C. The new grown phase is named α_{pt} . Fig. 2a shows the microwave conductivity in agreement with dc measurements. In Fig. 2b the resistivity is plotted versus temperature. In the range of 200–300 K the resistivity is proportional to the temperature corresponding to the metallic character. The measurements shown in Fig. 2 are done during the cooling down process. Measurements of the microwave conductivity during cooling down and warming up show a hysteresis between 160–300 K with a maximum at 230 K, probably due to phase transitions in the material.

To investigate the transformation from the α_{p} -phase into the α_{pt} -phase stepwise annealing was applied beginning with short duration and going to longer times. After every annealing step the microwave conductivity was measured in dependence of the temperature. Fig. 3 summarizes results for annealing times from 10 min to 42.7 h. All curves are crossing in an isosbestic point at 190 K. Therefore the assumption is made that the 10 min curve corresponds to the α_{p} -phase and the 42.7 h curve to the α_{pt} -phase, respectively. Then all curves between these two curves are due to the mixture of the two phases. That means that the conductivity can be described by a parallel arrangement of these two conductivities rated by the volume fraction x of the growing pt-phase:

$$\sigma(T) = (1-x)\sigma_{\text{p}}(T) + x\sigma_{\text{pt}}(T).$$

The two extremal curves $\sigma_{\text{p}}(T)$ and $\sigma_{\text{pt}}(T)$ are fitted stepwise parabolically. All other curves between these two curves are fitted by using the above equation and so determining the volume fraction x . Fig. 3 shows a good agreement between this equation and the data.

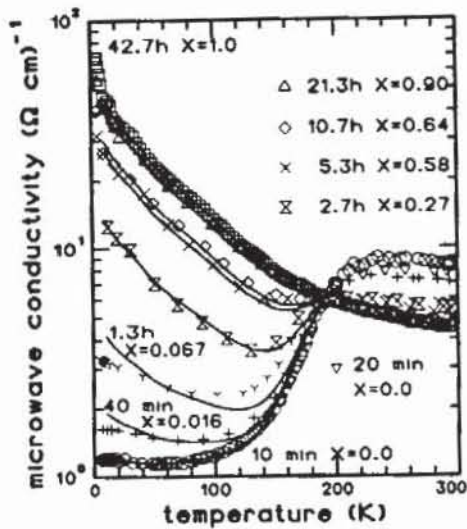


Fig. 3. Microwave conductivity of the pressed sample C of α_p, α_{pt} -(BEDT-TTF) $_2$ I $_3$ after stepwise annealing at 70°C. Parameter: added up annealing duration and volume fraction x of the growing α_{pt} -phase. x is determined by fitting the curves from $\sigma_p(T)$ and $\sigma_{pt}(T)$ using $\sigma(T) = (1-x)\sigma_p(T) + x\sigma_{pt}(T)$.

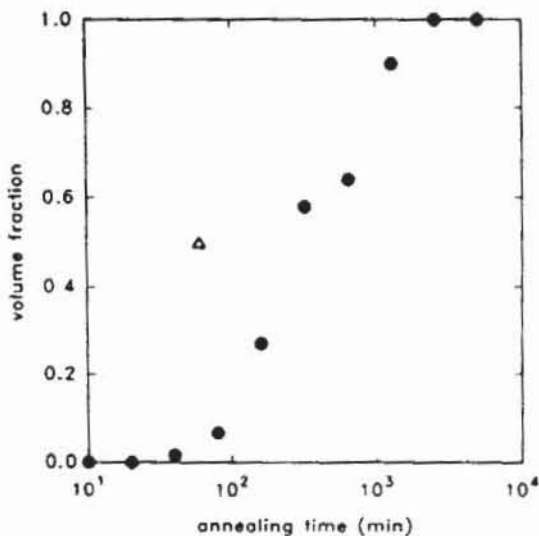


Fig. 4. Volume fraction of the growing α_{pt} -phase in the pressed sample C of α_p, α_{pt} -(BEDT-TTF) $_2$ I $_3$ taken from Fig. 3 (o) versus annealing duration. Sample A is annealed for 1 h without interruption (Δ). See Fig. 5.

In Fig. 4 the values of the volume fraction x of the pt -phase taken from Fig. 3 are plotted versus annealing duration. The volume fraction increases with annealing duration and saturates above two days. Half the material is transformed after about 5 h for the interrupted annealing shown in Fig. 3. The annealing of another sample (A) is interrupted not before 1 h. These results plotted in Fig. 5 in comparison to the results of sample C show that half of the material is transformed after 1 h if the annealing is applied without interruptions. Obviously the interrupted annealing causes barriers to the transformation process.

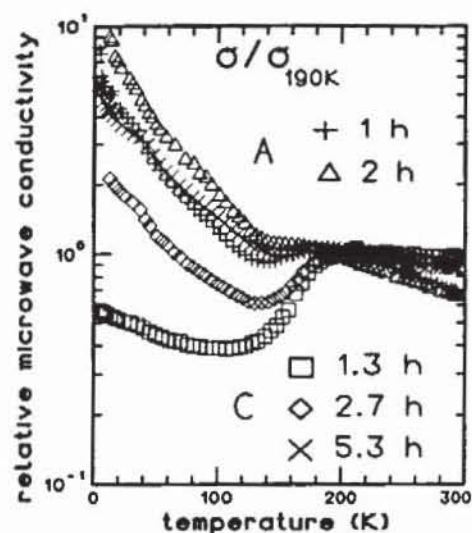


Fig. 5. Microwave conductivity of the pressed sample A of α_p, α_{pt} -(BEDT-TTF) $_2$ I $_3$ after 1 h (+) and 2 h (Δ) annealing at 70°C. Results of sample C are plotted for comparison (from Fig. 3).

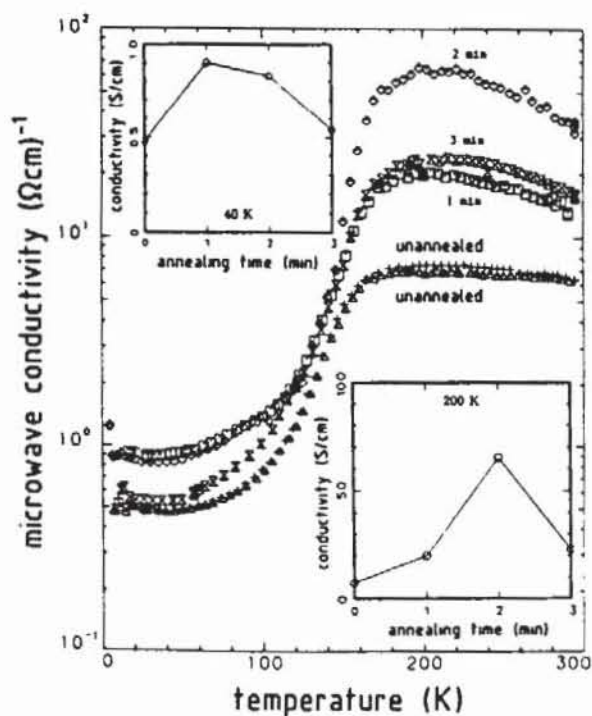


Fig. 6. Microwave conductivity of the pressed sample D of α_p, α_{pt} -(BEDT-TTF) $_2$ I $_3$ after stepwise annealing at 70°C. Parameter: added up annealing duration. Inserts: conductivity at 40 K and 200 K, respectively, versus annealing duration.

In the beginning of annealing there is another unexpected phase transformation. The values measured for a few minutes of annealing duration therefore are omitted in Fig. 3 and investigated in more detail on sample D. Fig. 6 shows the results. The conductivity increases with increasing annealing time and decreases after passing a maximum. Inserts in Fig. 6 describe this behaviour at 40 K and 200 K, respectively. In the high temperature range (200 K) the increase of the conductivity is more than one order of

magnitude. The origin for this behaviour is not known yet. Probably the high pressure procedure yields metastable phases disappearing in the first minutes of annealing. Due to the high heat conductivity and the small thicknesses of the samples annealing works in the whole sample volume, particularly in the case of short annealing times, too, ruling out surface effects.

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