

OPTICAL STUDY OF THE TRANSFORMATION OF THE α -PHASE OF $(\text{BEDT-TTF})_2\text{I}_3$ INTO THE SUPERCONDUCTING α_t -PHASE ($T_c = 8 \text{ K}$)

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ABSTRACT

The tempering of α - $(\text{BEDT-TTF})_2\text{I}_3$ crystals above 70°C for several days leads to the transformation into the superconducting α_t -phase ($T_c = 8 \text{ K}$ at ambient pressure). This process was observed in very small crystals by polarizing microscope techniques in the visible and near infrared spectral range. Premature termination of the tempering yields to crystals containing both phases in the same crystal. This allows direct comparison of the optical properties of the both phases. The orientation of the polarizability tensor and the transmission spectra parallel to the principal axes were measured. The spectra are similar to the spectra of the β -phase. But the indicatrix orientation rather indicates a new phase than the β -phase.

INTRODUCTION

In the family of organic conductors and superconductors the salts of BEDT-TTF* are of considerable interest, especially due to the highest T_c so far observed [1-5]. BEDT-TTF salts with I_3^- as counter anions crystallize in several crystallographic phases. The phase α - $(\text{BEDT-TTF})_2\text{I}_3$ undergoes a metal-insulator phase transition at 135 K and shows no transition to superconductivity even under high pressure [6-7]. The β -phase of $(\text{BEDT-TTF})_2\text{I}_3$ exhibits metallic conductivity down to 1.4 K and then becomes superconducting at ambient pressure [8-10]. After a particular pressure temperature cycling procedure volume superconductivity at ambient pressure and at a $T_c = 8.1 \text{ K}$ was obtained (high T_c -phase of β - $(\text{BEDT-TTF})_2\text{I}_3$ [3]. But this superconducting state is only stable for temperatures below 125 K.

*BEDT-TTF = 4,5-4',5'-bis(ethylenedithio)tetrathiafulvalene

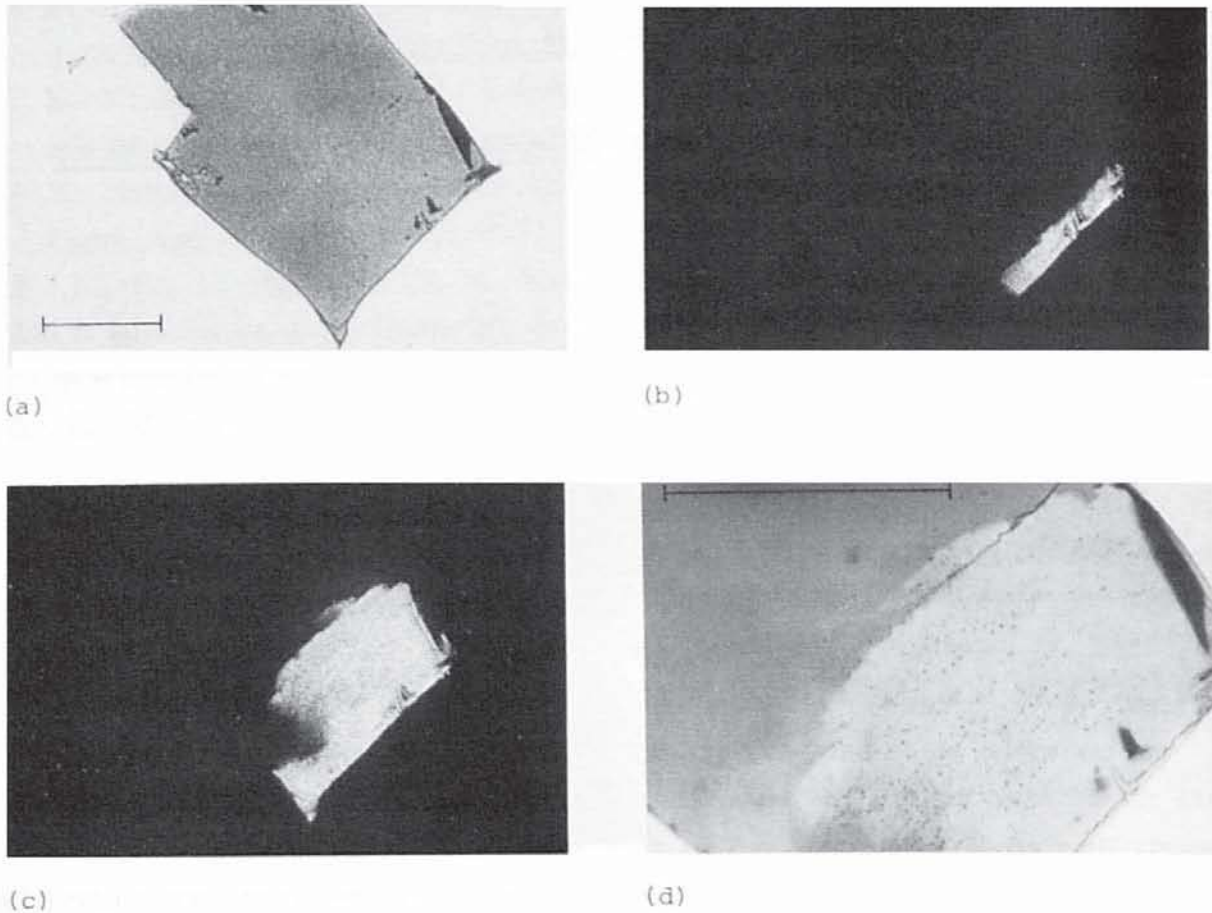


Fig. 1. Temper process in a crystal of α -(BEDT-TTF) $_2$ I $_3$. View perpendicularly to (001), stack direction [100] vertically. (a) before tempering. (b) and (c) after 4 and 6.5 days of tempering, resp., at 79°C. Crystal between crossed polarizers. α -phase in extinction position. The new α_t -phase appears bright. Boundary between α - and α_t -phase $\approx \parallel$ [110]. (d) same crystal, magnified, after terminated transformation (6.5 days). Upper left part remaining α -phase, lower right part grown α_t -phase (horizontal polarizer). - Scales 50 μ m.

Tempering of α -(BEDT-TTF) $_2$ I $_3$ above 70°C for several days yields a new phase the so-called α_t -(BEDT-TTF) $_2$ I $_3$, which is a stable superconductor at ambient pressure ($T_c = 8$ K) [11-12]. The properties of the α_t -phase and the high T_c -phase of β -crystals are found similar comparing the transition temperatures T_c , the temperature dependence of the conductivity, the critical fields H_{c2} etc. [11-12]. This gives reason to suppose that the tempering of the α -phase leads to some kind of the β -phase.

The method described in this paper allows direct comparing of the structural properties of the different phases in the same crystal sample by using polarizing microscope techniques and microspectroscopy.

RESULTS AND DISCUSSION

Tempering

Typical size of the used microcrystals of α -(BEDT-TTF) $_2$ I $_3$ is 0.1 x 0.1 mm and few μ m thick ((001) faced). Fig. 1a shows a crystal before starting the temper process. The stack direction [100] in Fig. 1 is vertical. In this orientation the α -crystal is in extinction position between crossed (vertical and horizontal) polarizers and appears dark (Fig. 1b and 1c) [13]. Tempering was performed by controlled heating (78°C) directly under the polarizing microscope. The transition to the α_t -phase starts after 2 days along the lower right edge (approximately parallel [110] direction) beginning from the right corner. The α_t -phase appears bright. Fig. 1b and 1c show the growth of the α_t -phase into the α -crystal after 4 days and 6.5 days, respectively. Then the transition is interrupted by slow cooling down to room temperature. During this procedure a small crack along the boundary between α - and α_t -phase grew into the crystal indicating the stress in the boundary. Fig. 1d shows the crystal in a magnified view. The boundary is not straight rather cloudy. The reason for this may be an inclined growth of the α_t -phase from the surface (001) varying in depth or the arising of dislocations. The crystal in Fig. 1d contains both phases and allows direct comparison of the two phases.

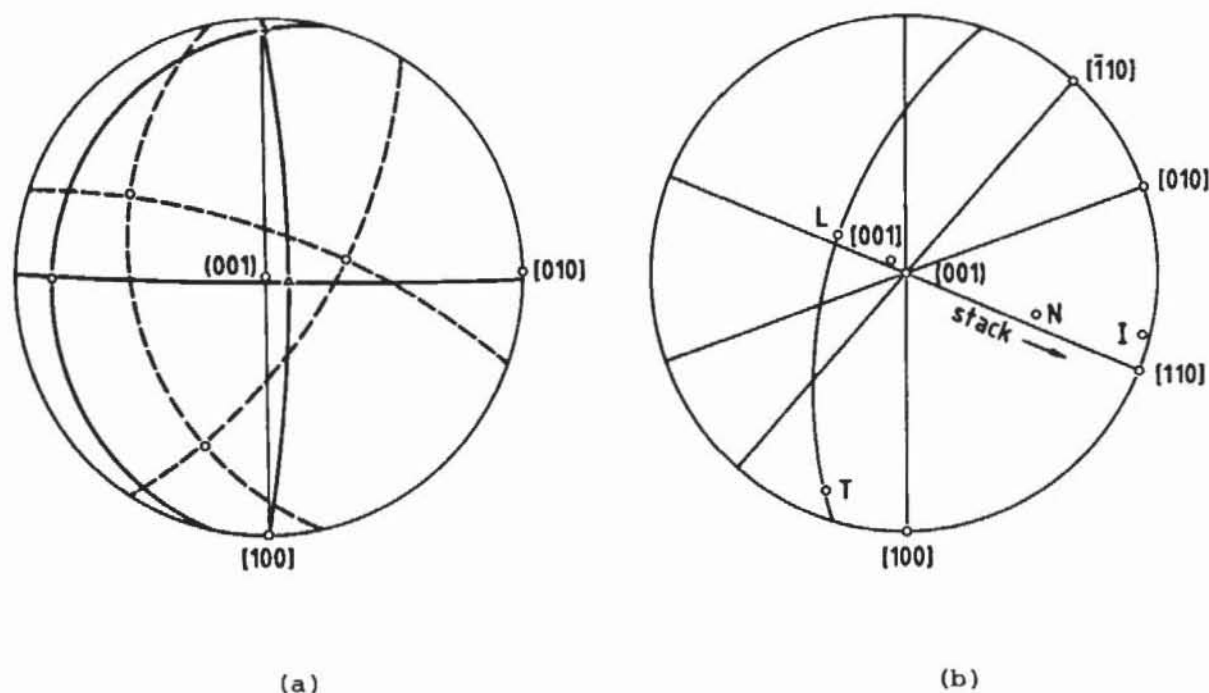


Fig. 2. Stereographic projection (a) related to the plane (001) of α -(BEDT-TTF) $_2$ I $_3$. Measured indicatrix orientation in the α -phase (full line) and in the α_t -phase (broken line). Principal axes X(o), Y(+), Z(Δ). (b) related to the plane (001) of β -(BEDT-TTF) $_2$ I $_3$. L longitudinal, T transversal, N normal molecule axis, I iodine molecule axis.

Indicatrix Orientation

In α -(BEDT-TTF)₂I₃ the BEDT-TTF molecules are arranged in two nonequivalent stacks [14]. Stack directions are [100]. The molecules are in three different positions (A, B, C), but the directions L of the longitudinal axes of all molecules are approximately the same. L stands perpendicularly to the stack L \perp [100] and inclined to the plane (001) by 18.5° [15]. Fig. 2a shows the measured indicatrix orientation of the α -phase. The indicatrix orientation is governed by the direction L and by the stack direction. The principal axis Z approximately parallels L and the principal axis Y coincides with the stack direction [100] [13]. The principal axes of the indicatrix related to the principal refraction indices n_α , n_β , n_γ , are X, Y, Z, respectively ($n_\alpha < n_\beta < n_\gamma$).

Fig. 2a contains also the indicatrix orientation of the α_t -phase measured in the transformed part of the same crystal (Fig. 1). Assuming that the α_t -phase is a kind of β -phases the indicatrix orientation should be compared to the structure of β -(BEDT-TTF)₂I₃ (Fig. 2b). In the β -phase all BEDT-TTF molecules have the same orientation [16-17]. The longitudinal axes L of the molecules are inclined to the stack direction [110] by 56.4° [15]. The transversal molecule axes T are lying approximately in the plane (001) (only $\approx 5^\circ$ out of the plane).

Assuming that the plane (001) remains always the plane of the iodine anions in all phases and that the longitudinal molecule axis L always coincides with the optic direction Z at high energies one way of the transformation is the following (compare Fig. 2a and Fig. 2b). Transforming the β -structure by rotating around \vec{c}^* so that $[\bar{1}00]_\beta$ parallels $[100]_\alpha$ the direction L coincides with the direction Z of the α_t -phase (index α or β indicates referring to the α -phase or β -phase, resp.). But then the transversal axis T does not coincide with the measured direction (Fig. 2). A transformation of this kind (α -phase into this transformed β -phase) needs large movements of the molecules. In a first step the molecules of the α -phase should be rotated around the L axis by 78° (A), 42° (B), 30° (C) and then all L axes should be further inclined by 15°.

On the other hand the transformation from the α -phase into the measured α_t -phase orientation needs a rotation of only 34° (A), 3° (B), 16° (C) around L and then the same inclination by 15°. This leads to the assumption that the α_t -phase is rather a new phase than the β -phase.

Transmission Spectra

Fig. 3 shows the transmission spectra of the α_t -phase measured in the two observable principal directions. Comparing with the spectra of the α -phase [18] points out to the shift of the two main absorption peaks at $1.90 \cdot 10^4 \text{ cm}^{-1}$ ($\parallel Y$) and $2.26 \cdot 10^4 \text{ cm}^{-1}$ ($\parallel X$) to higher energies (Fig. 3). But the α_t -spectra agree with spectra of the β -phase (Fig. 4) [19].

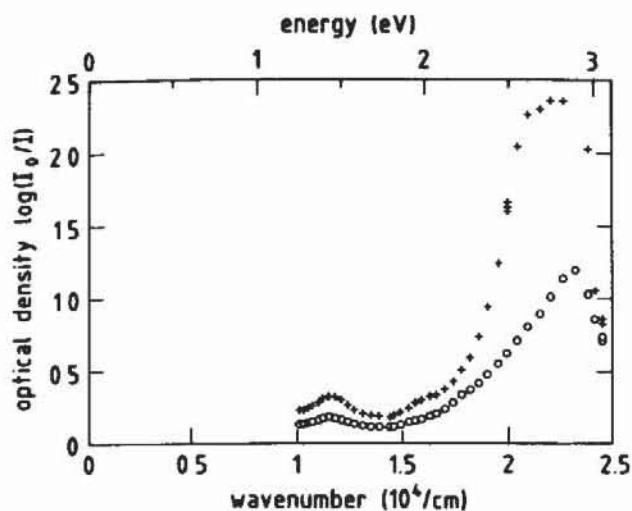


Fig. 3. Absorption of transmitted light polarized along two principal directions in α_t -(BEDT-TTF) $_2$ I $_3$ versus wavenumber.

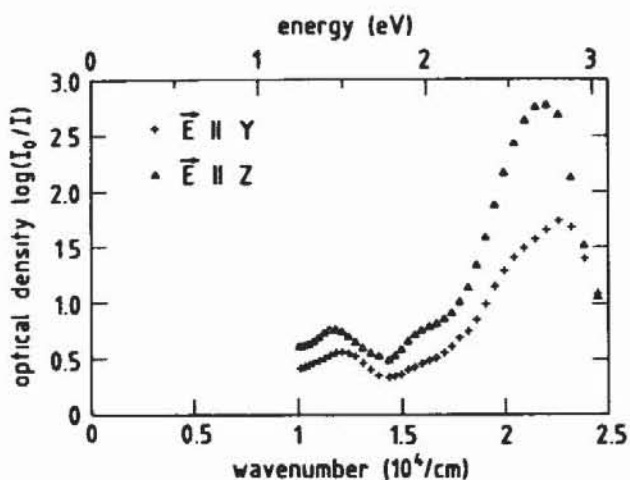


Fig. 4. Absorption of transmitted light polarized along the principal directions Y(+) and Z(Δ) in β -(BEDT-TTF) $_2$ I $_3$ versus wavenumber.

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