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Systematic Study of the $(\text{ET})_2\text{I}_3$ Reticulate Doped Polycarbonate Film: Structure, ESR, Transport Properties and Superconductivity

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Abstract. — The crystalline network structure of conducting $(\text{ET})_2\text{I}_3$ reticulate doped polycarbonate (RDP) films were analysed by X-ray as well as ESR, transport properties and superconducting characteristics of the films were investigated. It was found that under certain conditions of the second step of the RDP-film preparation, an oriented α - $(\text{ET})_2\text{I}_3$ crystalline network is formed. The c -axis of the linked α - $(\text{ET})_2\text{I}_3$ crystallites are perpendicular to the film surface and consequently their conducting layers are parallel to this surface. Moreover, this type of crystalline network orientation is kept during the α - \rightarrow β_t - $(\text{ET})_2\text{I}_3$ transition which takes place under film annealing. Thus, the conducting layers of the linked superconducting β_t - $(\text{ET})_2\text{I}_3$ crystals are also parallel to the film surface. It was demonstrated that superconducting properties are present in all parts of the β_t - $(\text{ET})_2\text{I}_3$ RDP film.

1. Introduction

The reticulate doping technique is a fine method for the production of conducting polymeric composites named Reticulate Doped Polymeric (RDP) films [1]. The method consists in the creation of the organic metallic crystalline network in an inert polymeric matrix [1, 2]. The RDP-composites can be obtained in different modifications yielding either bulk or surface conductors. Two kinds of reticulate doping techniques have been elaborated, one consisting of one step method and the other one has two steps [2–4]. Recently, by a modified two step method [5], we have succeeded in the preparation of the RDP-composites revealing metallic behaviour down to the helium temperatures and moreover an onset of superconducting transition around 7 K. These composites are polycarbonate films with a conducting surface layer due

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to a crystalline network of the well known organic superconductor so called: $\beta^*-(\text{ET})_2\text{I}_3$ [6] or $\alpha_t-(\text{ET})_2\text{I}_3$ [7] with $T_c \sim 7.5$ K, that seems to be the same and analogous to $\beta_{\text{H}}-(\text{ET})_2\text{I}_3$ [8], where ET is bis(ethylenedithio)tetrathiafulvalene. Below, following to [9], we will call this phase as $\beta_t-(\text{ET})_2\text{I}_3$.

The modified two-step method, described in [5,10], should be considered to be in fact a three-step composite preparation. In this modified method, the film with molecularly dispersed ET in the polymeric matrix was obtained at the first step. At the second step the film surface was treated with vapours of the *saturated* iodine solution in CH_2Cl_2 . During this stage the ET molecules were oxidized by iodine in the swollen film surface, resulting in mainly a creation of a conducting $\alpha-(\text{ET})_2\text{I}_3$ crystalline network. At the third step the film was annealed, the $\alpha-(\text{ET})_2\text{I}_3$ phase being converted to the superconducting $\beta_t-(\text{ET})_2\text{I}_3$ phase, like in single crystals [7, 11].

In this paper we present the results of a systematic investigation of the RDP-films with both $\alpha-$ and $\beta_t-(\text{ET})_2\text{I}_3$ crystalline network as well as the $\alpha \rightarrow \beta$ network conversion by means of detailed X-ray analysis, ESR studies and transport properties, including superconducting features of the $\beta_t-(\text{ET})_2\text{I}_3$ RDP-film.

2. Results and discussion

PREPARATION OF SUPERCONDUCTING $\beta_t-(\text{ET})_2\text{I}_3$ RDP-FILM AND X-RAY ANALYSIS. — The first step of the superconducting RDP composite preparation is the creation of the film with molecularly dispersed ET in a polymeric matrix. To perform this, the polycarbonate film (typical thickness was 10-15 mkm) was casted with 2 wt.% of molecularly dispersed ET, as previously described in [5, 9, 10].

As mentioned above, in the second step the film surface was treated with vapours of a *saturated* iodine solution in an organic solvent providing a way to modify strongly the nature of the composite. What could have happened under this treatment? Similar to the film treatment by the *non-saturated* iodine solution, considered in [12], the following events are possible:

- 1) ET oxidation by iodine and formation of the $\alpha-$ and/or $\beta-(\text{ET})_2\text{I}_3$ separated crystals or clusters of them randomly distributed in the film surface, as well as the crystals of the other ET polyiodides; *i.e.* $\varepsilon-(\text{ET})_2\text{I}_7$, $\zeta-(\text{ET})_2\text{I}_{10}$, or $\eta-(\text{ET})\text{I}_3$ [6];
- 2) ET oxidation by I_2 and creation of the conducting $\alpha-$ and/or $\beta-(\text{ET})_2\text{I}_3$ crystalline *networks* as well as the nonconducting crystalline *networks* of the $\varepsilon-$, $\zeta-$, $\eta-$ ET polyiodides;
- 3) crystallization of the unreacted ET crystals and/or formation of the ET crystalline *network*.

In addition, the occurrence of one or more of these three possibilities can lead to homogeneous or inhomogeneous properties of the films.

In order to clarify all these points we have performed a detailed X-ray analysis of the film which revealed the best metallic and superconducting properties. In Figure 1a the X-ray diffractogram of the RDP-film after the second step is shown. The intensive diffraction line at $2\theta = 5.18^\circ$ corresponds to the $\langle 00l \rangle$ reflection of the $\alpha-(\text{ET})_2\text{I}_3$ structure with parameters: $a = 10.785 \text{ \AA}$, $b = 9.172 \text{ \AA}$, $c = 17.39 \text{ \AA}$; $\alpha = 82.08^\circ$, $\beta = 96.92^\circ$, $\gamma = 89.13^\circ$ [13]. All other lines correspond to its higher order reflections. There are no lines related with either the neutral ET or the $\beta-$, $\varepsilon-$, $\zeta-$, $\eta-$ ET polyiodides [14-16]. It means that the proper conditions were found to crystallize mainly the $\alpha-(\text{ET})_2\text{I}_3$ in the viscous film surface. Moreover, the observation of only the $\langle 00l \rangle$ reflections seems to be evidenced that the α -crystals, formed in the film surface, are oriented. The c -axis of the $\alpha-(\text{ET})_2\text{I}_3$ crystals was found to be perpendicular to the film surface and consequently their conducting layers are parallel to this surface.

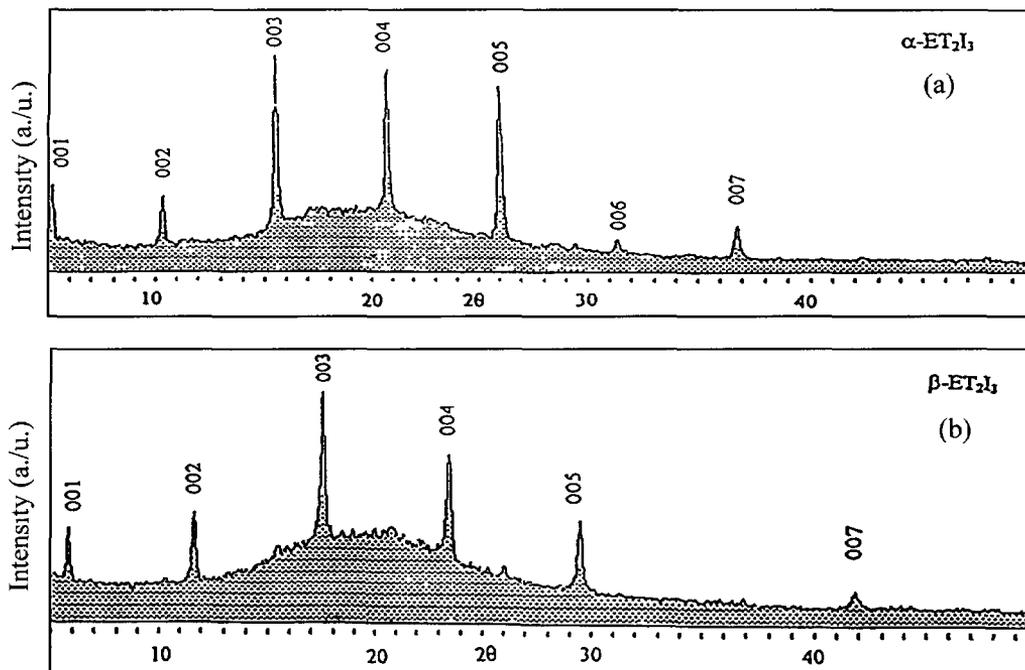


Fig. 1. — X-ray diffractograms of the conducting oriented α - and β_t - $(\text{ET})_2\text{I}_3$ crystalline networks in the RDP film after the 2nd (a) and the 3rd (b) step, respectively.

The formation of the single crystals of the other ET polyiodides and/or unreacted ET crystals can not be ruled out, but the amount of them in the considered case is likely not sufficient for X-ray detection. We would like to note that for the films treated in *non-saturated* iodine solution the X-ray diffraction clearly shows neutral ET [12].

In the third step, the film was annealed at 150 °C during 24 hours. All reflections belonging to the α - $(\text{ET})_2\text{I}_3$ -phase disappeared in the X-ray diffractogram for the annealed film. Instead of them a new strong line at $2\theta = 5.84$ and its higher order reflections appeared in the diffractogram (Fig. 1b). They correspond to $\langle 00l \rangle$ reflections of the β - $(\text{ET})_2\text{I}_3$ -phase [17]. This $\langle 00l \rangle$ reflection family suggests that the conducting layers of β_t - $(\text{ET})_2\text{I}_3$ crystals (*ab* plane) are parallel to the film surface as well.

3. ESR Characterization

Since the ESR linewidth of the α - $(\text{ET})_2\text{I}_3$ phase is much larger than that corresponding to the β^* - $(\text{ET})_2\text{I}_3$ or α_t - $(\text{ET})_2\text{I}_3$ [18, 19], ESR spectroscopy is a suitable technique to investigate the composition of the films after the second and third steps of the preparation as well as to follow the evolution of the film annealing. In addition, the anisotropy of the linewidth and *g* factor provide a powerful tool to study the crystallite orientations in the film.

In Figure 2 the evolution of the ESR signal with temperature for the film obtained after the second step is presented together with that of the α - $(\text{ET})_2\text{I}_3$ single crystal. From the signal at 300 K it is clearly seen that the film obtained after the second step contains some proportion of the β - $(\text{ET})_2\text{I}_3$ phase. The quantitative analysis of this signal, taking into account the ESR

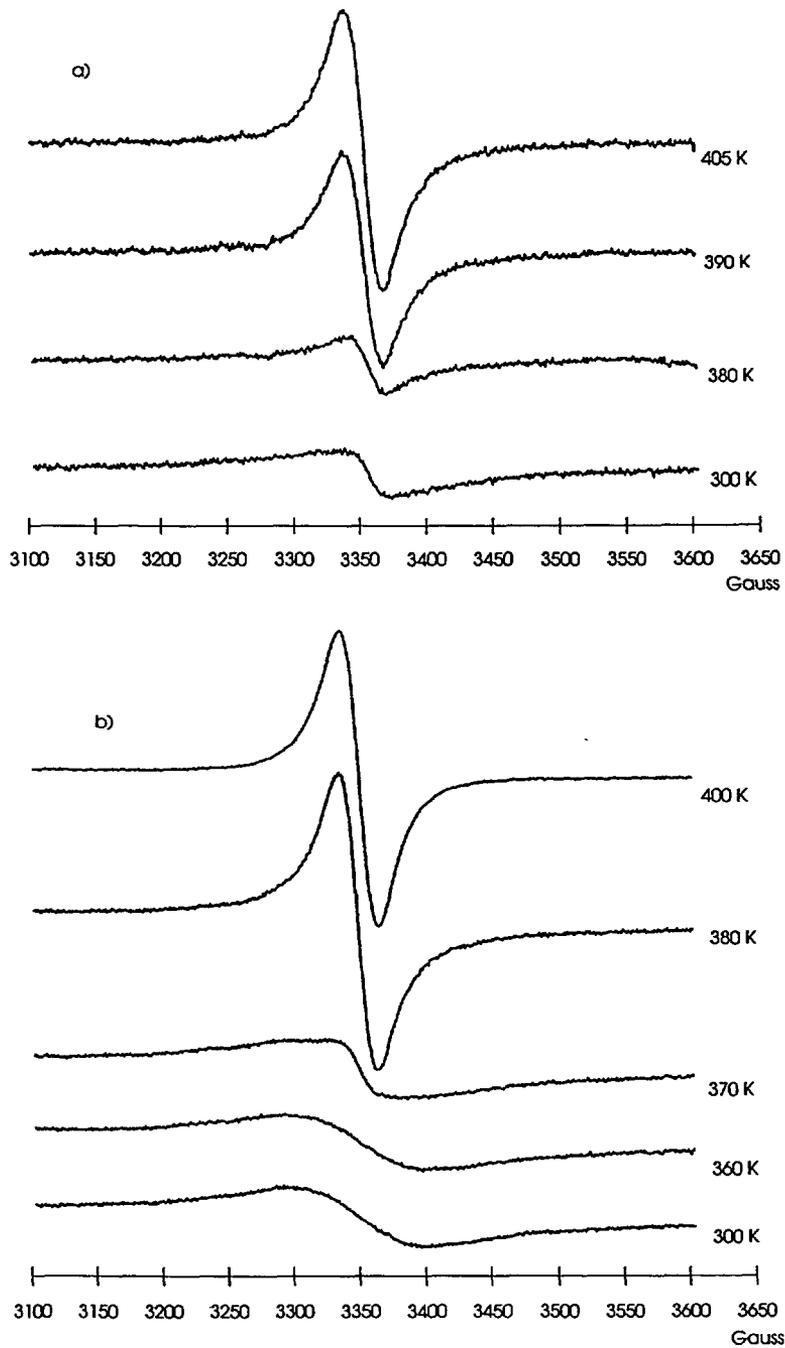


Fig. 2. — ESR signals at different temperatures for the $(\text{ET})_2\text{I}_3$ RDP film (a) and $(\text{ET})_2\text{I}_3$ single crystal (b) evidencing the $\alpha \rightarrow \beta_t$ conversion.

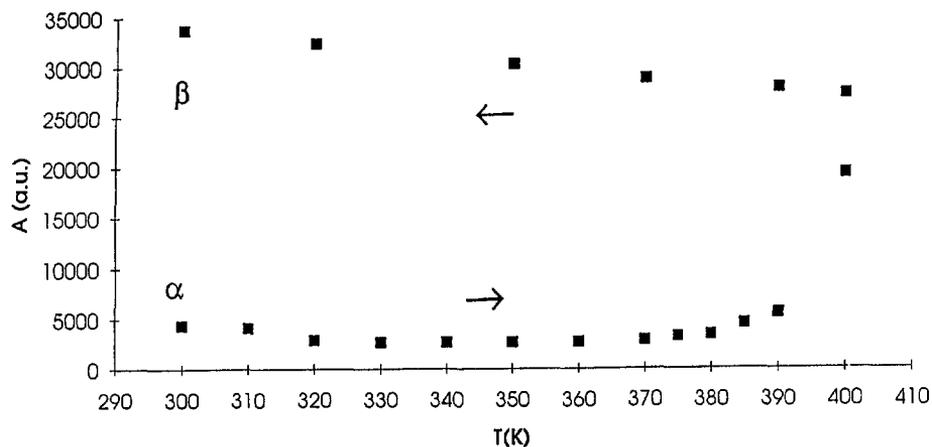


Fig. 3. — Temperature dependence of the ESR signal amplitude for the $(\text{ET})_2\text{I}_3$ RDP film after the second step of preparation (see text).

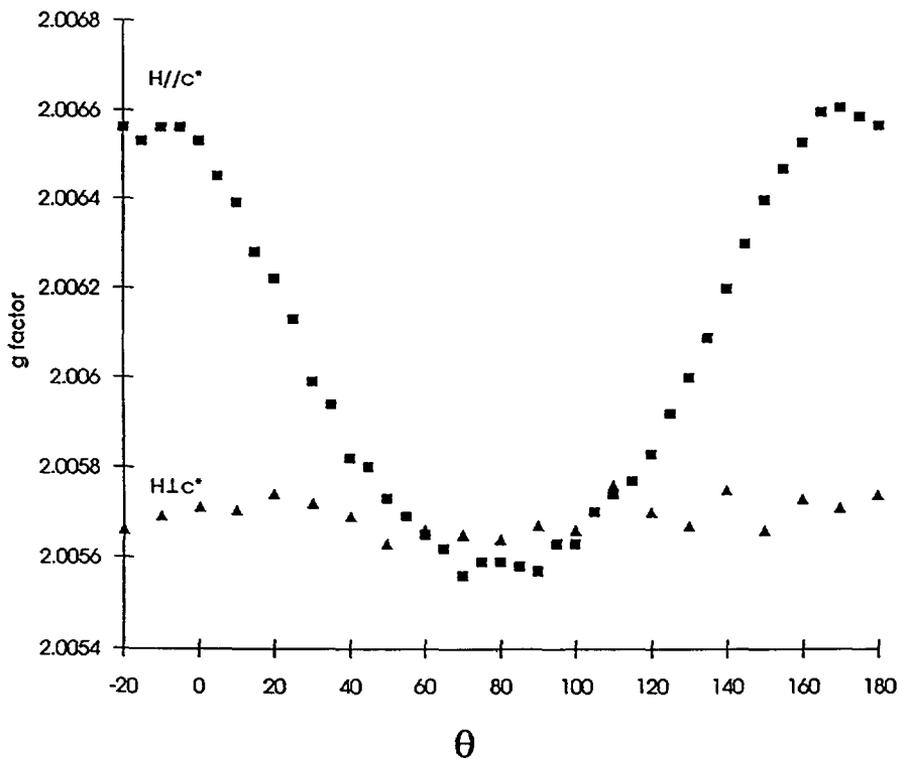


Fig. 4. — Angle dependence of the g factor for the β_t - $(\text{ET})_2\text{I}_3$ RDP film. (■) θ is the angle between the c axis and the external magnetic field; (▲) rotation around c axis.

and χ_s characteristics of both phases [18], is consistent with a small (5-6%) proportion of the β -phase which is in agreement with the X-ray results that show a majority α -phase composition. Temperature dependence of the ESR line amplitude of the film oriented perpendicular to the static magnetic field is shown in Figure 3. The thermal behaviour is almost constant from room temperature up to 390 K where an abrupt change is observed. This result indicates that a phase transition of the crystallites from the α - $(\text{ET})_2\text{I}_3$ to the β_t - $(\text{ET})_2\text{I}_3$ takes place at this temperature which is very close to that used in the third step of the RDP film preparation. On the basis of ESR line shape analysis [18, 19] we can conclude that the film reaches almost 100% conversion to the β_t - $(\text{ET})_2\text{I}_3$ when it is annealed at 390-400 K; the result that is in accordance with the X-ray data.

In order to verify the orientation of the β_t - $(\text{ET})_2\text{I}_3$ crystallites in the film, ESR of the RDP annealed film in different orientations with respect to the static magnetic field were also performed. The g factor variation is plotted in Figure 4. The g value is maximum when the magnetic field is perpendicular to the film plane and minimum when it is parallel. This minimum g value does not change upon rotation in the film plane. Since the maximum g value for the single crystal [19] is found when the static magnetic field is parallel to the c crystallographic axis, the above results allow us to conclude that the β_t - $(\text{ET})_2\text{I}_3$ crystallites are oriented with the c axis perpendicular to the film plane. This result is in good agreement with the X-ray analysis. In addition the isotropic behaviour found upon rotation around the c axis indicates that there is not a predominant in-plane orientation.

3.1. TRANSPORT PROPERTIES AND SUPERCONDUCTIVITY. — In order to study transport properties, the rectangular pieces ($\approx 1.5 \times 0.5 \text{ mm}^2$) were cut out from different parts of the film after the 2nd and 3th stage of preparation and a temperature dependence of the resistance

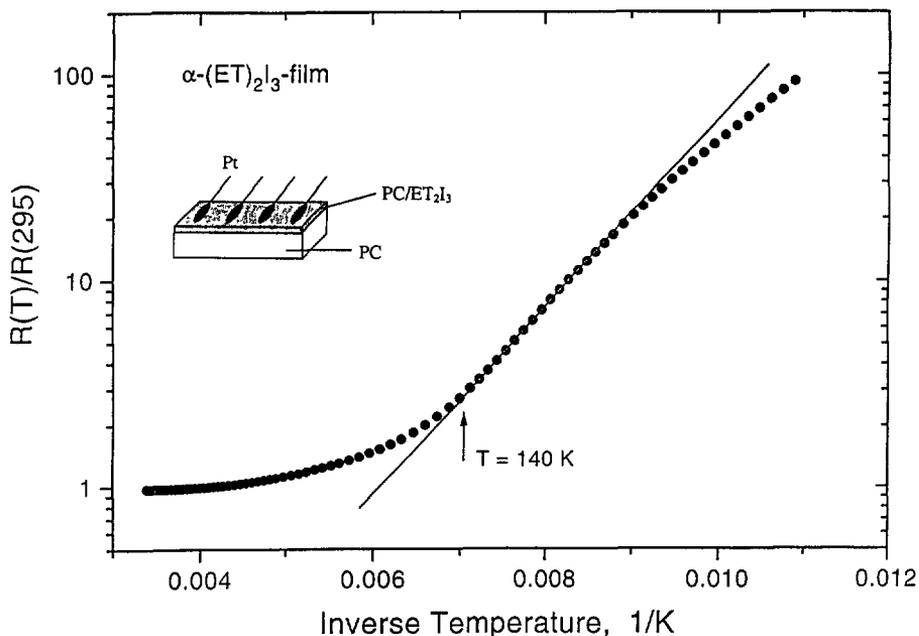


Fig. 5. — Normalized resistance of the conducting surface layer of the α - $(\text{ET})_2\text{I}_3$ RDP film versus inverse temperature (the second step of preparation). Inset shows a geometry of the electrical contacts to the film sample.

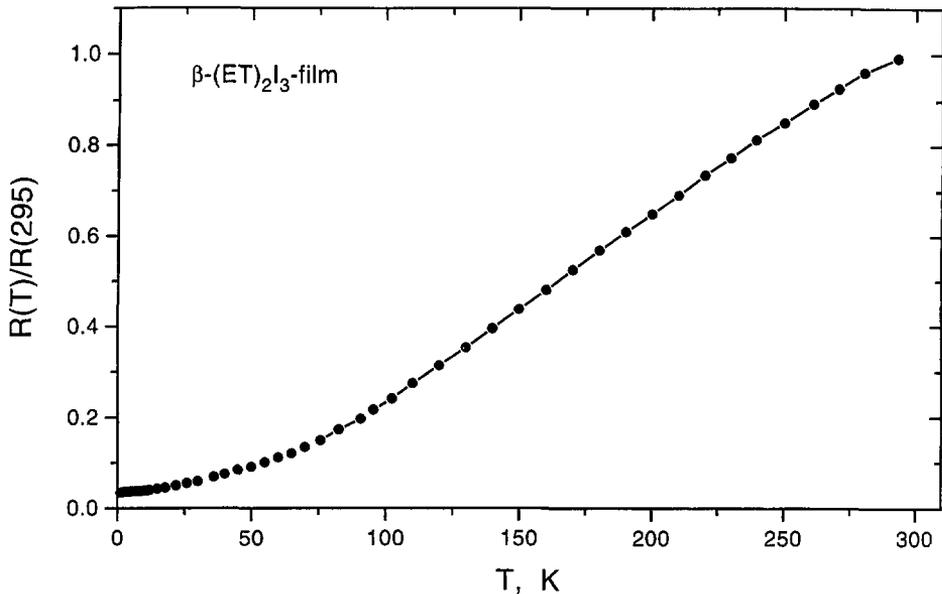


Fig. 6. — Temperature dependence of the normalized resistance for the conducting surface layer of the $\beta_t-(\text{ET})_2\text{I}_3$ RDP film (the third step of preparation).

was measured down to 1.5 K using the standard 4-probe dc method. Four annealed platinum wires (20 mkm in diameter) were contacted to the conducting surface of the film by means of a conductive graphite paste (see inset in Fig. 5). Unfortunately, the surface conductivity of our films cannot be directly calculated, since the real thickness of the conducting surface layer is still unknown. According some estimations performed in [12], the thickness of such a layer would be about 140 nm. Assuming a thickness of 140 nm for our conducting films, the calculated conductivity at room temperature is about 30 S cm^{-1} after the 2nd stage of preparation (the film containing mainly $\alpha-(\text{ET})_2\text{I}_3$ crystals) and around 10 S cm^{-1} after the 3th stage (the final $\beta_t-(\text{ET})_2\text{I}_3$ RDP film), that is very close to conductivity of the $\alpha-$ and $\beta_t-(\text{ET})_2\text{I}_3$ single crystals in the ab conducting plane [6, 7].

Temperature dependence of the normalized resistance of the conducting composite formed after the second step is presented in Figure 5. In the high temperature region, as the temperature decreases the resistivity decreases down to $\sim 280 \text{ K}$, and then it increases slowly. Below 145 K the resistivity increase becomes much stronger and can be interpreted as being associated with the well known metal-insulator (M-I) phase transition of the $\alpha-(\text{ET})_2\text{I}_3$ single crystals [20]. The non well pronounced metallic behaviour observed at high temperatures as well as the very broad phase transition revealed for this film, in contrast to the $\alpha-(\text{ET})_2\text{I}_3$ single crystals, seems to be resulted from both stress and defects in the conducting surface layer as well as intergrain barriers in it (see the SEM microphotograph in [9], Fig. 1a). In addition, the formation of minor amounts of crystallites of other ET polyiodides and/or unreacted ET could also partially disturb the metallic character of the conductivity and widen the M-I phase transition.

As it was shown previously [2, 21], the conductivity of the RDP composites results from the electrical properties of the crystalline network. It means that X-ray reflections as well as the ESR signal (see above) can be related to the conducting $\alpha-$ and $\beta_t-(\text{ET})_2\text{I}_3$ crystalline

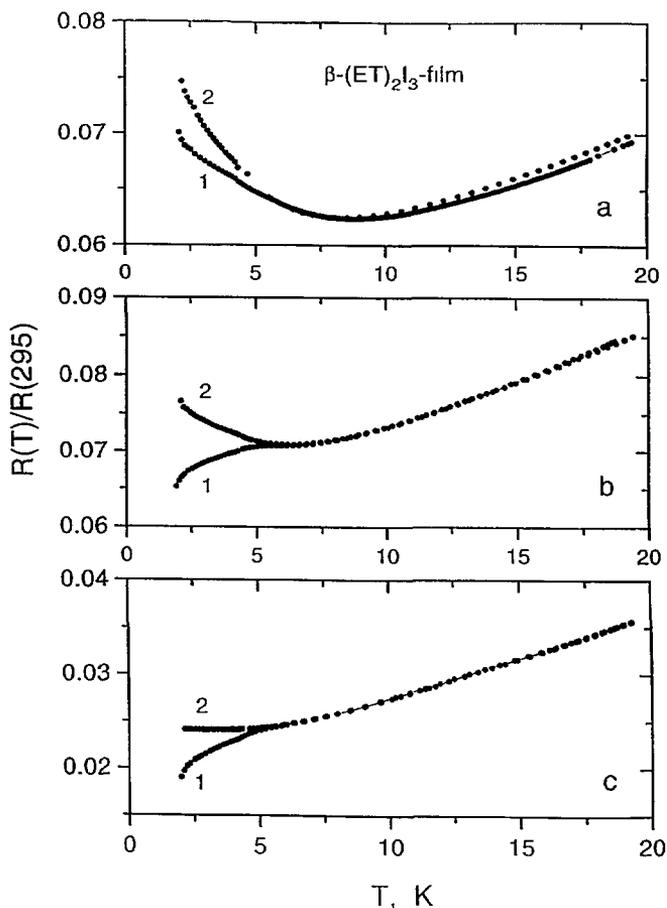


Fig. 7. — Typical low temperature behaviours of the resistance for different pieces of the $\beta_t-(\text{ET})_2\text{I}_3$ RDP film. (1) $B = 0$, (2) $B = 3.2$ T.

networks, which are formed during the second and third step of the RDP-film preparation, respectively.

After the third step (film annealing at 150 °C during 24 hours), the film resistivity reveals a metallic temperature dependence down to helium temperatures (Fig. 6), like in the other cases for $\beta_t-(\text{ET})_2\text{I}_3$ [5, 9, 22]. But in all these previous examples there were not evidences for a very important point: whether the obtained $\beta_t-(\text{ET})_2\text{I}_3$ RDP films are homogeneous enough in respect to *their superconducting properties*. In order to clarify this question, the plate-like film samples were cut out from different parts of the intact circle-like annealed film \varnothing 30 mm) and the temperature dependence of their resistance was measured down to ~ 1.5 K. In order to identify superconducting features, the influence of the magnetic field (3.2 T) on the low temperature resistance behaviour of the samples was investigated too.

The most typical behaviours of the low temperature normalized resistance for sample cut out from different parts of the annealed film are shown in Figure 7. The overall decrease of the resistance R_{300}/R_7 was found to be 15-45 for the different film samples. This fact can be considered to indicate some inhomogeneity of the obtained RDP films, even if all of

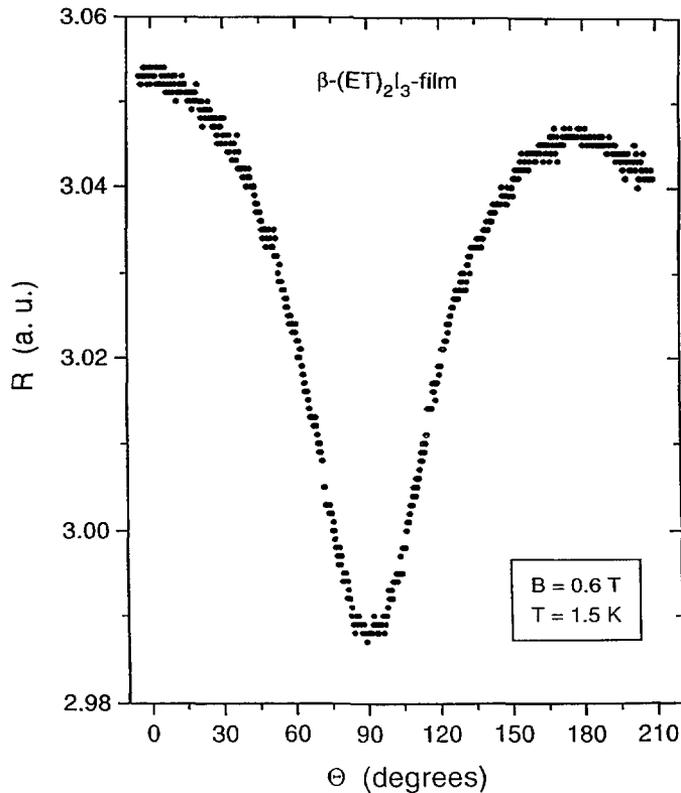


Fig. 8. — Angle dependence of the resistance for one of the pieces of the superconducting $\beta_t-(\text{ET})_2\text{I}_3$ RDP film in the magnetic field $B = 0.6$ T at $T = 1.5$ K. θ is the angle between the direction perpendicular to the film surface and the magnetic field.

them are characterized by a metallic behaviour. Low value of a residual resistance ratio (RRR) amounting to ≈ 15 can be related with high content of impurities and defects in the conducting surface layer of the film. When RRR increases, indicating on a higher quality of samples, small increase of the resistance below 6-8 K disappeared and an onset of the superconducting transition became more pronounced. It should be noted that in all parts of the $\beta_t-(\text{ET})_2\text{I}_3$ RDP film, obtained under the conditions mentioned above, we observed an appearance of superconducting phase below 5-6 K, which can be suppressed by magnetic field (Fig. 7). On the one hand, this temperature is close to the T_c (7-8 K) for the $\beta_t-(\text{ET})_2\text{I}_3$ crystals [6]. On the other hand, the superconducting transition is evidently incomplete even down to 2 K (Figs. 7b, c) and seems to be very broad. The last feature as well as some insignificant increase of the resistance below 6-8 K (Fig. 7a) can be considered to result from the polycrystalline structure of conducting network and intergrain barriers (see the SEM microphotograph, Fig. 1b, in [9]). In additional the formation of the neutral ET crystals (see above) can partially disturb and widen the superconducting transition.

According to the X-ray and ESR measurements as well as the SEM pictures [9, 23], the c -axis of the linked $\beta_t-(\text{ET})_2\text{I}_3$ crystals in the crystalline network was found to be perpendicular to the film surface and consequently their conducting layers are parallel to that. It should result in an anisotropy of the critical magnetic fields (*e.g.* H_{C2}) for the superconducting $\beta_t-(\text{ET})_2\text{I}_3$

surface layer in the RDP film, like in the case of the β^* -(ET)₂I₃ single crystals [24]. Figure 8 shows the angle dependence of the resistance for one of the pieces of the β_t -(ET)₂I₃ RDP film in the magnetic field $B = 0.6$ T, which is higher than H_{C2} directed perpendicular to the ab -conducting plane ($B \parallel c$), but smaller than H_{C2} for the direction parallel to the ab -plane at $T = 1.5$ K. Taking into account that the magnetoresistance of the film mainly results from a suppression of superconductivity, since there is no magnetoresistance above $T = 5-6$ K (see Fig. 7), we can suggest the angle dependence of the magnetoresistance in Figure 8 exhibits the anisotropy of the H_{C2} for the superconducting β_t -(ET)₂I₃ surface layer in the RDP film. Thus, Figure 8 provides us an additional evidence that the linked crystals which create the superconducting network are oriented so that their conducting planes are dominantly parallel to the film surface in agreement with the X-ray and ESR data.

4. Summary

- 1) X-ray data showed that the conductive (ET)₂I₃ crystalline networks are formed on the surface of the obtained RDP film, the conducting ab -plane of the network microcrystals of both α -(ET)₂I₃ and β_t -(ET)₂I₃ phases being dominantly parallel to the RDP film surface.
- 2) ESR spectra revealed quantitatively that the phase transition from α -(ET)₂I₃ to β_t -(ET)₂I₃ phase in the RDP film takes place in a narrow (390-400 K) temperature range. ESR studies showed that while the crystallites are preferentially oriented with the crystallographic c axis perpendicular to the film plane there is not a predominant in-plane orientation.
- 3) In the RDP film, obtained under certain conditions described above, the β_t -(ET)₂I₃ phase, showing the onset of the superconducting transition around 5-6 K, appeared in any parts of the film.

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