

ELECTRICAL AND OPTICAL PROPERTIES OF α -(PEDTTTF) $_2$ BF $_4$ AND
 α -(PEDTTTF) $_2$ IBr $_2$

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Conductivity measurements and polarized reflectance spectra,
carried out in single crystals of the compounds α -(PEDTTTF) $_2$ BF $_4$
and α -(PEDTTTF) $_2$ IBr $_2$ (where PEDTTTF=Pyrazino-ethylenedithio-²
tetrathiafulvalene), showed metallic behaviour.

Introduction

Cation radical salts of the type (PEDTTTF) $_2$ X [where BEDTTTF=bis
(ethylenedithio)tetrathiafulvalene and X=I $_3$, IBr $_2$, BF $_4$, ClO $_4$ etc] have
recently attracted many investigators since they exhibit a number
of interesting physical properties (see for example [1]). In this
paper we report preliminary results on the electrical and optical
properties of the salts α -(PEDTTTF) $_2$ BF $_4$ (I) and α -(PEDTTTF) $_2$ IBr $_2$ (II)
(where PEDTTTF=pyrazinoethylenedithiotetrathiafulvalene, namely a
modification of BEDTTTF molecule) [2,3].

Preparation and crystal structure data

The crystals were prepared by electrocrystallization of the
donor (PEDTTTF) in presence of Bu $_4$ NX (X=BF $_4$, IBr $_2$) in CH $_2$ Cl $_2$ [4].

Compound (I) crystallizes in the monoclinic system, space group C2/2, with $a=34.655$, $b=12.122$, $c=14.213 \text{ \AA}$, $\beta=97.13^\circ$, $V=5925 \text{ \AA}^3$, $Z=8$, $d=1.748 \text{ g/cm}^3$, $R=0.105$. Cations in (I) pack side by side, in a planar arrangement, through S---S and S---N contacts the shortest of which are 3.471 and 3.384 \AA , respectively. There is also a partial stacking along the c-axis [4,5].

Compound (II) crystallizes in the triclinic system, space group $P\bar{1}$, with $a=8.847$, $b=5.671$, $c=15.818 \text{ \AA}$, $\alpha=98.44$, $\beta=89.66$, $\gamma=107.13^\circ$, $V=749.6 \text{ \AA}^3$, $Z=1$, $d=2.17 \text{ g/cm}^3$, $R=0.031$. Cations in (II) pack side by side, in a planar arrangement, through S---S and S---N contacts the shortest of which are 3.427 and 3.331 \AA , respectively. Also, there is a partial stacking along the a-axis and intrastack contacts the shortest being S---S= 3.748 \AA [4,6].

Fig.1 shows the morphology of single crystals of (I) and (II). Z-axis is almost parallel to the stacking direction.



Fig.1 Morphology of single crystals of (I) and (II).

Results and discussion

Fig.2 shows the variation of dc-conductivity (σ) with the T and $1/T$ for single crystals of (I) and (II) in the Z-axis direction, while Fig.3 shows the room temperature polarized reflectance spectra on 100 and 001 faces of single crystals of (I) (II), respectively.

Compound (I) exhibited a dc-conductivity ca $13-21 \Omega^{-1} \text{ cm}^{-1}$ at room temperature. Fig.1a shows that there is a metallic region to ca 180 K in which the conductivity is almost temperature independent but below this temperature, the compound undergoes a metal to insulator transition. The behaviour in the semiconductor region however, does not give a linear dependence of $\ln \sigma$ upon $1/T$, and therefore no activation energy can be determined in the low temperature region. The reflectance spectra (Fig.3a) show a metallic behaviour in both directions, namely parallel and perpendicular to the Z-axis, at room temperature.

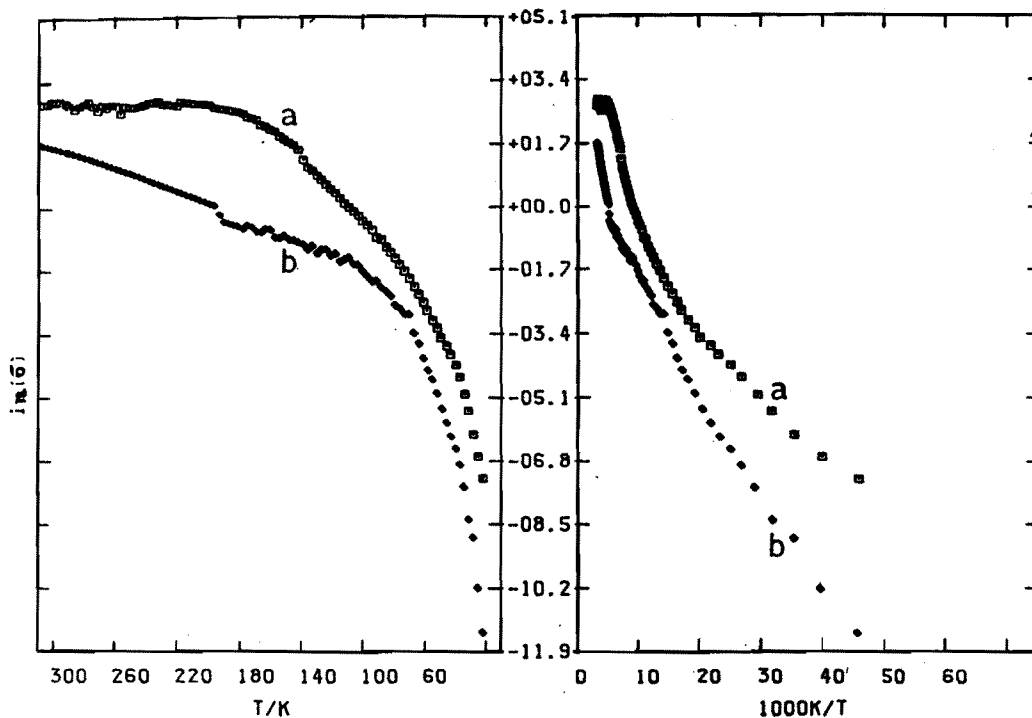


Fig.2. Variation of the conductivity (σ) with the T and $1/T$ for single crystals of (I) (a) and (II) (b) in the Z-axis direction.

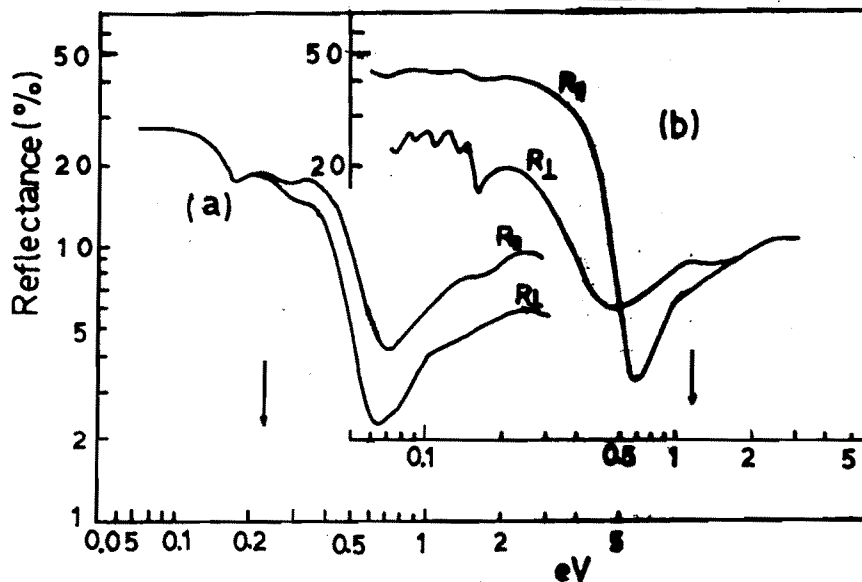


Fig.3. Reflectance spectra of (I) (a) and (II) (b) with polarization parallel (\parallel) and perpendicular (\perp) to the Z-axis.

Compound (II) exhibited a dc-conductivity ca $2-5 \Omega^{-1} \text{cm}^{-1}$ at room temperature. Fig.2b shows that for the temperature region 290-200 K the compound behaves as a semiconductor with an activation energy of ca 100meV. At approximately 200K there is a step in the conductivity versus temperature curve and subsequently down

to 100K, the conductivity is more or less temperature independent ("metallic"). Between 100 and 50K there is a second transition (metal-insulator) and subsequently the compound behaves as a semiconductor with an activation energy of ca 20meV (namely much smaller than that at room temperature). Preliminary conductivity measurements carried out with the Montgomery method showed that the behaviour in the Z-axis direction is very unusual: the semiconducting behaviour observed down to just below 200K is changed to a behaviour in which the conductivity rises with decreasing temperature (i.e. metallic). The reflectance spectra (Fig.3b) show a metallic behaviour in the Z-axis direction at room temperature.

It is concluded that the crystals show metallic behaviour at least in one direction. However, more accurate measurements are required in the directions of the crystallographic axes.

References

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