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STRUCTURAL AND PHYSICAL PROPERTIES OF τ-(EDO-*S,S*-DMEDT-TTF)$_2$ $(AuBr_2)_1(AuBr_2)_y$

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Abstract The crystal structure and physical properties of τ-(EDO-*S,S*-DMEDT-TTF)$_2$ $(AuBr_2)_1(AuBr_2)_y$ (where EDO-*S,S*-DMEDT-TTF is ethylenedioxy-*S,S*-dimethylethylenedithiotetrathiafulvalene and $y \approx 0.75$) showed that this is a two-dimensional metal.

INTRODUCTION

During the last fifteen years a large number of cation radical salts based on symmetrical or unsymmetrical tetrachalcogenafulvalenes have been prepared and studied[1,2]. Among them, the salts which are crystallized in the α-, β-, θ-, λ- and κ-phases were found to be the most important due to their unique relations between structural and physical properties. In all these phases, the cations (organic) and anions or polyanions (inorganic) form separate layers and the degree of ionicity usually is ρ=0.5. Some of these salts with linear or nonlinear anions were found to be superconductors at low temperatures[1-3]. In 1990, it was discovered that some salts with linear anions, based on unsymmetrical tetrachalcogenafulvalenes with an ethylenedioxy-group as an additional group to the tetrachalcogenafulvalene-core, are crystallized in the tetragonal system, i.e. in the so-called τ-phase[4-7]. In this phase mixed cation (organic)-anion (inorganic) layers alternate with anion (inorganic) layers and the resulting crystals are metallic in directions parallel to the layers (i.e., in-ab-plane) and semiconducting in the direction (c-axis) perpendicular to these layers (i.e., out-of-plane)[4,7]. In other words, these salts are two-dimensional (2D) metals.

Recently, it has been found that some salts based on pyrazino-*S,S*-dimethylethylenedithio-tetrathiafulvalene (hereafter abbreviated as P-*S,S*-DMEDT-TTF)[7-9] as well as salts based on ethylenedioxy-*S,S*-dimethylethylenedithio-tetrathiafulvalene (abbreviated as EDO-*S,S*-DMEDT-TTF)[7] in combination with linear anions (i.e. $AuBr_2$, I_3, IBr_2 etc) are crystallized in the τ-phase. In this paper the structural and some physical properties of τ-(EDO-*S,S*-DMEDT-TTF)$_2$ $(AuBr_2)_1(AuBr_2)_y$ (with $y \approx 0.75$) are reported.

EXPERIMENTAL

The π-donor EDO-*S,S*-DMEDT-TTF was prepared by cross-coupling reaction[1,10] of 4,5-ethylenedioxy-1,3-dithiole-2-one[11] and 4,5-*S,S*-dimethylethylenedithio-1,3-dithiole-2-one[12], via triethyl phosphite, followed by separation of the desired compound from the self-coupling by-products using liquid chromatography on a silica gel column with CS_2 as eluent. Crystals of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_y$ were obtained by electrooxidation of the donor in CH_2Cl_2 in presence of Bu_4NAuBr_2 with a constant current of 0.2 μA. They are black-greenish plates; from elemental analysis it was found C=21.07, H=1.66, S=27.20 Br=20.00, Au=25.3 %, while the corresponding calculated values are 20.79 1.73, 27.73, 20.22 and 24.89% for y=0.75. It has been observed that the solution around the anode became green as in the cases of similar salts based on other donors[13]. The density of single crystals was measured by floatation technique using 1,1,2,2-tetrabromoethane and 1,2-dibromoethane. Crystal structure determination was performed on a $P2_1$ Nicolet difractometer using MoKα radiation, by refining the angular setting of 25 automatically centered reflections in the range $11^o<2\theta<23^o$. One octant of data (h,k,l) were collected, Lorentz polarization and psi-scan absorption were applied. Final R=0.0499 for 1280 observed reflections ($F_o>4\sigma(F_o)$), 119 parameters were refined. The electronic band structure and Fermi surface (of a single layer) have been calculated by using extended Hückel tight binding method[6]. dc-Conductivity measurements on single crystals were done by a four probe technique. ESR spectra were recorded on a Bruker ER100 spectrophotometer. Reflectance spectra on a pressed pellet and optical absorption spectra were recorded on aVarian model 2390 spectrophotometer and a Bruker 1FS113v spectrophotometer.

RESULTS AND DISCUSSION

The salt is crystallized in the tetragonal system (τ-phase), space group $I4_122$ with a=7.4048 [4], c=67.995 [4] Å, and V=3728.23 [3] Å^3. Fig.1 shows the structure of the donor molecule (EDO-*S,S*-DMEDT-TTF) the molecular organization of a (conducting) layer of the salt seen along the largest molecular axis and a stereoview of the crystal structure. The final positional parameters are summarized in Table 1. The crystallographic results are similar to those obtained for the corresponding pyrazino-containing salts,[7,9] i.e. mixed organic-inorganic layers alternate with inorganic layers. Each unit cell contains eight donor molecules, four well-behaved $AuBr_2$ plus four disordered $(AuBr_2)_y$, which are "smeared" all along the b-axis at a=0 and c=0.125, as the disordered anions of other τ-phases.[4-9] Because of this disorder, we cannot have much confidence on the occupancy factors for the corresponding Au- and Br-atoms. The calculated value of density is 2.46 g/cm^3, for y=0.75, while the determinated value by flotation value is 2.51 g/cm^3. In contrast to the pyrazino-analogue[9], where the dimethylethylenedithio-group was disordered, in the present structure this group is ordered but the ethylenedioxy-group is disordered. There are S(1)---S(2)=3.517-3.599 Å and S(2)---O=3.36-3.37 Å intermolecular contacts which are smaller than or close to the sum of the corresponding van der Waals radii (3.70 and 3.25 Å, respectively).

Fig.2 shows the calculated electronic band structure and Fermi surface of a single organic layer of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$. The overall interactions between organic molecules are isotropic in the ab-plane and the ratio of the inte-

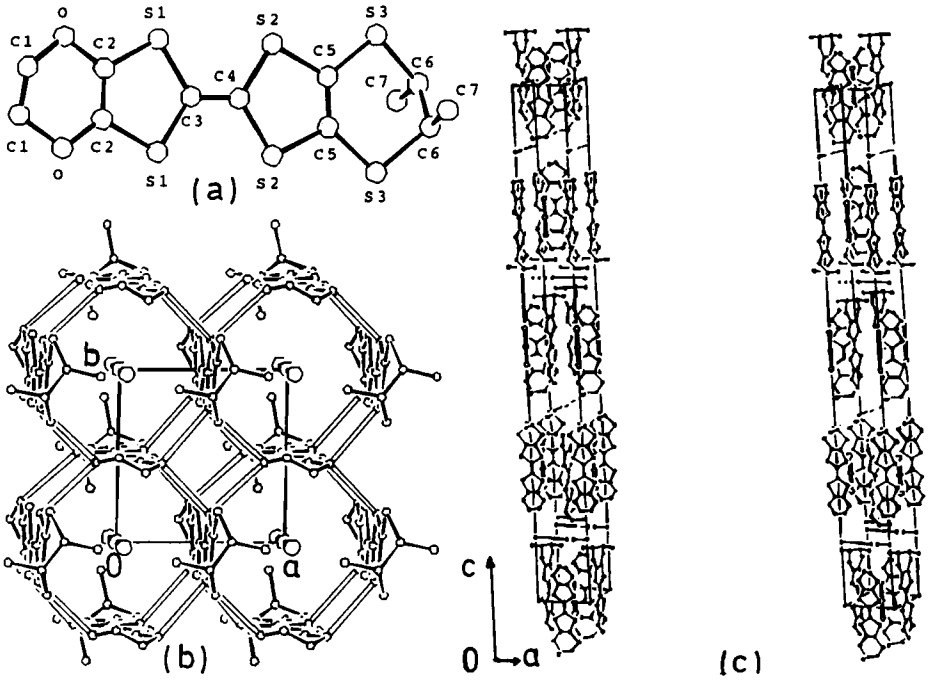

Fig.1. Molecular structure of EDO-*S,S*-DMEDTTTF (double bonds $C_2 = C_2$, $C_3 = C_4$ and $C_5 = C_5$) (a), molecular organization of a conducting layer in τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$ seen along the largest molecular axis (thin lines indicate the S(1)---S(2) and S(2)---O intermolecular contacts) (b) and stereoview of crystal structure of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$ (c).

ractions between perpendicular molecules to the interactions between parallel ones is around 10. Thus, the resulting band structure shows large and almost zero dispersions along different directions of the reciprocal space. There is an almost zero gap in the vicinity of the Γ point. These results as well as Fermi surfaces calculated for y=1, y=0.75 and y=0 are identical to those of τ-(P-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$[9]. They are similar to those of τ-(EDOVDT-TTF)$_2$(I$_3$)(I$_3$)$_y$[6] except for the degeneracy at the Γ point which is a consequence of the different space groups. The degree of ionicity (for y=0.75) is ρ=0.875. These results predict that the salt is a 2D metal.

Fig.3 shows the temperature dependence of the in-plane dc-resistivity for two crystals of τ-(EDO-*S*-*S*-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_{0.75}$. One can see that the crystals are metallic over a large temperature range and become semiconducting at lower temperatures (T<25 K). The room temperature in-plane dc-conductivity is $\sigma_{||}$(RT)=140-200 S/cm. Fig.4 shows the temperature dependence of the out-of-plane dc-resistivity for two crystals. In contrast to τ-(P-*S*, *S*-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_{0.75}$ and τ-(EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$ which show semiconductor behaviour[1,6,7,9] in the out-of- plane direction, in the present case the crystals show a weak metallic behaviour. The room temperature out-of-plane dc-conductivity is $\sigma_{\perp}$(RT)=3.6-6.5 x 10^{-3} S/cm. Thus, the room temperature anisotropy in the conductivity is extremely large (i.e., $\sigma_{||}$(RT)/$\sigma_{\perp}$(RT)=3-4x10^4). The in-plane Hall

Table I.Atomic coordinates (10^4) and equivalent isotropic displacement parameters (10^3) with standard deviations in square brackets. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au	0	5000	7500	65[1]
Br	0	5000	7852	75[1]
S(1)	1976[2]	-15[7]	7624[1]	40[1]
S(2)	-1963[2]	-42[7]	7149[1]	39[1]
S(3)	-2409[2]	-40[7]	6719[1]	48[1]
O	1952[6]	-39[18]	8013[1]	48[3]
C(1)	809[15]	- 428[34]	8177[2]	121[5]
C(2)	892[10]	-80[21]	7851[1]	35[4]
C(3)	0	0	7486[1]	33[5]
C(4)	0	0	7283[1]	33[6]
C(5)	- 888[9]	- 64[24]	6920[1]	34[3]
C(6)	- 808[13]	- 632[13]	6524[1]	48[5]
C(7)	- 371[15]	-2637[15]	6529[2]	63[10]
Au(1)	0	5000	1240[2]	189[3]
Br(1)	-160[17]	3327[12]	1253[2]	169[3]

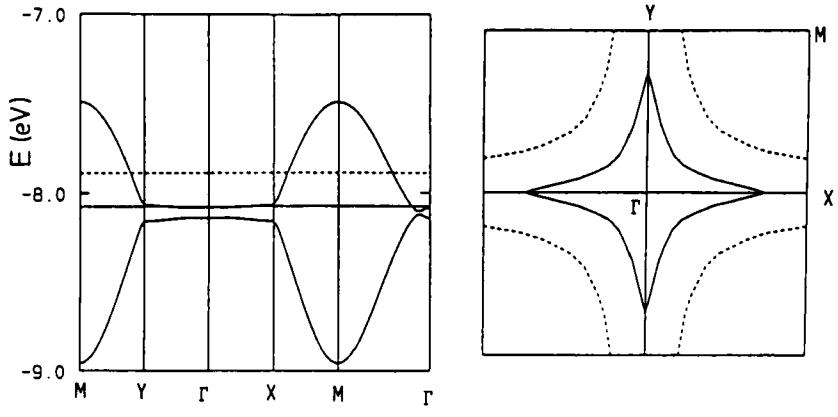

Fig.2 Calculated electronic band structure and Fermi surface of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_y$; dotted line corresponds to y=0 (i.e., 3/4 filled band) and solid line to y=0.75.

coefficient (R_H) is very temperature dependent (Figure 5). At room temperature it is rather positive, and by lowering temperature, R_H decreases to negative value crossing zero around 250 K. Below 150 K, R_H shows almost a constant negative value. This implies that the electron scattering in the Fermi surface is very anisotropic and temperature dependent. The UV-visible absorption spectrum shows maxima close to those observed from the green solution obtained fromthe anode region. The reflectance spectrum shows an upward slope from 3500 cm^{-1} to lower frequencies, which

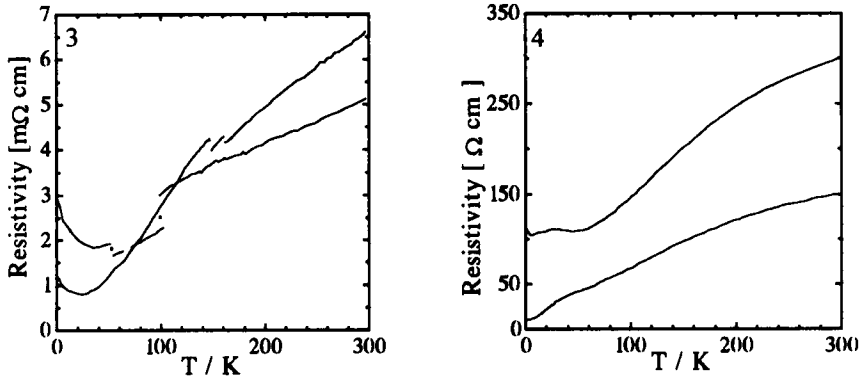

Fig.3 Temperature dependence of in-plane resistivity for two crystals of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$.
Fig.4 Temperature dependence of out-of-plane resistivity for two crystals of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$.

indicates a metallic behaviour. These experimental results indicate that the material is a 2D metal in accordance to the electronic band structure calculations for (y=0.75). The resistance upturn observed at low temperature (Fig.3) might be due to a weak localization effect.[14] However, more detailed experiments such as low temperature x-ray investigations, angular dependence of magnetoresistance and temperature dependence of conductivity are needed to clarify the origin of this effect. The room temperature ESR spectrum is shown in Fig. 6. One can see that the linewidth is larger than 500 gauss as in the case of pyrazino-analogues[7] and other τ-phases based on EDOVDT TTF[6]. In addition to structural data, the spectroscopic data (for a comparison see

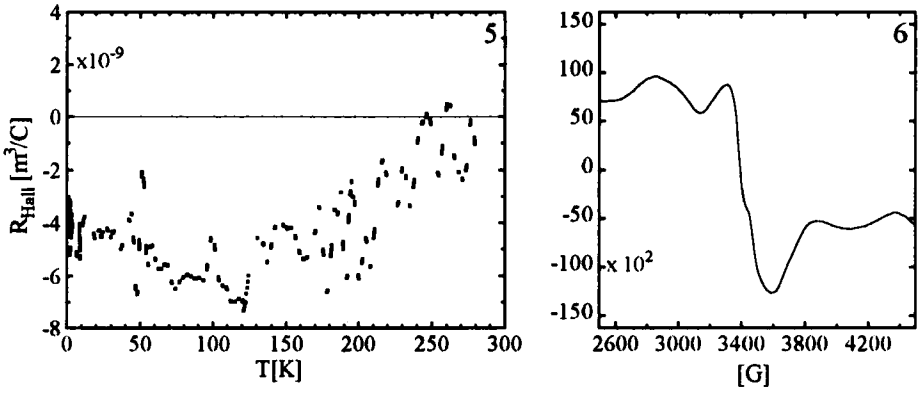

Fig.5. Temperature dependence of Hall-coefficient of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$.
Fig.6 Room temperature ESR spectrum of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_1$(AuBr$_2$)$_{0.75}$.

also [13]) indicate that the compound contains the species D^{2+}, $D^{+\cdot}$ and D^{0}, which means that a possible formula is

$$[0.5\ D^{2+} + 0.75\ D^{+\cdot} + 0.75\ D^{0}]\ [1(AuBr_2^-) + 0.75(AuBr_2^-)]$$

where D is the donor molecule EDO-*S,S*-DMEDT-TTF.

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