# (BEDT-TTF)$_2$X(TCE)$_{0.5}$ [X: BF$_4$, FSO$_3$, IO$_4$] NEW ORGANIC METALS

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## ABSTRACT

The structure, the temperature dependence of the resistivity, thermopower, ESR-linewidth and the spin susceptibility of a new series of organic metals (BEDT−TTF)$_2$X·(TCE)$_{0.5}$ [X = BF$_4$, FSO$_3$ and IO$_4$] is presented and discussed.

## INTRODUCTION

New radical salts of the donor BEDT−TTF [bis(ethylenedithio)tetrathiofulvalene] are of great interest because many of the known salts are organic metals down to low temperatures and some become even superconducting. So at the moment the organic superconductors with the highest transition temperatures are all radical salts of the donor BEDT−TTF.

An important parameter in the electrochemical process which has to be optimized in order to obtain new phases of radical salts of good quality is the concentration of the donor cations as well as of the anions in the solution. Hereby the concentration of the anions can be varied f.i. by the choice of the type of electrolyte salt or by the solvent which is used in the electrochemical crystallisation. By using the crown ether route [1] we have varied the conditions for the electrocrystallisation of BEDT−TTF radical salts in order to obtain new structural phases.

## EXPERIMENTS AND RESULTS

In the solvent 1,1,2 trichloroethane (TCE) the donor BEDT−TTF (1.8 m mol), 18-crown-6-ether (10 m mol) and the electrolyte salts KBF$_4$ or KFSO$_3$ or KIO$_4$ (10 m mol) were dissolved. The solution with a remainder of undissolved electrolyte salt was filled under nitrogen in the electrochemical cell. At 20$^0$C and under constant voltage conditions with a current density of about 1 µA/cm$^2$ crystals of (BEDT−TTF)$_2$X(TCE)$_{0.5}$ [X = BF$_4$ (1), FSO$_3$ or IO$_4$] were grown in about two weeks. All crystal structures are similar to the structure of the radical salt (BEDT−TTF)$_2$ClO$_4$(TCE)$_{0.5}$ (2) which was the first quasi two dimensional organic metal of the BEDT−TTF salts, synthesized by Saito and coworkers [2]. The crystals of 2 were obtained under conditions where using BF$_4^-$ anions instead of ClO$_4^-$ only the phase (BEDT−TTF)$_3$(BF$_4$)$_2$ (3) [3] can be obtained, which has a metal insulator phase transition around 250 K and a different structure with respect to the compounds 1 and 2.
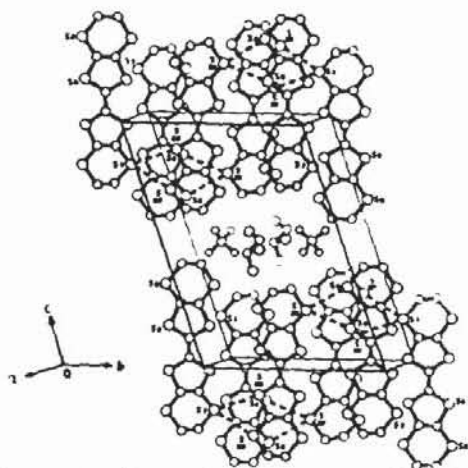
Figure 1: Crystal structure of 1 viewed along the a-axis.



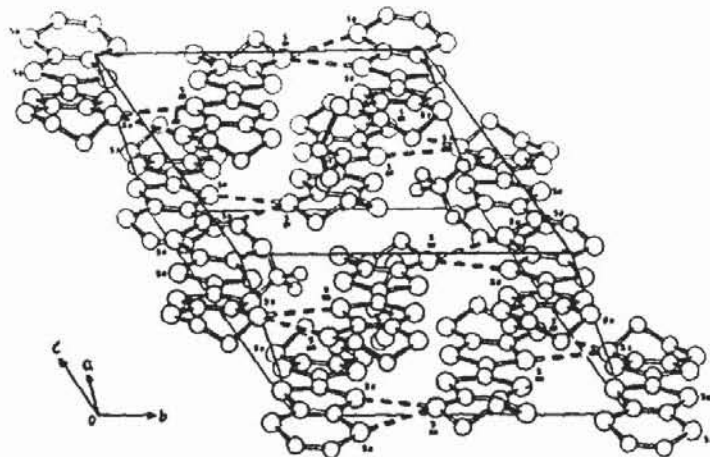Figure 2: Crystal structure of 1 viewed along the c-axis

In the following only the properties of $(BEDT-TTF)_2BF_4(TCE)_{0.5}$ (1) will be presented and discussed. The properties of the analogue $FSO_3$ and $IO_4$ compounds are very similar. The crystal data of $(BEDT-TTF)_2BF_4(TCE)_{0.5}$ (1) are the following: triclinic space group $P\bar{1}$, a = 7.735 (6), b = 13.006 (11), c = 18.450 (10) A, $\alpha$ = 110.11 (5), $\beta$ = 90.53 (6), $\gamma$ = 104.41 (6)°, Z = 2, V = 1679 (2) A$^3$. Figure 1 shows the crystal structure of 1 viewed along the a-axis. Two layers of BEDT−TTF ribbons are shown with the top layer being drawn darker. The intermolecular S....S contacts less than the van der Waals distance (3.6 A) in the layer are shown by broken lines. In fig. 2 the crystal structure viewed along the c-axis is shown.

The room temperature conductivity in the ab-plane of the crystals is typically between 5 and 40 S/cm, while in the c-direction this value is about a factor of 1000 smaller. The figs. 3 and 4 show the temperature dependence of the resistivity (normalized to the room-temperature starting value) of crystals of 1 along the a- and b-direction in a cooling down and warming up cycle. While below 60 K the resistivity values are identical in both cycles, above 60 K the resistivity shows in both directions a large hysteresis. Such a behaviour was already observed before in crystals of $\alpha_t$-$(BEDT-TTF)_2I_3$ [4] as well as in polycrystalline pressed samples of $\alpha_t$-$(BEDT-TTF)_2I_3$ [4] and $\beta_p$-$(BEDT-TTF)_2I_3$ [5]. After reaching again 300 K in the warming up cycle the resistivity is much higher than the starting value but relaxes back to the starting value within a few hours. We have observed a similar behaviour as well in the organic metal $(BEDT-TTF)_2ClO_4(TCE)_{0.5}$ (2) [2].

It is interesting to notice that the ratio $\rho_a/\rho_b$ (see fig. 5) is identical for the cooling down and warming up cycle in the whole temperature range between 4.2 and 210 K and only above 210 K this ratio differs. At room temperature the anisotropy in the resistivity in the ab-plane is with $\rho_a/\rho_b \approx 4$ in the usual range of BEDT−TTF radical salts. This ratio becomes smaller with decreasing temperature and below 50 K $\rho_a$ is even smaller than $\rho_b$.
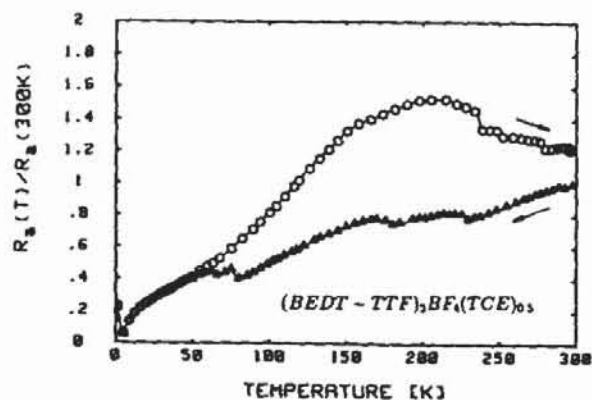


Figure 3: Resistivity of 1 versus temperature in a-direction (see text).
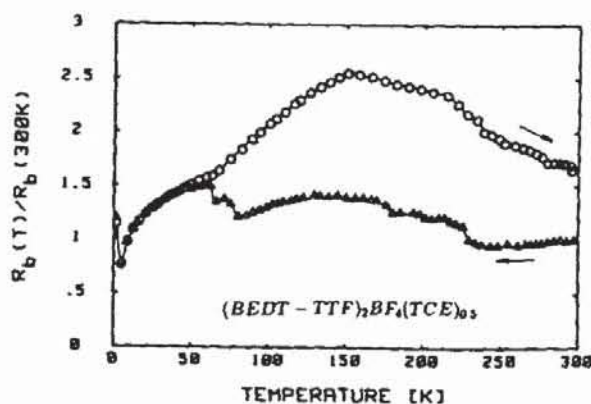


Figure 4: Resistivity of 1 versus temperature in b-direction (see text).

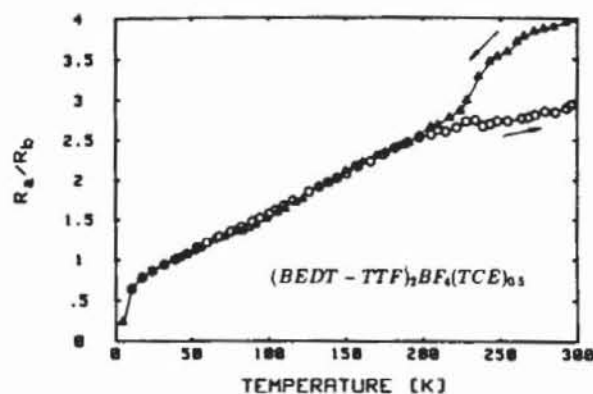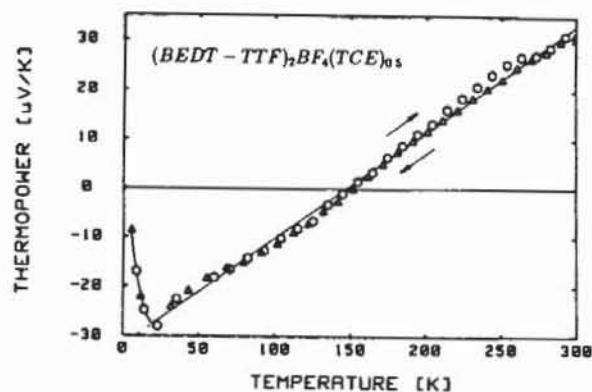Figure 5: $\rho_a/\rho_b$ of $\underline{1}$ versus temperature



Figure 6: Thermopower of $\underline{1}$ versus temperature

In fig. 6 the temperature dependence of the thermopower of $\underline{1}$ parallel to the a-direction is shown. In the whole temperature range between 20 and 300 K the thermopower increases linearely with the temperature as expected for a metal. At around 20 K a phase transition seems to occure, which was not observed in the resistivity measurement. From the slope of the thermopower a bandwidth of the conductionband in the a-direction of about 0.5 eV can be estimated.

At room temperature the ESR-linewidth varies between 26 and 35 Gauss, depending on the orientation of the crystal with respect to the magnetic field. Figure 7 shows the typical temperature dependence of the ESR-linewidth for the magnetic field parallel to the c-direction and the orientation in the ab-plane for a minimum ESR-linewidth. Down to 150 K the ESR-linewidth is constant, while below 150 K the linewidth decreases with lowering the temperature. In fig. 8 the spin-susceptibility versus temperature is presented as calculated from the ESR data. The susceptibility is more or less temperature independent in the temperature range between 30 and 300 K as expected for a metal. Below 30 K the susceptibility increases which is probably due to paramagnetic impurities.

It was shown that polycrystalline pressed samples of organic metals can display metallic properties down to low temperatures and can even become superconducting [4-6]. Nevertheless up to now such a metallic behaviour in polycrystalline pressed samples was only observed for quasi two-dimensional materials and not for quasi one-dimensional systems. Therefore we have measured the resistivity of polycrystalline pressed samples of (BEDT—TTF)$_2$BF$_4 \cdot$ (TCE)$_{0.5}$ ($\underline{1}$). In fig. 9 the temperature dependence of the resistivity of a polycrystalline pressed sample of $\underline{1}$ in a cooling down and warming up cycle is presented. The resistivity of this sample decreases slowly by lowering the temperature down to about 150 K indicating a metallic behaviour. Below 150 K the sample becomes semiconducting. Above 60 K again a hysteresis in the resistivity is observed as in single crystals. After annealing the samples at 80$^0$ C for several days no change in the resistivity characteristic was observed.
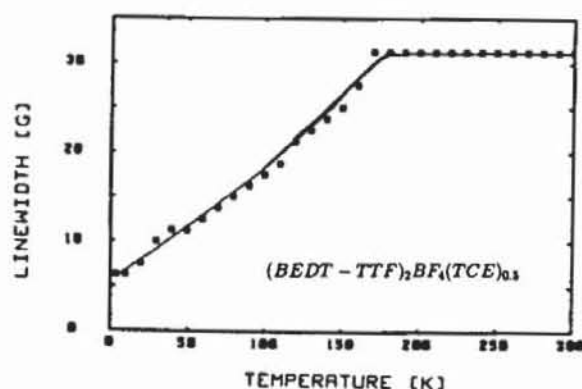


Figure 7: ESR-linewidth of $\underline{1}$ versus temperature (see text).
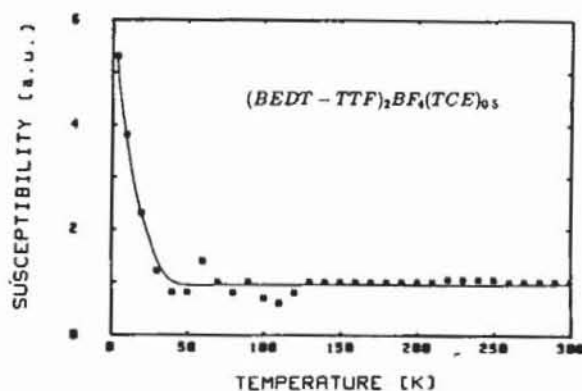


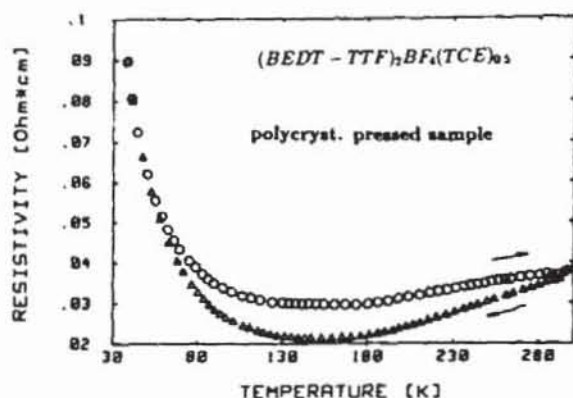Figure 8: Spin susceptibility of $\underline{1}$ versus temperature (see tex).

Figure 9: Resistivity of polycrystalline pressed samples of 1 (see text).

## DISCUSSION

From the resistivity measurements shown in fig. 3—5 we would conclude that the crystals of $(BEDT-TTF)_2BF_4 \cdot (TCE)_{0.5}$ (1) are quasi two-dimensional organic metals down to about 3 K where a metal-semiconductor phase transition seems to occur. The metallic state is confirmed down to 20 K by the thermopower measurement (fig. 6) and the temperature dependence of the spin susceptibility (fig. 8). At the moment it is not clear whether there exist two phase transitions at 20 K and 3 K or only one in this temperature range.

The temperature dependence of the ESR linewidth is typical as expected for a quasi two-dimensional metal. The ESR linewidth at room temperature can be used for sample identification [7]. The constant linewidth down to about 170 K and the monotonic decrease of the linewidth with decreasing temperature below 170 K can be attributed to temperature dependent scattering processes and the ESR linewidth can be described by the Elliot formula [8] for the spin relaxation in metals.

The resistivity characteristic of the polycrystalline pressed samples of 1 also demonstrates the quasi two-dimensional character of the material. Due to the anisotropic pressure during the preparation of the samples a phase transition might be induced because the polycrystalline samples display a metal-semiconductor phase transition at about 150 K which can not be suppressed, even by annealing the samples at higher temperatures for a longer time.

## LITERATURE

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