



## (BEDO-TTF)<sub>2</sub>ReO<sub>4</sub>·(H<sub>2</sub>O): A NEW ORGANIC SUPERCONDUCTOR<sup>+</sup>

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The structure and the temperature dependence of the resistivity, thermopower and ac-susceptibility of the new organic metal (BEDO-TTF)<sub>2</sub>ReO<sub>4</sub>(H<sub>2</sub>O) was investigated. The resistivity and thermopower data indicate phase transitions at 213K, around 90K and 35K. Below 2.5K an onset to superconductivity is observed in the resistivity data. Superconductivity was suppressed in the resistivity at 1.3K by applying a magnetic field of about 0.2T. Ac-susceptibility data indicate that superconductivity is a bulk effect in (BEDO-TTF)<sub>2</sub>ReO<sub>4</sub>(H<sub>2</sub>O) but the onset for superconductivity observed in the ac-susceptibility is only at 0.9K and the transition seems to be complete only at temperatures below 50 mK. This broad transition might be due to some disorder in the structure created by the low temperature phase transitions.

### Introduction

The discovery of superconductivity in (TMTSF)<sub>2</sub>PF<sub>6</sub> [1] has been followed by the synthesis of approximately forty further organic superconductors. The highest values of the superconducting transition temperature T<sub>c</sub> have involved radical salts obtained from the organic donor BEDT-TTF (bisethylenedithiolotetrathiafulvalene). Therefore after the synthesis of the new donor BEDO-TTF [2] (bisethylenedioxytetrathiafulvalene, see insert in fig. 3), which is structurally strongly related to BEDT-TTF, the expectation was that similar radical salts with superconducting properties can be obtained

by electrochemical preparation as for the donor BEDT-TTF. In fact, up to now a large number of organic metals was prepared with the donor BEDO-TTF, but only in one case an indication for superconductivity was observed. RF penetration depth measurements on crystals of (BEDO-TTF)<sub>3</sub>·Cu<sub>2</sub>(NCS)<sub>3</sub> [3] show the occurrence of superconductivity below 1K.

Usually the crystal quality of the BEDO-TTF salts is rather poor and in fact up to now only a few have been characterized structurally [3-6]. Even in the few cases where the structures were solved, relative large R-values are given in the structural data, indicating dis-

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order and bad crystal quality, in contrast to radical salts of the donor BEDT-TTF, which show normally a quite good crystal quality.

The electrocrystallisation of radical salts of the donor BEDO-TTF results - similar as in the case of BEDT-TTF - often in several structural different phases, depending on the condition of the electrocrystallisation. By varying those condition we obtained a new organic metal, single crystals of  $(\text{BEDO-TTF})_2\text{ReO}_4 \cdot (\text{H}_2\text{O})$ . Here we report structural data, the temperature dependence of the resistivity and thermopower as well as the observation of superconductivity in resistivity data and RF penetration depth measurements for  $(\text{BEDO-TTF})_2\text{ReO}_4 \cdot (\text{H}_2\text{O})$ .

### Experimental

BEDO-TTF was synthesised as described by Suzuki et al [2]. Crystals of  $(\text{BEDO-TTF})_2\text{ReO}_4 \cdot (\text{H}_2\text{O})$  were prepared using the crown ether route in the electrochemical preparation [7]. Instead of using a high concentration of  $\text{ReO}_4^-$  anions, as obtained by the electrolyte salt  $(n\text{-Bu}_4\text{N})\text{ReO}_4$ , we used a rather low concentration by taking  $\text{KReO}_4$  and 18-crown-6 ether in 1,1,2-trichlor-

ethane (TCE). The crystal preparation was similar as described earlier for  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  [8].

For the crystal structure determination a black plate-like crystal ( $0.05 \times 0.25 \times 0.65 \text{ mm}^3$ ) was used. Lattice parameters were obtained from setting angles of 15 reflections ( $4 < 2\theta < 21^\circ$ ) centered on a diffractometer (Syntex R3, Mo  $K\alpha$  radiation). Data collection at room temperature by  $\Omega$  scan ( $3 < 2\theta < 58^\circ$ ) yielded 3112 observed independent reflections with  $I > 2\sigma(I)$ . The structure was solved by direct methods and Fourier synthesis. Calculations were performed with the SHELXTL program package [9].

The resistivity measurements were carried out by the usual four point method. On all measured crystals four gold contacts were deposited by evaporation techniques and gold wires with gold paint connected to these contacts. The measurements between 1.3K and 300K were carried out in a specially prepared  $^4\text{He}$ -bath-cryostat while the measurements between 0.5K and 1.3K were performed with a  $^3\text{He}$ -cryostat.

Thermopower measurements were done with an apparatus described earlier [10] in the temperature range between 5K and 300K.

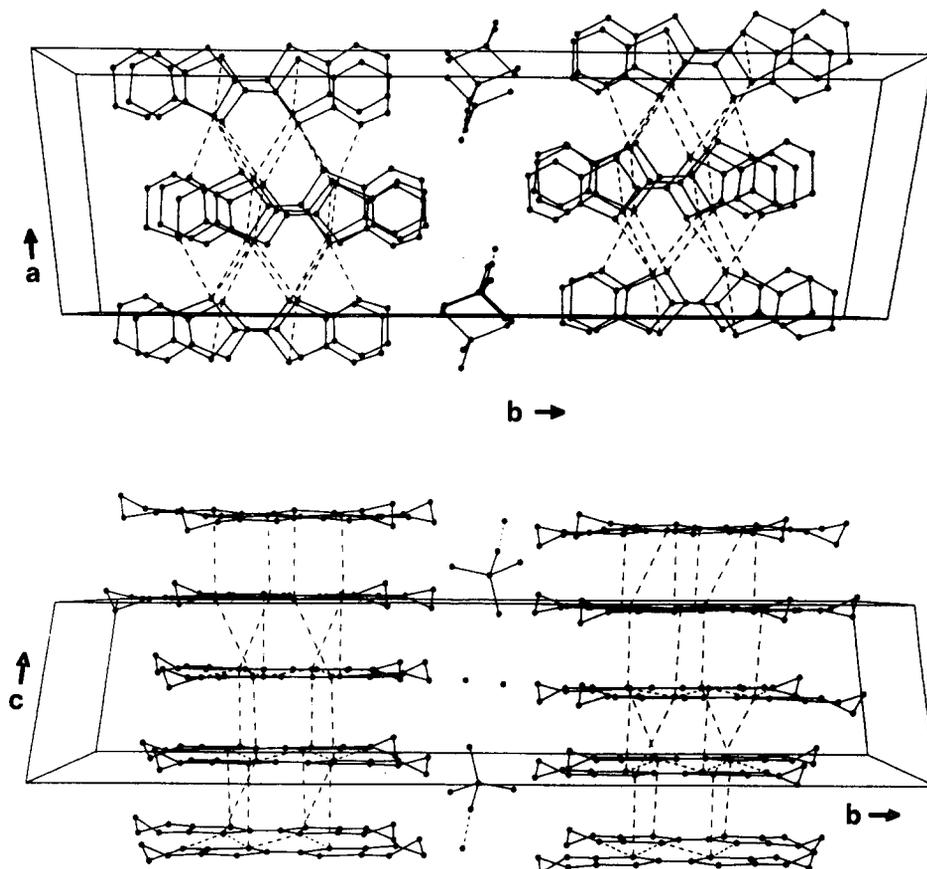


Figure 1: Projection of the unit cell of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4 \cdot (\text{H}_2\text{O})$  along (top) and perpendicular to the columns of the BEDO-TTF molecules.

The real part of the complex susceptibility was measured by using a standard low frequency (117 Hz) mutual inductance technique. Several ribbon like samples were arranged parallel to each other to obtain the desired mass of about  $10^{-4}$  g for the susceptibility measurement. The ac- magnetic field of  $5 \cdot 10^{-5}$  Tesla was applied perpendicular to the ribbons. The measurements were performed in an adiabatic demagnetization cryostat down to 30mK.

### Results

The crystal structure determination of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$  at room temperature gives a monoclinic cell P2 1/a, with  $a=12.16$  (1) Å,  $b=34.05$  (3) Å,  $c=8.091$  (4) Å,  $\beta=123.44$  (4)°,  $V=2795.5$  Å<sup>3</sup>,  $d_c=2.16$  g/cm<sup>3</sup>,  $Z=4$ . Refinement of 280 variables converged with  $R_w=0.069$ . The  $\text{ReO}_4^-$ - anions are slightly disordered. A detailed discussion of the structure will be given later.

Figure 1 shows a projection of the unit cell of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$  along and perpendicular to the columns of the BEDO-TTF molecules. Strong S-S and S-O contacts between the molecules are shown as well, indicating the typical two dimensional electronic character of the material. Hydrogen atoms are not drawn in the figures but the hydrogen bonds between the water molecules and the oxygens of the  $\text{ReO}_4^-$ -anions are indicated.

A typical temperature dependence of the resistivity of crystals of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$  between 1.3K and 300K is given in fig. 2. The increase in resistivity below 35K and the height of the maximum at 2.5K depends somewhat on the cooling procedure of the crystals (typical cooling rate 1K/minute). The jump in resistivity at 213 K is not due to a crack in the crystal, but probably due to a phase transition because this jump in resistivity at this temperature is not only observed

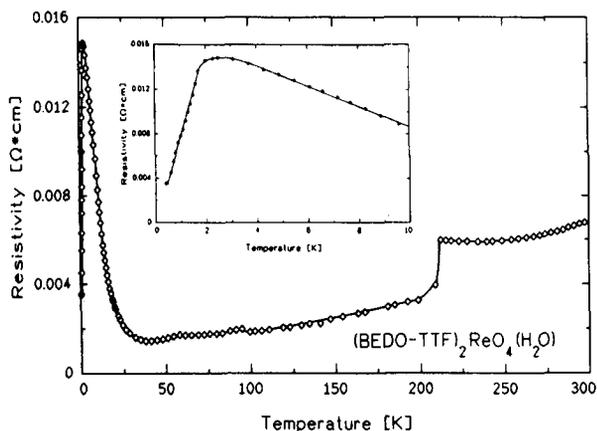


Figure 2: Temperature dependence of the resistivity parallel to the  $c^*$ -axes of single crystals of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$ . The insert shows the resistivity in the temperature range 0.5K to 10K (see text).

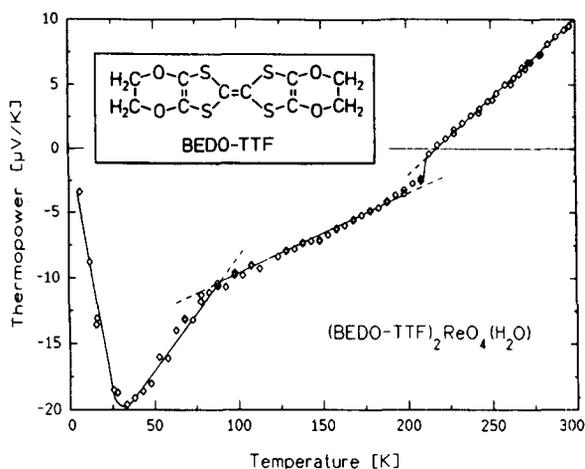


Figure 3: Temperature dependence of the thermopower parallel to the  $c^*$ -axes of single crystals of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$ . The insert shows the molecule BEDO-TTF.

in the cooling down cycle but also in the warming up cycle. This metal-metal phase transition can be seen as well in the measurement of the temperature dependence of the thermopower (fig. 3), where at the same temperature a small jump in thermopower is observed and the slope of the thermopower changes.

The insert in fig. 2 shows the temperature dependence of the resistivity of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$  between 0.5K and 10K. In this figure the measurements of two independent experiments (first run down to 1.3K and second run between 0.5K and 1.3K) are drawn in one graph. Since in the experiment in the <sup>3</sup>He-cryostat the sample was cooled faster from room temperature down to 1.3K a number of cracks were observed

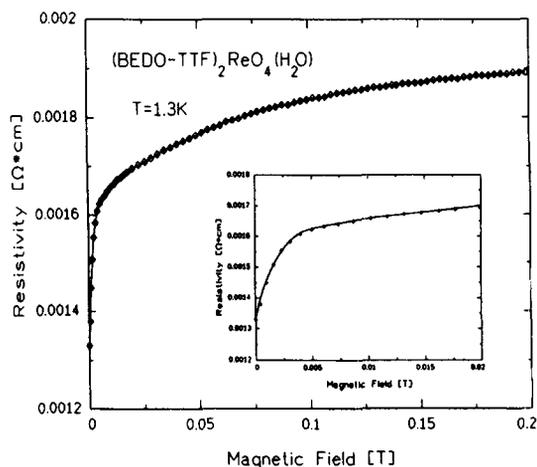


Figure 4: Resistivity parallel to the  $c^*$ -axes of single crystals of  $(\text{BEDO-TTF})_2 \cdot \text{ReO}_4(\text{H}_2\text{O})$  versus an applied magnetic field parallel to the  $b$ -axes at 1.3K.

in the resistivity data. Therefore at 0.5 K still a resistivity of 0.0035  $\Omega\text{cm}$  was obtained. In an additional measurement of the resistivity on another sample down to 1.3 K a magnetic field was applied at this temperature. In fig. 4 the dependence of the resistivity with respect to the applied magnetic field at 1.3 K is shown, indicating the suppression of superconductivity at a field of about 0.2 T. Above 0.2 T a rather strong magnetoresistance of additional 30% at a field of 1.8 T was observed.

Since the resistivity measurements below 2.5 K indicated that the samples become superconducting at this temperature, the ac-susceptibility was measured in an adiabatic demagnetization cryostat. Below 1 K the ac signal of the mutual inductance bridge becomes diamagnetic indicating a broad transition into the superconducting state which seems to be complete only at temperatures below 50 mK. Figure 5 shows the normalized susceptibility signal as a function of temperature. Due to the irregular size and the very small mass of the samples, the absolute value of  $\chi$  is not exactly known. The half value of the transition is obtained at  $T=0.36$  K while the onset temperature is observed at 0.9 K. This onset temperature for superconductivity in ac-susceptibility is much smaller than in resistivity ( $\approx 2.5$  K). Usually an onset in change in ac-susceptibility in organic superconductors is observed at about the temperature where zero resistivity is found. This is not the case here, since even at 0.5 K still a non-zero resistivity is observed which is probably due to the cracks in the sample generated in the cooling cycle.

### Discussion

The structural data indicate a slight disorder in the  $\text{ReO}_4^-$  anions at room temperature. The fact that the anions are not totally disordered is due to the hydrogen bonds between the oxygens of the anions and the water molecules. At the moment it is assumed that the  $\text{ReO}_4^-$  anions do order at the phase transition at 213 K observed in resistivity (fig. 2) and thermopower (fig. 3) data, similar as in  $(\text{TMTSF})_2\text{ReO}_4$  where the ordering of the  $\text{ReO}_4^-$  anions appears at 180 K and leads to a metal-insulator transition [11]. Here this transition is a metal-metal transition as can be seen from the temperature dependence of the resistivity and the thermopower (fig. 2, 3). In addition, both the resistivity and the thermopower characteristics in fig. 2 and 3 indicate two further phase transitions at around 80 K to 90 K and at about 35 K. These transitions might be caused by order-disorder phenomena either in the anionic or (and) cationic sublattices. Disorder could lead to the increase in resistivity below 35 K. Nevertheless below 2.5 K the resistivity decreases again rather strongly (fig. 2) and this decrease can be suppressed by applying a magnetic field to the sample (fig. 4). Together with the observed change

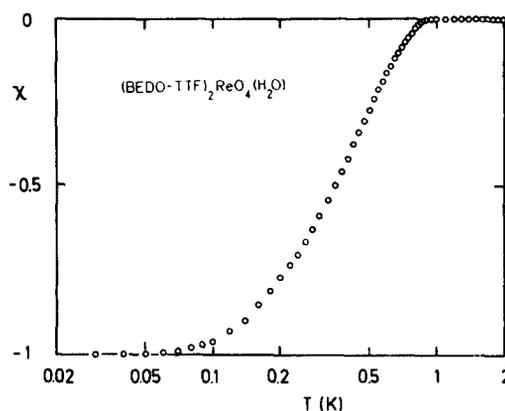


Figure 5: Normalized susceptibility signal as a function of the temperature for crystals of  $(\text{BEDO-TTF})_2\text{ReO}_4(\text{H}_2\text{O})$  (see text).

in ac-susceptibility below 1 K (fig. 5) these experiments show a clear evidence for bulk superconductivity in the single crystals of  $(\text{BEDO-TTF})_2\text{ReO}_4(\text{H}_2\text{O})$ .

The onset temperature for superconductivity in the resistivity is much higher ( $\approx 2.5$  K) than in the ac-susceptibility ( $\approx 0.9$  K). This is not surprising if disorder-order effects are presumably responsible for the increase in resistivity below 35 K. A disorder in the structure would result in a lower superconducting transition temperature with respect to a totally ordered structure but in addition the superconducting transition would be rather broad. Further experiments are necessary in order to clarify this assumption. Special cooling cycles or experiments under pressure might suppress the phase transitions at 80 K to 90 K and 35 K leading to an totally ordered state and hopefully resulting in an even higher superconducting transition temperature. The additional large magnetoresistance effect above 0.2 T of about 30% until a field of 1.7 T might be an indication for such a possible higher transition temperature. The fact that the increase in resistivity below 35 K and the height of the maximum in resistivity depends somewhat on the cooling rate might be a further indication.

The results discussed above show that the crystals of  $(\text{BEDO-TTF})_2\text{ReO}_4(\text{H}_2\text{O})$  become superconducting below 2.5 K and that superconductivity is a bulk effect.

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