PRESSURE DEPENDENCE OF THE RESISTIVITY

OF (BEDO-TTF)$_2$ ReO$_4$·(H$_2$O)

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The temperature dependence of the resistivity under pressure (up to 6 kbar) of the organic metal (BEDO-TTF)$_2$ReO$_4$(H$_2$O) was investigated. The increase of the resistivity below 35 K, which is observed at ambient pressure, is already totally suppressed at 1 kbar. In addition at this pressure the superconducting transition sharpens drastically and the onset temperature of 2.3 K is nearly the same as at ambient pressure.

Introduction

Recently [1] the observation of superconductivity below 2.5 K in single crystals of (BEDO-TTF)$_2$ReO$_4$·(H$_2$O) was reported. (BEDO-TTF)$_2$ReO$_4$·(H$_2$O) is the second crystal system in the large family of the radical salts of the electron donor BEDO-TTF (bisethylenedithiolo-tetrathiafulvalene [2]) in which superconductivity in the bulk was observed. Before only in single crystals of (BEDO-TFF)$_3$·Cu$_2$(NCS)$_3$ [3] superconductivity (below 1 K) was found.

In (BEDO-TTF)$_2$ReO$_4$·(H$_2$O) a first order metal-metal phase transition at 213 K in resistivity (see figure 1) and thermopower measurements was observed [1]. Additional phase transitions exist at around 90 K and 35 K. The most striking fact in the resistivity characteristic of the crystals at ambient pressure is the increase in resistivity below 35 K (see figure 1) and the strong decrease below 2.5 K. Nevertheless, the superconducting transition at ambient pressure is rather broad and the onset temperature is much lower in the ac-susceptibility with respect to the resistivity data [1]. Therefore it was assumed that structural disorder might be responsible for the increase in resistivity below 35 K and the rather broad superconducting transition.

In order to clariefy the nature of the phase transitions and the question whether the superconducting transition sharpens under pressure we have investigated the resistivity under pressure up to 6 kbar.

Experimental

Crystals of (BEDO-TTF)$_2$ReO$_4$·(H$_2$O) were prepared as described in reference 1. The resistivity data have been obtained by the usual four contact methods on needle shaped crystals of a typical length of 2-3 mm. Gold contacts were evaporated on these crystals and thin gold wires were attached using gold paint. The resistance has been measured with a low frequency lock-in technique passing a current of 10-100 µA through the sample. The high pressure was provided by either a helium gas hydrostatic medium using a Cu-Be pressure vessel, or a clamped pressure cell with isopentane as a pressure fluid. In the first cell, the measurements were performed at temperatures between 130 K and room temperature, up to 6 kbar with a good accurracy for the pressure determination as the helium gas pressure can be regulated when the temperature is decreased. The measurements in the second type of
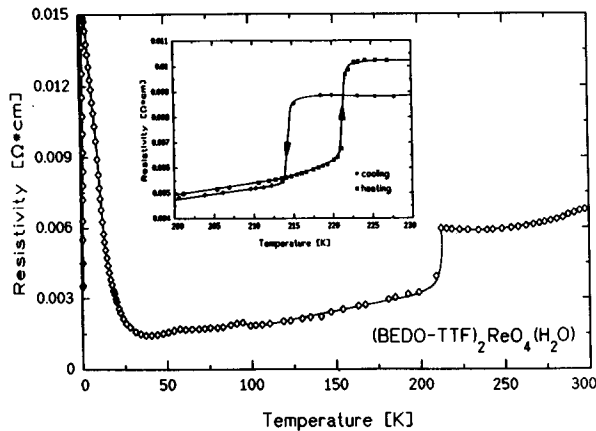
Figure 1: Temperature dependence of the resistivity parallel to the c^*-axes of single crystals of $(BEDO\text{-}TTF)_2 \cdot ReO_4(H_2O)$. The insert shows the temperature region of the resistivity characteristic where the metal-metal phase transition occurs in the cooling down and warming up cycle.

cell were done between 350 mK and 300 K using a He^3 system, with applied pressure up to 5 kbar but without any pressure regulation at low temperature.

Results

The typical resistivity of single crystals of $(BEDO\text{-}TTF)_2ReO_4 \cdot (H_2O)$ at room temperature and ambient pressure parallel to the c^*-axes is of the order $\rho_{c^*} = 0.005 \, \Omega cm$ and the resistivity ratio $\rho_{c^*} : \rho_a : \rho_b \approx 1 : 3 : 1000$. The pressure (p) dependence of the conductivity σ_{c^*} at room temperature in the investigated region up to 6 kbar is linear and the slope $\Delta\sigma_{c^*} / \Delta p = 28 \, (\Omega cm \cdot kbar)^{-1}$.
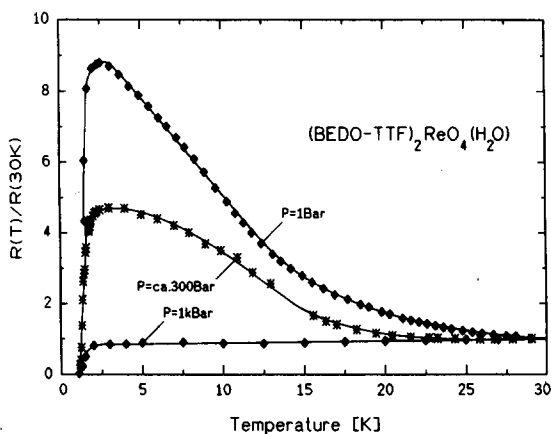
Figure 2 shows the temperature dependence of the re-

Figure 2: Temperature dependence of the resistivity (normalized at 30 K) parallel to the c^*-axes of single crystals of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ below 30 K at ambient pressure and an isotropic pressure of about 300 bar and 1 kbar.
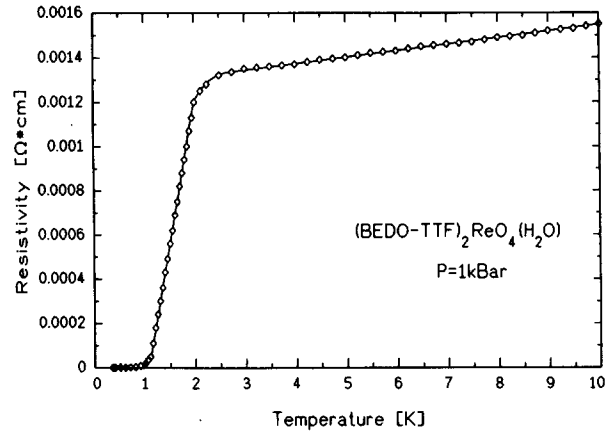

Figure 3: Resistivity parallel to the c^*-axes of a single crystal of $(BEDO\text{-}TTF)_2 \cdot ReO_4(H_2O)$ below 10 K at an isotropic pressure of 1 kbar.

sistivity of single crystals of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ at ambient pressure, about 300 bar and 1 kbar in the temperature range below 30 K. Since the experiments were done on different crystals the resistivity in fig. 2 is normalized to the resitivity values at 30 K. It can be seen that already a pressure of 1 kbar is sufficient in order to suppress the increase in resistivity below 30 K and the crystals show a metallic like behaviour down to about 2.3 K where the onset to superconductivity is observed. Figure 3 shows again the low temperature part (below 10 K) of the resistivity characteristic of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ under an isotropic pressure of 1 kbar.

In additon the pressure dependence of the first order phase transition temperature T_{MM} (213 K at ambient pressure) was studied. Figure 4 shows the dependence of the phase transition temperature with respect to the applied pressure in the cooling down and warming up cycle.

Discussion

The resistivity ratio at room temperature of $\rho_{c^*} : \rho_a : \rho_b \approx 1 : 3 : 1000$ ($t_{c^*} : t_a \approx 2.5$; where t is the transfer integral) indicates that the electronic properties of the $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ crystals are not so ideal two dimensional as observed in the radical salts of the BEDT-TTF family where the typical ratio of the resistivities in the conducting plane is about $1 : 1.5$ ($t_a : t_b \approx 1$). On the other hand the electronic properties of the $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ crystals are certainly less anisotropic than those of the TMTSF radical salts where the resistivity ratio is about $1 : 25 : 400$ ($t_a : t_b \approx 10$) [4].

Since the structural data indicate a slight disorder in the ReO_4^--anions at room temperature [1] it was assumed that the ReO_4^--anions do order at the phase transition at 213 K (see fig. 1) similar as in $(TMTSF)_2ReO_4$ where the ordering of the ReO_4^--anions appears at 180 K and leads to a metal-insulator transition [5]. Here in $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ the observed transition
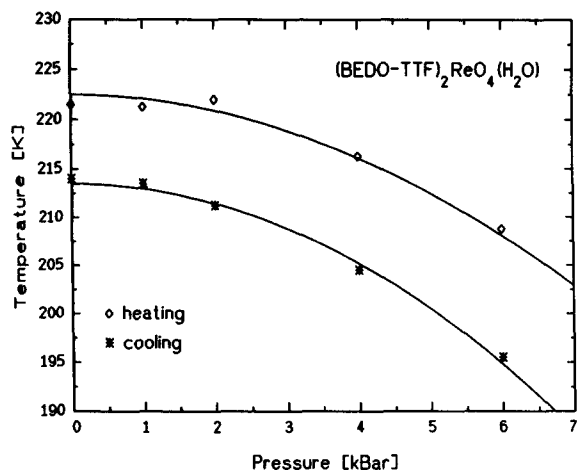
Figure 4: Pressure dependence of the metal-metal phase transition temperature T_{MM} of single crystals of (BEDO -TTF)$_2$ReO$_4$(H$_2$O) in the cooling down and warming up cycle. The drawn curves represent the equation

$$T_{MM} = T_{MM}(0) + a \cdot p^2$$

where $T_{MM}(0)$ is the phase transition temperature at ambiet pressure and p the applied isotropic pressure. The constant $a = \Delta T_{MM}/\Delta p^2 = -0.55$ K(kbar)$^{-2}$ in the cooling down cycle and $a = -0.40$ K(kbar)$^{-2}$ in the warming up cycle.

is a metal- metal phase transition (T_{MM}). Therefore it was expected that pressure might increase the transition temperature. In contrast to this expectation the phase transition temperature decreases as can be seen from fig. 4. Recent structural investigations at a temperature below 200 K [6] seem to indicate that in fact a structural phase transition into a phase with lower symmetry occurs. Therefore it can be understood that the phase transition temperature lowers by applying pressure to the system. Nevertheless, the nature of this structural phase transition seems to be of first order which can be seen from the hysteresis in the resistivity (and thermopower) data (see inset in fig.1) and the data shown in fig. 4 in the cooling down and warming up cycle. The data in fig. 4 show that by increasing hydrostatic pressure the phase transition temperature T_{MM} shifts to lower values. Hereby the change in phase transition temperature ΔT_{MM} is almost proportional to the square of the applied pressure. This indicates that a pressure of about 19 kbar would be nessecary in order to suppress this structural phase transition.

In reference 1 it was assumed that disorder phenomena either in the anionic or (and) cationic sublattice might drive the phase transition at around 35 K and that such disorder could lead to the increase in resistivity below 35 K. From figure 2 it can be seen that in fact already an isotropic pressure of 1 kbar is sufficient in order to suppress the increase in resistivity below 35 K. In addition at this pressure the superconducting transition sharpens strongly (see fig. 3) and the onset temperature for superconductivity is shifted to lower temperatures only about 0.2 K. At a pressure of 5 kbar the onset for superconductivity is shifted to 1.4 K. Nevertheless, in order to clear up the nature of the phase transition at 35 K further experiments are in progress.

Acknowledgement

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