TEMPERATURE DEPENDENT RESISTIVITY UNDER PRESSURE AND MAGNETORESISTANCE DATA OF THE ORGANIC SUPERCONDUCTOR (BEDO-TTF)$_2$ReO$_4$(H$_2$O).

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ABSTRACT

The temperature dependence of the resistivity under pressure (up to 6 kbar) of the organic metal (BEDO-TTF)$_2$ReO$_4$(H$_2$O) is reported. An increase of the resistivity below 35 K, which is observed at ambient pressure, is already suppressed at 1 kbar. In addition at this pressure the superconducting transition sharpens and the onset temperature of 2.3 K is nearly the same as at ambient pressure. Magnetoresistance data observed at 1.3 K and 6.7 Tesla show a strong angle dependence. In addition at 1.3 K first SdH-oscillations in the magnetoresistance are found already at such low fields as 5 Tesla.

INTRODUCTION

(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 (bisethylenedithiolotetrathiafulvalene [1]) in which superconductivity in the bulk is observed [2,3]. The first crystal system which showed superconductivity (below 1 K) in this donor family was (BEDO-TFF)$_3$Cu$_2$(NCS)$_3$ [4]. 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 is observed [2]. 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 [2]. 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 clarify the nature of the phase transitions and the question whether the superconducting transition sharpens under pressure the resistivity under pressure up to 6 kbar was investigated. In addition, in order to obtain information about the dimensionality of the electronic system, the anisotropy of the resistivity was measured as well as first magnetoresistance measurements on crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) in magnetic fields up to 7 Tesla were performed. As a main result it can be noticed that first Shubnikov de Haas (SdH) oscillations in the magnetoresistance can be observed already at such low fields as 5 Tesla. Furthermore the angle dependence of the magnetoresistance at fixed magnetic field shows oscillations as well.
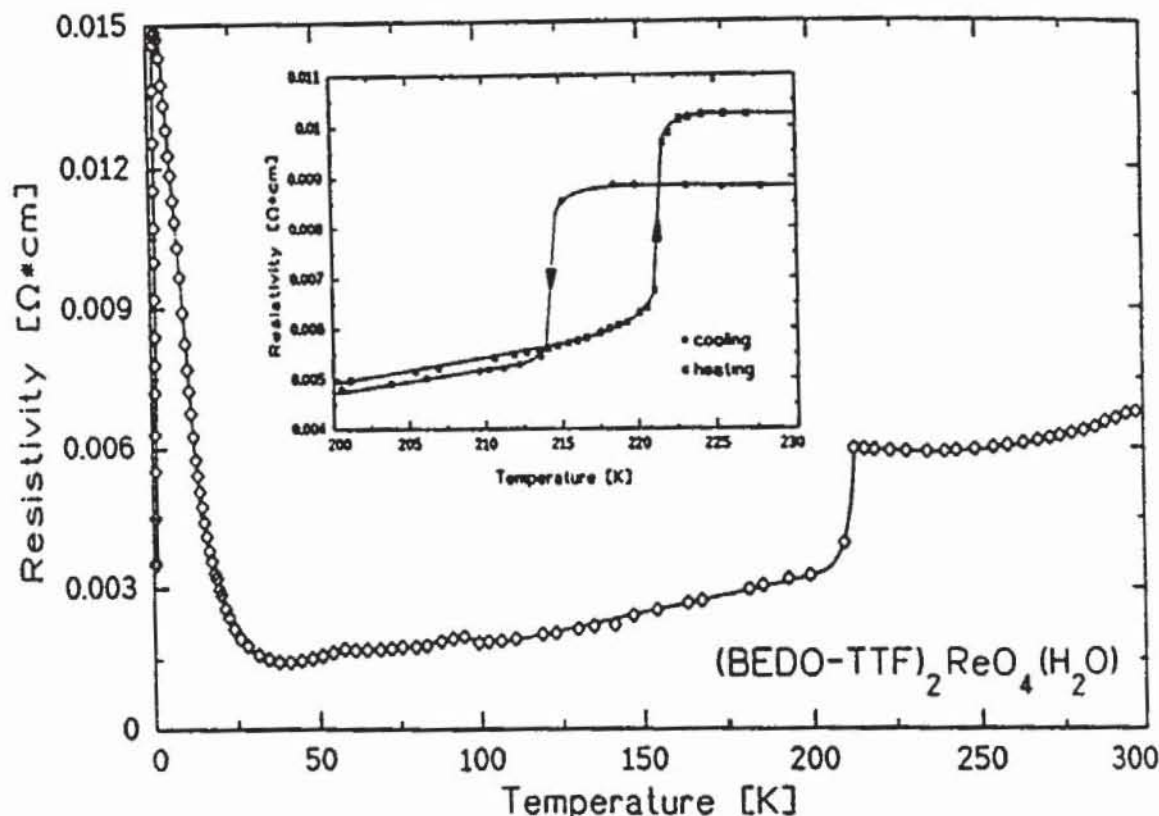
Fig. 1. Temperature dependence of the resistivity parallel to the c*-axis of single crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O). The insert shows the temperature region of the resistivity characteristic where the metal-metal phase transition occurs in the cooling down and warming up cycle.

EXPERIMENTAL

Crystals of (BEDO-TTF)$_2$ReO$_4$·(H$_2$O) were prepared as described in reference 2. 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 this 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 Be-Cu pressure vessel or a clammed pressure cell containing 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 accuracy for the pressure determination as the helium gas pressure can be regulated when the temperature is decreased. The measurements in the second type of 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. The magnetoresistance measurements were performed in a magnet system with a maximum field of 7 Tesla.

RESULTS

The typical resistivity of single crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) at room temperature and ambient pressure parallel to the c*-axis is of the order of $\rho_{c*} = 0.005$ Ωcm and the resistivity ratio $\rho_{c*} : \rho_a : \rho_b \approx 1 : 3 : 1000$. The pressure (p) dependence of the resistivity ρ_{c*} at room temperature in the investigated region up to 6 kbar is linear and the slope $\Delta\rho_{c*}/\Delta p = -0.0357$ Ωcm/kbar.

Figure 2 shows the temperature dependence of the resistivity of single crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) 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 resistivity values at 30 K. It can be seen that already a pressure of 1 kbar
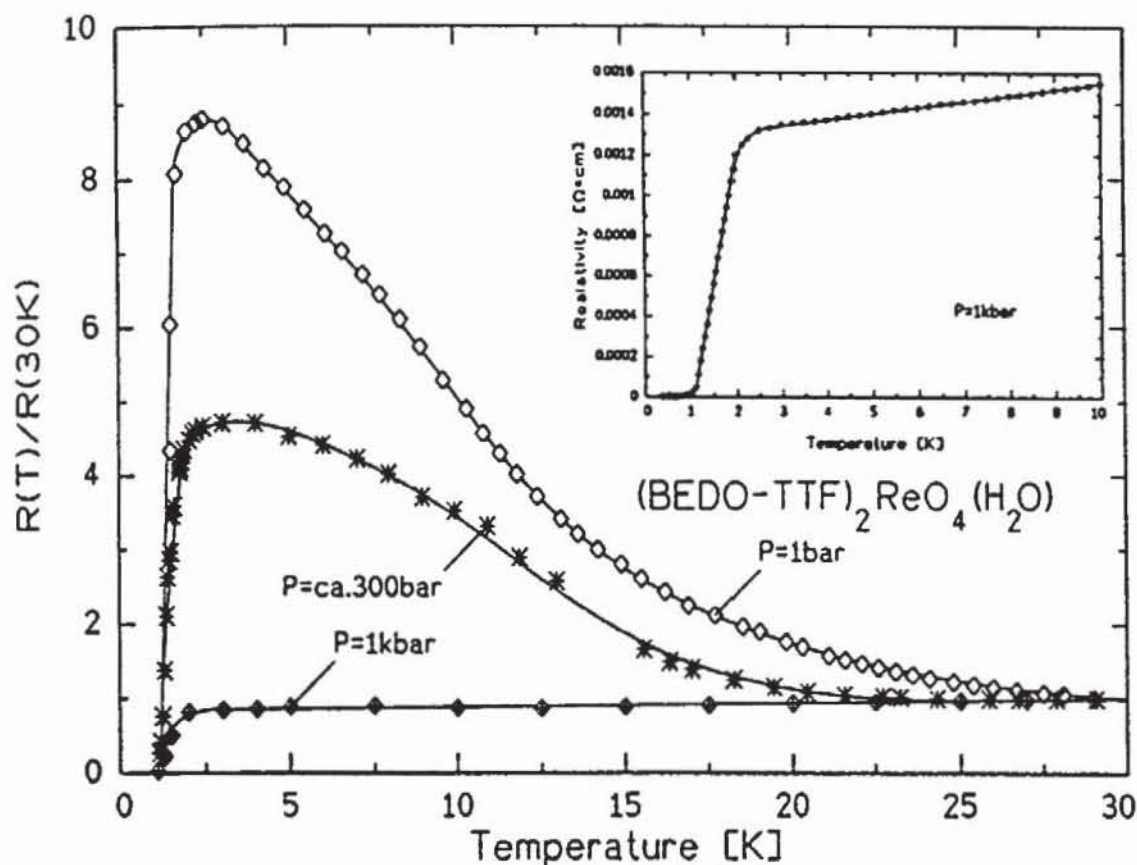
Fig. 2. Temperature dependence of the resistivity (normalized at 30K) parallel to the c^*-axis of single crystals of $(BEDO\text{-}TTF)_2 ReO_4(H_2O)$ below 30 K at ambient pressure and an isotropic pressure of about 300 bar and 1 kbar. The insert shows the resistivity below 10 K at an isotropic pressure 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. The insert in fig. 2 shows again the low temperature part (below 10K) of the resistivity characteristic of $(BEDO\text{-}TTF)_2 ReO_4(H_2O)$ under an isotropic pressure of 1kbar.

In additon the pressure dependence of the first order metal-metal phase transition at 213 K (see insert in fig. 1) was studied. The phase transition temperature T_{MM} at pressure p can be represented by an equation of the form: $T_{MM}(p) = T_{MM}(0) + a \cdot p^2$, where $T_{MM}(0)$ is the phase transition temperature at ambient pressure (213K) 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.

Figure 3 shows the magnetic field dependence of the resistivity (up to 6.8 Tesla) at a temperature of 4.2 K for the magnetic field parallel to the crystal axes a, b and c^*. In these experiments the current flow was parallel to the c^*-direction. It should be noticed, that for the magnetic field of 6.5 Tesla parallel to the b-direction (that means perpendicular to the conducting donor sheets) the increase in resistivity is nearly 100 %, while for this magnetic field parallel to the a-direction the increase is only of the order of 10 %. In fig. 4 the angle dependence of the magnetoresistance in the bc^*-plane in a magnetic field of 6.8 Tesla at a temperature of 1.3 K is drawn. The insert in fig. 4 shows oscillations of the magnetoresistance occuring in the angle dependence. Figure 5 shows the magnetic field dependence of the resistivity at a temperature of 1.3 K (where the crystal is superconducting without a magnetic field) for the magnetic field parallel to the c^*-direction. At low field (below 0.2 Tesla) the resistivity increases strongly due to the suppression of the superconductivity. At fields above 5 Tesla first oscillations in the magnetoresistance can be observed as can be seen in the
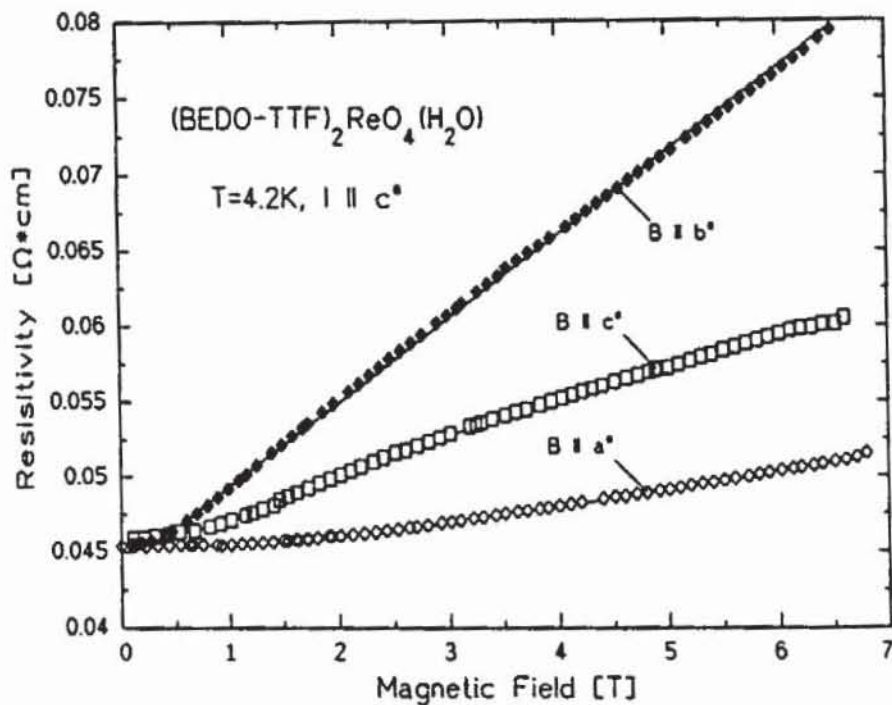
Fig. 3. Magnetic field dependence of the resistivity (at 4.2 K) for the magnetic field parallel to the a-, b- and c*- direction of single crystals of $(BEDO-TTF)_2ReO_4(H_2O)$ (see text).
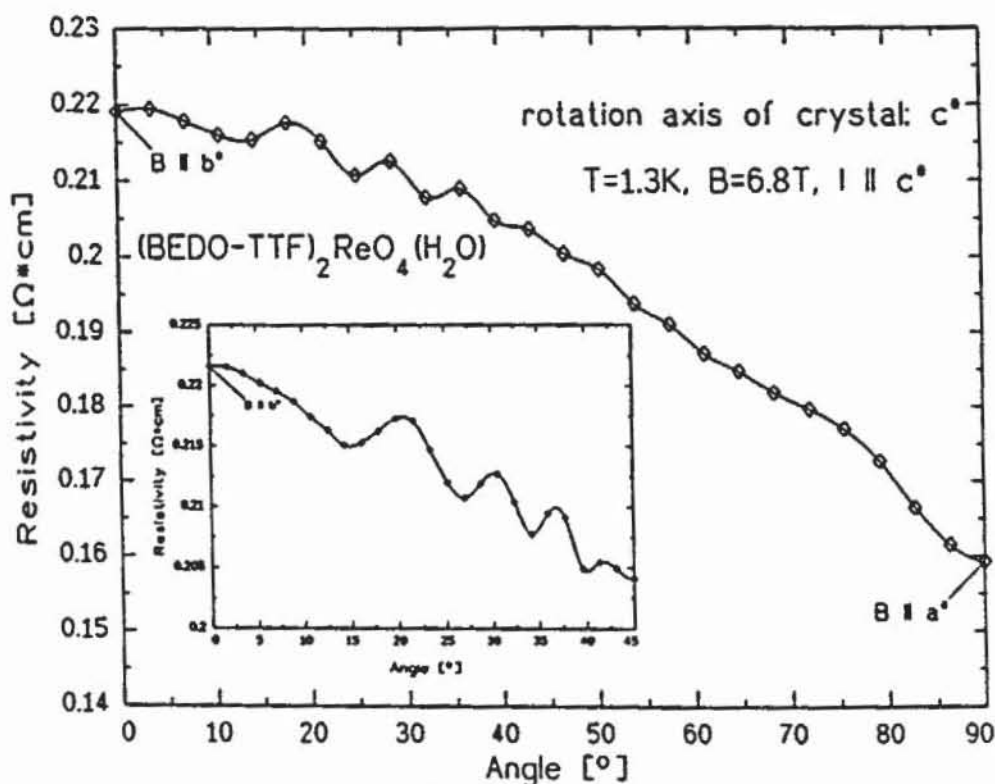

Fig. 4. Angle dependence of the magnetoresistance in the bc*- plane in a magnetic field of 6.8 Tesla (at 1.3 K) of single crystals of $(BEDO-TTF)_2ReO_4(H_2O)$ (see text).

insert in fig. 5. It should be mentioned that in an analogue experiment with the magnetic field parallel to the a-direction such oscillations were not observed in fields up to 7 Tesla.

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 $(BEDO-TTF)_2ReO_4(H_2O)$
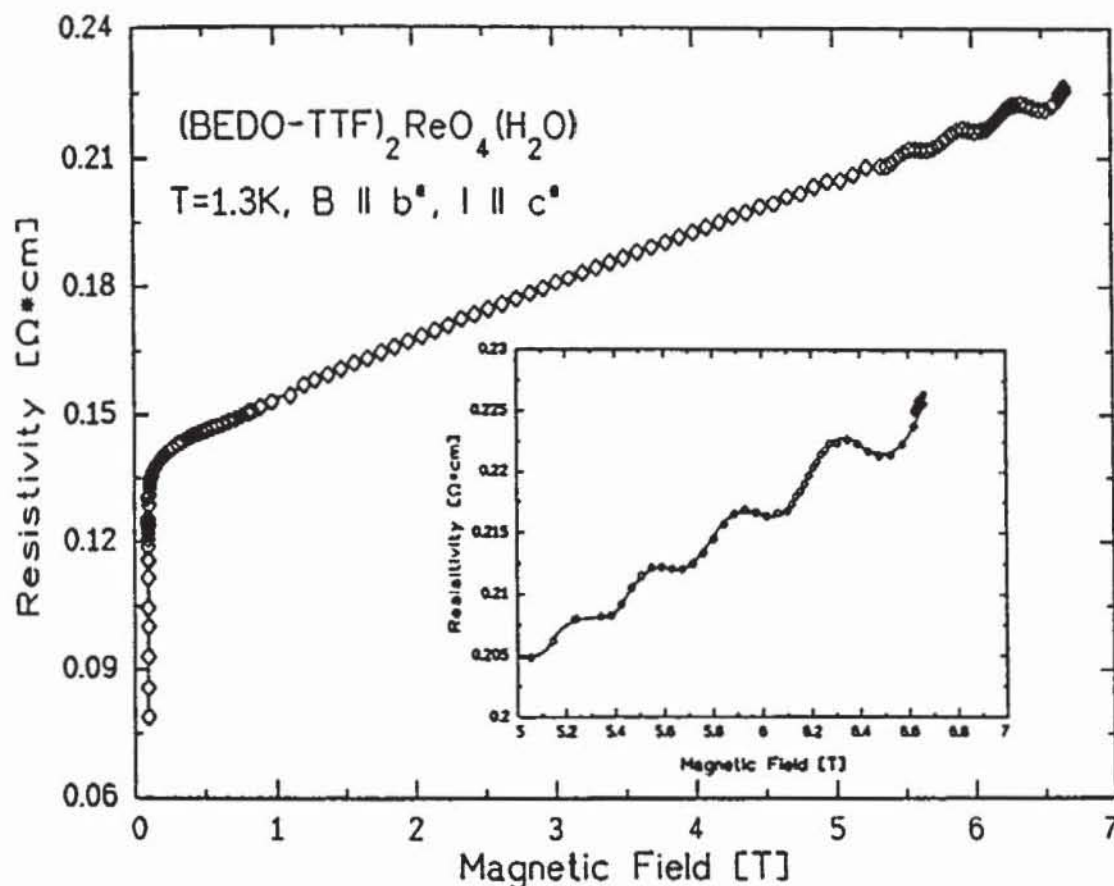
Fig. 5. Magnetic field dependence of the resistivity (at 1.3 K) for the magnetic field parallel to the c*- direction of single crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) (see text).

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 ≈ 1). On the other hand the electronic properties of the (BEDO-TTF)$_2$ReO$_4$(H$_2$O) 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 ≈ 10) [5].

Since the structural data indicate a slight disorder in the ReO$_4^-$ - anions at room temperature [2] it was assumed that the ReO$_4^-$- anions do order at the phase transition at 213 K (see fig. 1) similar as in (TMTSF)$_2$ReO$_4$ where the ordering of the ReO$_4^-$-anions appears at 180 K and leads to a metal-insulator transition [6]. Here in (BEDO-TTF)$_2$ReO$_4$(H$_2$O) the observed transition 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 the sign of the constant a in the equation for the transition temperature T$_{MM}$. Recent structural investigations at a temperature below 200 K [7] 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 insert in fig.1) and the data for the constant a in the cooling down and warming up cycle. By increasing the hydrostatic pressure the phase transition temperature T$_{MM}$ shifts to lower values. Hereby the change in phase transition temperature ΔT$_{MM}$ is 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 2 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 1kbar is sufficient in order to suppress the increase in resistivity below 35K. In addition at this pressure the superconducting transition sharpens strongly (see insert in fig. 2) but 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.

The presented first measurements of the magnetoresistance on crystals of $(BEDO-TTF)_2$ $ReO(H_2O)$ are incomplete and specially measurements in magnetic fields above 7 Tesla are needed. Nevertheless, a few interesting preliminary results can be learned. The fact that first SdH-oscillations (at 1.3 K) can be seen in such low fields as 5 Tesla seems to indicate that we deal with a two dimensional electronic system with a cylindrical Fermi surface. The observed SdH-oscillation has a frequency of about 90 Tesla. The quasi-two-dimensionality of the electronic system can further be seen from another oscillation in the magnetoresistance which is observed when the magnetic field is kept at a fixed strength (6.8Tesla in fig. 4) and is rotated from the direction normal to the conductive two dimensional plane (0°) to a direction parallel to the plane (90°). Such an oscillatory peaking of the magnetoresistance was first observed by Kajita et al [8] in crystals of $\Theta-(BEDT-TTF)_2I_3$ at low temperature as the constant magnetic field inclines from the normal of the conducting plane towards the plane and such a behaviour was theoretically explained by Yamaji [9] in a picture of a typical quasi-two-dimensional organic superconductor with a cylindrical Fermi surface. In such a quasi-two-dimensional system he calculated for the minima of the oscillations a dependence from the angle Θ and obtained an equation of the form: $\tan \Theta = c(n-1/4)$, with integer n and where c is a constant. In fact the observed oscillations here in fig. 4 for the single crystals of $(BEDO-TTF)_2ReO_4(H_2O)$ satisfy this equation remarkably good.

ACKNOWLEDGEMENTS

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