Possible localization behavior of the inherent conducting polymer $(CH_3)_{0.9}ReO_3$

E.-W. Scheidt[a], R. Miller[a], Ch. Helbig[a], G. Eickerling[a], F. Mayr[a], R. Herrmann[a], P. Schwab[b], W. Scherer[a,*]

[a]Chemische Physik und Materialwissenschaften, Universität Augsburg, 86159 Augsburg, Germany
[b]Theoretische Physik II, Universität Augsburg, 86159 Augsburg, Germany

Abstract

Polymeric methyltrioxorhenium (poly-MTO) represents the first example of an inherent conducting organometallic oxide. It adopts the structural motives and transport properties of some classical perovskites in two dimensions. In this study we present resistivity data down to 30 mK which exhibit a crossover from a metallic ($d\rho/dT > 0$) to an insulating ($d\rho/dT < 0$) behavior at about 30 K. Below 30 K an unusual resistivity behavior, similar to that of some doped cuprate systems, is observed: initially the resistivity increases approximately as $\rho \sim \log(1/T)$ before it starts to saturate below 2 K. Furthermore, a linear positive magnetoresistance is found (up to 7 T). Temperature dependent magnetization and specific heat measurements in various magnetic fields indicate that the unusual resistivity behavior may be driven by spatial localization of the d^1 moments at the Re atoms.

Polymeric methyltrioxorhenium (poly-MTO), $\{(CH_3)_{0.9}ReO_3\}_\infty$, is a unique representant of a conductive organometallic polymer in metal-oxide systems, with a moderate high resistivity of $6\,m\Omega\,cm$ at room temperature [1]. The conductivity is attributed to a fraction of demethylated Re atoms. Instead of a crossover from a Re(VII) (d^0) to a Re(VI) (d^1) state, these demethylated Re atoms are effectively oxidized and their electrons are transferred to the band system. Only a minor part (0.05% Re atoms [2]) remains located at the metal sites which are in the following treated as Re(d^1) centers. They model a two-dimensional dilute metal-oxide spin system. The attempt to increase the electronic conductivity of poly-MTO by employing the organic donor species tetrathiafulvalene (TTF) leads to a crossover from metallic to insulating behavior with increasing TTF concentration [2].

The resistivity of poly-MTO at low temperatures and in high magnetic fields within the ReO_2 planes resembles ρ of the CuO_2 planes of the Zn-doped high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) [3]. The scattering centers in Zn-doped YBCO are due to nonmagnetic Zn centers in the antiferromagnetic spin correlated CuO_2 planes. The scattering centers of poly-MTO mirror the inverse situation: the magnetic d^1 centers are placed in nonmagnetic ReO_2 planes. Therefore, poly-MTO might be a promising candidate to revitalize the discussion about the electron scattering mechanism in cuprates.

Poly-MTO was synthesized by auto-polymerization of MTO in flux at 120 °C during 48 h [2]. X-ray powder diffraction measurements suggest a two-dimensional $\{ReO_2\}_\infty$ layered structure. The missing $0\,0\,l$ series and the asymmetric shape of the $h\,k\,0$ reflections indicate ordering to occur solely in two dimensions.

Figs. 1a,b show the resistivity of $(CH_3)_{0.9}ReO_3$ on a semi–logarithmic and linear temperature scale, respectively. The high residual resistivity may be due to interlayer

*Corresponding author. Tel.: +49 821 5983356; fax: +49 821 5983227.
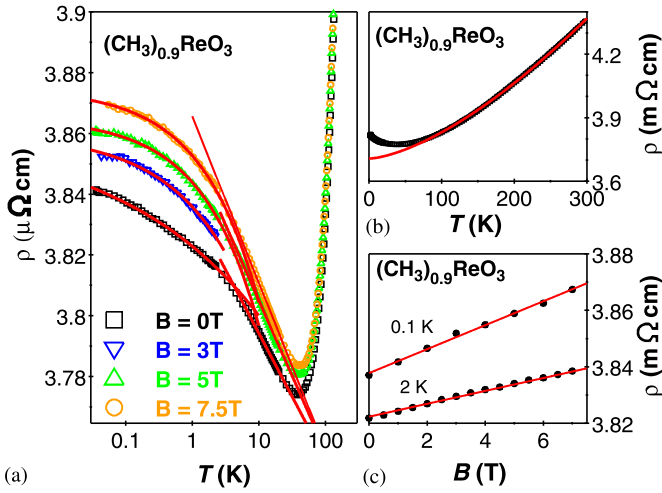 E-mail address: wolfgang.scherer@physik.uni-augsburg.de (W. Scherer).

Fig. 1. (a) Resistivity vs. log T in various magnetic fields B. The solid lines are logarithmic fits between 5 and 30 K and power-law fits below 2.5 K ($\Delta\rho \propto T^\alpha$ with $\alpha = 0.2; 0.4; 0.5; 0.5$ for $B = 0; 3; 5; 7\,T$, respectively). (b) Above 80 K the resistivity obeys a power-law $\Delta\rho \propto T^{1.5}$. (c) A positive magnetoresistivity is observed, similar to that seen in Ref. [3].
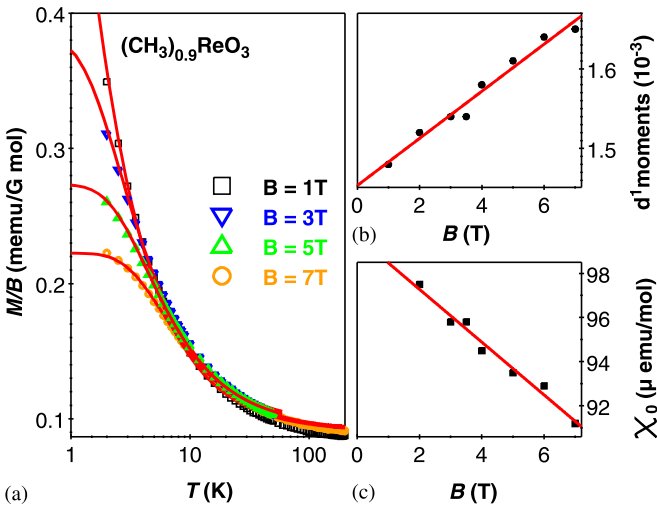

Fig. 2. (a) M/B of poly-MTO in several external magnetic fields. The solid lines are Brillouin-fits for a d^1 moment using the amount of Re(d^1) centers (b) and χ_0 (c) as fit parameters.

disorder [2]. The temperature dependence of the resistivity clearly exhibits a crossover from a metallic ($d\rho/dT > 0$) to an insulating ($d\rho/dT < 0$) behavior at about 30 K. Below 30 K a log($1/T$) divergence over one decade of T is observed, similar to that found in Zn-doped YBCO [3]. At lowest temperatures a crossover to a power-law dependence is detected, $\Delta\rho \propto T^\alpha$, with $\alpha \approx 0.5$ for $B > 3\,T$. In the insulating regime we observe a positive, linearly increasing magnetoresistivity as depicted for two temperatures in Fig. 1c.

Common scenarios predicting a log($1/T$) behavior like conventional Kondo impurities or 2D weak localization, cannot explain our experimental results. In both cases the logarithmic divergence of the resistivity should be reduced in the presence of a magnetic field.

For further information concerning the origin of the positive linear magnetoresistivity, temperature dependent magnetization measurements in various magnetic fields B were performed. In Fig. 2a the magnetization M divided by the applied magnetic field B is plotted vs. temperature. The solid lines are fits, which follow a Brillouin function, assuming that the paramagnetic behavior is only due to independent d^1 moments with a quenched orbital moment. The two fit parameters, the amount of Re(d^1) centers and the constant itinerant contribution $\chi_0 = \chi_{Pauli} + \chi_{Landau}$, are pictured in Figs. 2b and c, respectively. These two plots show clear evidence, that with increasing magnetic field, the amount of localized d^1 moments increases linearly with a simultaneous decrease of the itinerant electrons. This spatial localization of the d^1 moments at the Re atoms might be the origin of the unusual linear positive magnetoresistivity in poly-MTO.

This interpretation is also corroborated by the magnetic field dependence of the internal electric field gradient (V_{zz}) at the Re site. Analysis of specific heat data below 1 K with a crystal field model reveals a decrease of the Re nuclear quadrupole splitting with increasing magnetic field B, pointing to a decrease of V_{zz}. This indicates a reduction of the electronic and structural anisotropy at the Re site, which is in good agreement with density functional theory (DFT) geometry optimization of poly-MTO, where an increasing amount of localized d^1 centers leads to a reduction of strain in the ReO$_2$ planes [4].

The origin of the log($1/T$) and $\sqrt{T}$ dependence of ρ could be the Altshuler–Aronov [5] correction in the presence of a crossover from 2D to 3D diffusion at lower temperature. In a granular system a similar crossover is also expected between the high temperature incoherent tunnelling and the low temperature coherent intergrain tunnelling [6]. But at present we cannot exclude Kondo-like scenarios. In this respect we notice that the spatial localization of the d^1 moments in the ReO$_2$ planes might be a new approach for the understanding of the unusual resistivity of Zn-doped YBCO.

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