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Magnetic Transitions and Magneto-Transport in Epitaxial $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ Thin Films

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Abstract. Epitaxial thin films of the magnetic perovskite $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were prepared by dc-magnetron sputtering, structurally characterized by x-ray diffraction and their physical properties investigated by magnetization and electrical transport measurements. Ferromagnetic ordering appears in zero-field at 263 K, followed by a second transition into an antiferromagnetic state at 160 K. The zero-field resistivity has a semiconducting behaviour according to Mott's law and becomes quasi-metallic only within the ferromagnetic state, whose temperature range can be extended by applying an external magnetic field. The negative magnetoresistance effect increases systematically with decreasing temperature and reaches a value of 700 % at 1.5 K in a field of 12 T. For temperatures below 75 K we observed additionally a memory effect, showing up as a persistent, field induced lowering of sample resistivity.

1. INTRODUCTION

It is well known that LaMnO_3 is an antiferromagnetic (AFM) insulator, becoming a metallic conductor with a ferromagnetic (FM) ordering after doping with divalent ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) on the site of trivalent La [1]. The discovery of giant negative magnetoresistance (GMR) in $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ and the structurally related $\text{Nd}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ [2,3] increased considerably the interest in these compounds. Above the Curie-temperature T_C the doped La- and Nd-manganites are semiconductors and undergo at T_C a transition to a ferromagnetic metallic state. This state persists down to the lowest temperatures, while the maximum of the GMR effect shows up around T_C . The conductivity is supposed to emerge primarily from hopping of magnetic polarons above T_C [2,3], and from the double-exchange mechanism below T_C [4].

Another manganite compound, $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, behaves differently: neutron-diffraction studies of polycrystalline $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ revealed again ferromagnetism below 200 K, followed however by a coexistence of FM and AFM phases between 80 and 160 K, and a purely AFM phase below 80 K [5]. Magnetization and transport measurements on a high-quality single crystal confirmed the two transitions with a $T_C = 270$ K and a Néel temperature $T_N = 140$ K [6]. The conductivity was found to be metallic in the FM, and semiconducting in the AFM phase. Based on the jump-like resistivity increase at the transition from the FM to the AFM state, and the doping state with 0.5 charge carriers per Mn ion, it was speculated that the carriers in the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ undergo a charge ordering transition into an insulating, antiferromagnetic Wigner crystal [6]. The origin of this AFM behaviour of the Pr-manganite is related to the weakening of the ferromagnetic Mn^{3+} - Mn^{4+} double exchange coupling by the contraction of the chemical unit cell.

2. SAMPLE PREPARATION

Starting from a polycrystalline, disk-shaped target with nominal composition $\text{Pr}_{0.50}\text{Sr}_{0.50}\text{Mn}_{1.00}\text{O}_{\approx 3}$, thin films were deposited onto SrTiO_3 (1 0 0) substrates by dc-magnetron sputtering in on-axis geo-

metry. The target was prepared by mixing stoichiometric amounts of Pr_6O_{11} , SrCO_3 and MnCO_3 , calcinating (12 h at 900°C) and firing in air (24 h at 1250°C) with intermediate grinding. After pulverizing the reacted material, the powder was pressed into a 2 mm thick disk (38 mm diameter) with 40 MPa uniaxial pressure. The target was sintered in air for 24 h at 1250°C and an additional 6 h at 1350°C . During the sputtering of the films (120 min for a 3000 Å thick layer) the discharge current was 100 mA (-290 V) in a 1.5 hPa flowing O_2 atmosphere, and with a target-substrate distance of 20 mm. The SrTiO_3 substrates were glued with silver paint to an Al_2O_3 block, which was resistively heated up to $\approx 900^\circ\text{C}$ in order to achieve epitaxial film growth. The actual temperature at the substrate surface is estimated to be 200°C lower, while higher deposition temperatures resulted in polycrystalline films. Although the phase formation is complete after deposition, the films were kept an additional 30 min in 10 hPa O_2 at 900°C , and 30 min in 500 hPa O_2 at 600°C , in order to achieve homogeneous oxidation.

The x-ray diffraction spectra show that the films have no extra phases and are $\bar{c}$ -axis oriented with FWHM values for the Θ -scan of the (0 0 2) reflection between 0.19° and 0.39° . This indicates an excellent structural order, comparable to the 0.15° for the (2 0 0) reflection of the single crystalline substrates. The lattice constant is $3.818\text{ Å} \pm 0.002\text{ Å}$, in good agreement with the half c -axis length determined with neutron diffraction, i. e. 7.644 Å [5]. The difference by a factor of two arises from the existence of a superstructure, caused by deviations from the ideal cubic perovskite lattice. The half diagonal of the ab plane of the superstructure is 3.842 Å [5], in good agreement with the lattice constant of the SrTiO_3 substrate (3.905 Å). Therefore a strong in-plane texture can be expected, and $\bar{a}$ - or $\bar{b}$ -axis oriented film growth have not been observed. Scanning electron microscopy showed no trace of particles on the mirror-like film surfaces, while the average roughness of a $1\text{ }\mu\text{m}^2$ surface obtained with atomic force microscopy is 40 Å for a 3000 Å thick film. Composition analysis by means of Rutherford backscattering revealed the ratio $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1.25}\text{O}_{\approx 3}$ with an uncertainty of less than 10% for the cations. The correct concentration ratio of Pr^{3+} and Sr^{2+} is the essential precondition for the proposed charge ordering transition.

3. MAGNETIC PROPERTIES

The in-plane sample magnetization M was measured with a *Quantum Design* SQUID at fields between 20 mT and 5 T. Prior to applying a field, the sample was cooled from 300 K to 5 K in zero field in order to ensure equivalent preconditions for each measurement. The measurements were then performed by warming up to 300 K with subsequent cooling to 5 K, while Fig. 1 shows representative $M(T)$ curves for 20 mT, 50 mT and 1 T. Higher magnetic fields did not substantially alter the appearance of the data for 1 T.

The mean-field ferromagnetic Curie temperature T_C was determined by linearly extrapolating the $M(T)^{-1}$ data to zero. For 20 mT, close to the zero-field limit, we obtained $T_C = 263\text{ K}$, comparable to 270 K as reported for the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ single crystal [6]. By applying external fields, T_C is shifted slightly to higher temperatures. Although in the presence of fields above 20 mT no clear Curie-Weiss behaviour is found in the data, this shift is also reflected by the shift of T_C^* , defined as the high temperature inflection point of $M(T)$, see Fig. 1. The transition to the AF state occurs around $T_N = 160\text{ K}$ ($B_{\text{ext}}=20\text{ mT}$) as clearly indicated by the reduction of M with decreasing T . This implies that the Mn^{3+} and Mn^{4+} ions form independently two AF sublattices, if we assume different moments for Mn^{4+} ($4.0\mu_B$) and Mn^{3+} ($5.0\mu_B$), according to ref. [7]. With increasing external field the local magnetization maximum at T_N is less pronounced and shifts to slightly lower temperatures. The onset of the AF behaviour (Fig. 1) is at all fields also accompanied by a splitting of the cooling and the warming magnetization data, reflecting the occurrence of hysteresis effects. We note that the magnetic moment of the sample measured in 1 T at 5 K ($1.5 \cdot 10^{-3}\text{ emu}$) corresponds to a moment of only $0.62\mu_B$ per Mn ion, which is below the above mentioned values. The occurrence of relatively small Mn moments is however also known from La-manganites in form of thin films. At $T_A \approx 45\text{ K}$

(see Fig. 1) a small jump in the magnetization is observed, especially in the cooling runs. Two mechanisms may cause this jump: i) an ordering of the Pr^{3+} moments, and ii) the presence of magnetically ordering second phases. Concerning the first possibility, it is known that the Pr-moments in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ undergo antiferromagnetic ordering with a Néel temperature of 17 K [8], comparable to the 45 K observed for the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ films. Also in the $\text{Nd}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ system a susceptibility anomaly showed up at 30 K, which was associated with ordering in the Nd^{3+} lattice ($3.5 \mu_B$) [3]. A possible second phase could consist of amorphous traces of the Mn-rich PrMn_2O_5 with $T_N = 46$ K [9]. XRD reflections corresponding to the lattice constants of this compound were not detected for the sample under investigation, therefore we conclude the volume fraction to be probably below 10 %.

Figure 1: In-plane magnetic moment of a $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ film vs. temperature for fields of 20 mT, 50 mT, and 1 T in warming and cooling runs as indicated by arrows. The lines suggest the positions of (i) the Curie temperature T_C^* of ferromagnetism, (ii) the onset temperature T_N of antiferromagnetic correlations, and (iii) the low temperature anomaly T_A as discussed in the text.

Figure 2: Zero-field resistivity as a function of temperature of a $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ film. The fit functions are based on (1) thermally activated nearest neighbour hopping in the paramagnetic phase, (2) variable range hopping in the antiferromagnetic phase below 160 K, and (3) the empirical low temperature scaling $\rho \propto \exp(\Theta_1/(T + \Theta_2))$. The insert shows a detail of the metallic (ferromagnetic) regime.

4. CONDUCTIVITY MECHANISM IN ZERO FIELD

The resistivity measurements were performed on a stripe cut from a $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ film (10 mm long, 2.8 mm wide) after evaporating four gold contacts in one line across the sample and annealing them in air for 15 min at 700°C. These contacts had a resistance below 1 Ω and the measurements were carried out with an ac-bridge (28 Hz) at an effective excitation current of 0.3 μA . The current direction was within the ab plane of the film, parallel with the field axis of the cryostat, providing that the measurements of Sect. 5 were performed in the Lorentz-force free configuration.

Figure 2 shows the temperature dependence of the zero-field resistivity, with a magnification of the metallic-like region between 160 K and 220 K in the insert. This temperature dependence corresponds more or less to the single crystal data reported by Tomioka et al. [6], including comparable resistivity values, except for the smooth quasi-metallic to semiconducting transition at 160 K. Above the metallic-like region ($T > 250$ K) the resistivity scales with thermally activated nearest neighbour hopping ($\rho \propto \exp(U/k_B T)$, $U \approx 30 \text{ meV}$), which can be attributed to magnetic polarons, as assumed for the doped Nd- and La-manganites [2,3]. Below the metallic region ($50 \text{ K} < T < 160 \text{ K}$) a semiconducting behaviour is observed in accordance with Mott's law for variable range hopping (VRH), i. e. $\log \rho \propto (\Theta/T)^{1/4}$ [10]. Below 50 K the resistivity starts to deviate slightly from Mott's law and scales with $\log \rho \propto \Theta_1/(T + \Theta_2)$ ($\Theta_1 = 54.9 \text{ K}$, $\Theta_2 = 60.0 \text{ K}$). This temperature dependence resembles the susceptibility of an antiferromagnet above T_N and remains valid also in the presence of external magnetic fields, with slightly other values for Θ_1 and Θ_2 . Although there is no theoretical model for this $\rho(T)$ behaviour at $T < 50 \text{ K}$, the correspondence of the empirical relation with the data is excellent. The existence of two different scaling regimes below 160 K indicates again a change in magnetic ordering around 50 K, in accordance with the magnetization data.

5. GIANT NEGATIVE MAGNETORESISTIVITY

Figure 3: Field dependence of the magnetoresistivity at different temperatures. The curvature is positive for 298 K and negative for all temperatures below, indicating a unique GMR mechanism for $T \leq 250 \text{ K}$. Hysteretic behaviour is visible up to 150 K, with coercitive fields below 100 mT.

Resistivity measurements at fixed temperatures are shown in Fig. 3. Each curve consists of four field sweeps in the sense $0 \text{ T} \rightarrow 12 \text{ T} \rightarrow 0 \text{ T} \rightarrow -12 \text{ T} \rightarrow 0 \text{ T}$, starting with a zero-field cooled sample. The curves for 50 K, 100 K and 150 K exhibit a splitting due to hysteresis which becomes even more pronounced at 5 K. The data at 5 K are omitted, since the memory effect at low temperatures

(see Sect. 6) leads to further complications in interpreting the $\rho(B)$ changes. From the difference in curvature of the $\rho(B)$ data at 298 K and the lower temperature data we may conclude that a different mechanism is present in the paramagnetic and the ordered states. Double logarithmic plots of the field induced conductivity vs. field revealed the scaling:

$$\sigma(B, T) = \sigma(B = 0, T) + \sigma^*(T) \cdot B^\alpha \quad (1)$$

At 298 K the exponent $\alpha \approx 1.82$, a value close to 2, which was reported for the scattering of charge carriers by independent spins [11,12]. For all other temperatures up to 250 K, α varies between 0.99 and 1.20, while deviations are present mainly in the antiferromagnetic phase. Especially at 200 K, still in the ferromagnetic state the conductivity increase remains strictly linear for fields as high as 25 T [13]. It should also be pointed out that the scaling with Eq. 1 can only be a low field approximation, in the sense that saturation tendencies of the GMR effect, especially visible at the low temperature curves of Fig. 3, are not taken into account.

6. MEMORY EFFECTS

At temperatures below $T_M = 75$ K we observe an irreversible change of the sample resistivity after application of high external fields. The resistivity at e. g. 5 K, measured directly after zero-field cooling, is 17 % higher than the highest resistivities observed at the coercitive fields in a resistive hysteresis loop after a field sweep to 12 T. This result confirms similar observations of memory effects for $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films [12,14], as well as $\text{Pr}_{0.7}\text{Sr}_{0.04}\text{Ca}_{0.26}\text{MnO}_3$ bulk samples [15]. In these compounds, with comparatively high resistivities after ZF cooling, the field induced resistivity decay reaches several orders of magnitude. The most probable origin for this memory effect seems to be a persistent alteration of the spin structure, as found by neutron diffraction on $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ single crystals [16]. The antiferromagnetic spin arrangement, which is also the low-temperature spin structure of our $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ samples, was modified into a ferromagnetic structure, encouraging carrier transport by means of the double exchange mechanism. The temperature dependence of the memory effect was studied by first zero-field cooling of the sample to 4.2 K and applying an external field of 30 T. After sweeping the external field to zero, the resistivity was measured by warming (ρ_W) to room temperature and cooling (ρ_C) back to 4.2 K, where the memory effect $(\rho_C - \rho_W)/\rho_C$ reaches over 30 % (see Fig. 4).

Figure 4: Temperature dependence of resistivity in the remanent cryostat field after exposing the sample at 4.2 K to an external field of 30 T. The direction of warming and cooling is indicated by arrows, while the difference between both curves vanishes at 75 K.

As can be seen from the insert of Fig. 4, the difference between the two measurements vanishes above 70 K. We should note here, that the temperature of this irreversibility point does neither agree with the upper temperature limit for the low-temperature resistivity scaling from Sect. 4, nor with a characteristic anomaly of the magnetization curves in Sect. 3. However, it agrees well with the complete vanishing of a ferromagnetic signal in the neutron diffraction spectra of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powder at 80 K [5].

7. Conclusions

Thin films of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were prepared *in situ* with strong $\tilde{c}$ -axis orientation, and are characterized with respect to morphology and surface properties. The zero-field resistivity showed semiconducting behaviour according to nearest neighbour hopping in the paramagnetic, and variable range hopping in the antiferromagnetic state. Metallic conductivity was only observed in the temperature regime between 160 K and 220 K, where magnetization measurements reveal a ferromagnetic state. Surprisingly, the GMR mechanism in the antiferromagnetic state seems to be of a similar origin as for the ferromagnet, since both obey in good approximation the same scaling law for the conductivity increase, which is almost directly proportional to the strength of the externally applied field. We want to point out that for potential field sensing purposes it seems to be more interesting to use antiferromagnetic compounds since they exhibit GMR not only around the ferromagnetic transition temperature as the doped La-manganites, but at all temperatures below room temperature.

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