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Manuel Brando, R. Caciuffo, Joachim Hemberger, Alois Loidl, L. Malavasi, P. Ghigna

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Magnetic and electronic properties of $\text{La}_{0.85}\text{Na}_{0.15}\text{MnO}_{3-\delta}$

M. Brando^{a,*}, R. Caciuffo^a, J. Hemberger^b, A. Loidl^b, L. Malavasi^c, P. Ghigna^c

^a *INFN and Dipartimento di Fisica ed Ingegneria dei Materiali, Università Politecnica delle Marche,
Via Breccie Bianche, I-60131 Ancona, Italy*

^b *Experimental physik V, EKM, Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany*

^c *Dipartimento di Chimica Fisica, Università di Pavia, I-27100 Pavia, Italy*

Investigations of electronic and magnetic properties in the insulating systems LaMnO_3 in dependence on the oxygen content started more than 20 years ago [1,2]. It is well known that both oxygen excess and alkali-earth metal substitution for La induce holes on Mn sites, increasing Mn^{4+} content in the sample and therefore the valence state of Mn. When the amount of substitution is between 20% and 50% an insulator-to-metal transition (IM) occurs with simultaneous ferromagnetic ordering of the Mn spins [3]. The nature of the conductivity processes and of the resulting colossal magnetoresistance (CMR) can be understood in the framework of the double-exchange interaction between Mn^{3+} ($S=2$) and Mn^{4+} ($S=\frac{3}{2}$) ions [4]. It has been shown that in Ba-doped manganese oxides the Curie temperature T_C decreases by increasing the oxygen ion deficiency δ , amplifying the CMR effect [5]. The substitution with alkali metals like Na can induce twice the increase in valence state of Mn as compared to alkali-earth substitution. Since it was found that for divalent metal content close to 0.3 the samples show maximum T_C and minimum electrical resistivities ρ , our attention is

focused on those compositions that have a Na content close to 0.15 and different amounts of δ .

$\text{La}_{0.87}\text{Na}_{0.13}\text{MnO}_{3-\delta}$ (LNMO) samples were synthesised by solid-state reaction starting from stoichiometric amounts of La_2O_3 , Mn_2O_3 and Na_2CO_3 (Aldrich, 99.99%). Pellets were prepared from the thoroughly mixed powders and allowed to react at 900°C for a total time of at least 90 h, during which they were re-ground and re-pelletised at least twice.

Low reaction temperature and long firing times have been chosen in order to avoid Na evaporation during the synthesis procedure. According to EMPA and XRPD, the above synthetic procedures gave single-phase materials. To obtain different oxygen contents, the samples have been annealed under various T and $P(\text{O}_2)$ and then quenched to room temperature [2]. Thermogravimetric measurements were used to determine the oxygen content of each sample with a TA 2905 thermal analysis system.

The Ar-annealed sample crystallises in orthorhombic structure, while the other two samples did in the rhombohedral one. Lattice constants are shown in Table 1. These values agree with the results of early X-ray studies on sodium lanthanum orthomanganites [6,7]. By increasing the content of Mn^{4+} , the system changes from a highly distorted orthorhombic to a rhombohedral structure [8].

*Corresponding author. Tel.: +39-071-2204423; fax: +39-071-2204729.

E-mail address: manuel.brand@physik.uni-augsburg.de (M. Brando).

Table 1
Lattice parameters and transition temperatures

δ	Structure	a (Å)	b (Å)	c (Å)	T_R (K)	T_C (K)	Mn ⁴⁺ (%)
0.10	O	5.462	5.476	7.746	263	254	10
0.04	R	5.454	5.454	13.463	270	326	22
0	R	5.505	5.505	13.345	286	328	30

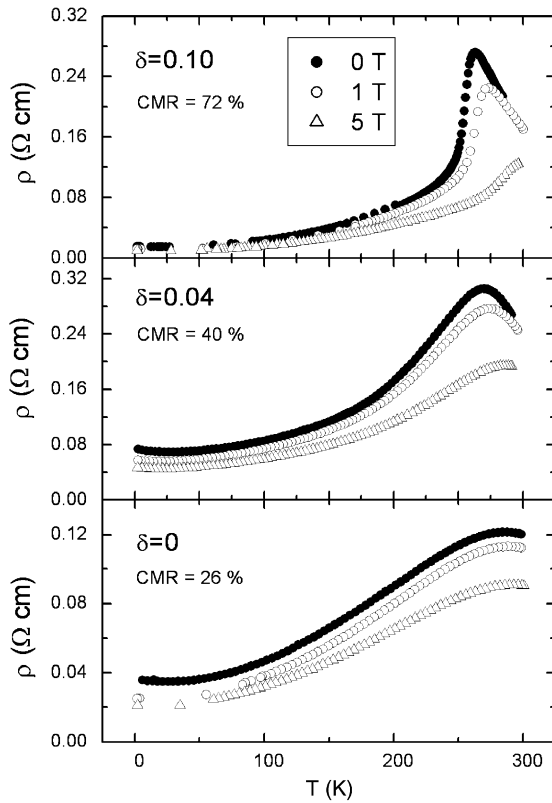


Fig. 1. Temperature dependence of the resistivity ρ at various magnetic fields.

In Fig. 1, ρ vs. T plots are given for all LNMO samples in three magnetic fields. All samples exhibit IM transition as T is decreased. The magnetic field greatly reduces the resistivity near T_C by shifting the resistivity maximum T_R to higher temperature, due to suppression of the spin scattering of e_g -state carriers [9]. T_R increases with increasing oxygen content. The CMR effect at T_R is of 72% in the first sample, 40% in the second sample and 26% in the last one. These values are slightly larger than in other thin films or bulk samples of the same composition [10].

The magnetic susceptibility measured with three different magnetic field amplitudes is shown in Fig. 2. The Curie temperature T_C is clearly lower only for the Ar-annealed sample, where the saturation magnetisation

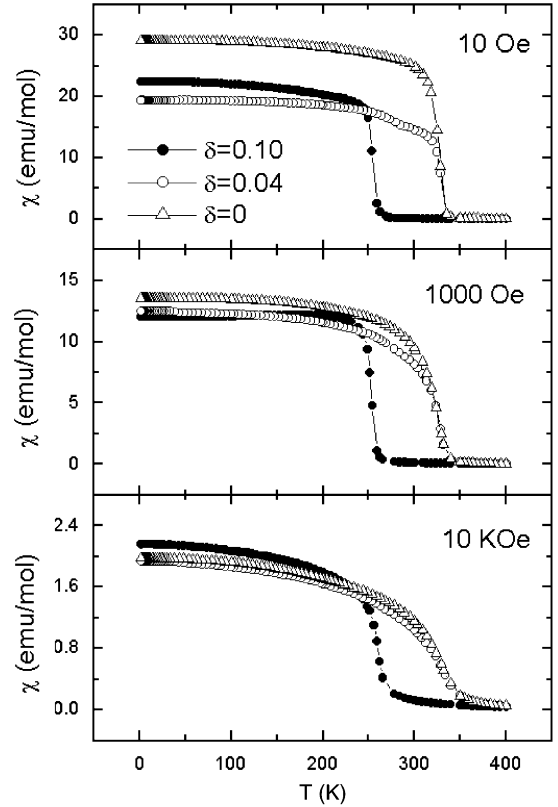


Fig. 2. Magnetic susceptibility as a function of temperature for the three samples at 10 Oe, 1 and 10 kOe.

$M_S = 3.85 \mu_B$ at 1.4 K and 10 kOe has the larger value, indicating the larger concentration of Mn³⁺. This result is similar to that obtained for La_{1-x}Sr_xMnO₃ with $x = 0.175$ [9]. The increasing of T_C with the Mn⁴⁺ content corresponds with the resistivity results and confirms the correlation between magnetoresistance and magnetisation of the specimens. T_C is about 50 K higher than T_R .

In conclusion, it can be confirmed that the direct relation between the oxygen deficiency δ , magnetisation and the magnetoresistance in these specimens. This behaviour is based on the combination of the valence of Mn and the crystal structure, which change systematically with δ . As δ decreases, more Mn⁴⁺ ions can contribute to double-exchange mechanisms raising therefore the transition temperatures.

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