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MAGNETIC PROPERTIES OF $La_{0.67}Ca_{0.33}(Co_xMn_{1-x})O_3$

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Detailed study of temperature dependencies of AC susceptibility, magnetization and electrical resistance was performed on $La_{0.67}Ca_{0.33}(Mn_{1-x}Co_x)O_3$ ceramics for x = 0.01, 0.03, 0.06, 0.1, 0.15. All compounds undergo the paramagnetic-ferromagnetic phase transition between 240 K, and 60 K. Basic magnetic characteristics, like the Curie temperature and the saturated magnetization, decrease with Co-substitution Very weak frequency dependence of the peak in AC susceptibility $\chi''(T)$, hysteretic behaviour between zero-field-cooled magnetization regime and field-cooled magnetization regime are typical features of all compounds. Anomalies in electrical resistance connected with the ferromagnetic transition at the Curie temperature, the insulator-metal transitions and the re-entrant metal-isolator transition are field dependent pointing to magnetic origin of these transitions. The colossal magneto-resistance was observed for all compounds. Sintering in different atmosphere (O_2 or Ar) affects electrical resistance significantly.

Keywords: mixed-valence perovskite manganese oxides, magnetic properties, colossal magneto-resistance

1 INTRODUCTION

The transition metal oxides are materials with a broad spectrum of electronic properties, which is given by variability of oxidation states and coordination environments. In perovskite or perovskite-related systems transition metal ions of $3d^n$ type (the "iron" series from titanium to copper) occupy positions with octahedral coordination by oxygen atoms. Recent works performed on the mixed-valence perovskite manganese oxides have been driven by a desire to understand and exploit the large negative magneto-resistance and magnetocaloric effects. Ca-doped lanthanum manganites were first reported during a study of ionic ferromagnets of the general composition $La_{1-x}M_xMnO_3$, where M was a divalent cation Ca, Sr, Ba Cd or Pb [1]. The compound $La_{1-x}Ca_xMnO_3$ is metallic ferromagnet for $0.23<x<0.45$; for all other calcium concentrations x, the ground state is insulating [2, 3]. A mixed valence of Mn^{3+}/ Mn^{4+} and the double exchange interaction is needed for both metallic behaviour and ferromagnetism in these materials [2].

Our recent studies [4] and [5, 6] were focused on the effect of Fe or Co substitution on crystal structure, magnetic and electrical transport properties of $La_{0.67}Ca_{0.33}Mn_{0.67}{}^{57}Fe_{0.94}O_3$ or $La_{0.67}Pb_{0.33}(Mn_{1-x}Co_x)O_3$ ceramics. The substitution does not change the crystal structure significantly. A decrease in the lattice parameters and the volume of the unit cell were observed with increasing Co-content in $La_{0.67}Pb_{0.33}(Mn_{1-x}Co_x)O_3$ [5]. This change can be assigned to the smaller ion size of Co^{3+} compared to Mn^{3+}. Throughout this study we assumed, as claimed in literature that trivalent Co replaces trivalent Mn sites. Our results confirmed that the substitution strongly affects magnetic and transport properties of the parent compound. Reduction of the double exchange interaction results in reduction of magnetization and the Curie temperature. In this paper we present detailed studies of AC susceptibility, temperature and field dependence of magnetization and electrical resistance of $La_{0.67}Ca_{0.33}(Mn_{1-x}Co_x)O_3$ ceramics sintered in argon or in oxygen.

2 EXPERIMENTS

Single phase samples of $La_{0.67}Ca_{0.33}(Mn_{1-x}Co_x)O_{3-\delta}$ for x = 0.01, 0.03, 0.06, 0.1, 0.15 were prepared in a two step procedure [7]. The preparation of the ceramic samples followed the malic acid gel method. Prepared gels were ground, dried and then calcined. The powders were compacted into discs. Discs were either sintered for 8 hours at 1200°C or at 1300 °C in flowing argon or oxygen. Samples of 1 mm x 1 mm x 15 mm were cut from the sintered discs for resistance and magnetic measurements by a wire saw. X-ray diffractograms were measured on an X'pert Pro (Panalytical) with Ni-filtered Cu K_α radiation (40 kV, 45 mA). Magnetization measurements were performed in magnetic fields up to 5 T and in the temperature range between 1.8 K and 350 K by a MPMS - SQUID magnetometer (Quantum Design, USA). Electrical resistance measurements were carried out on a Physical Properties Measuring System (PPMS) equipment (Quantum Design, USA) using the AC-transport method in magnetic fields up to 9 T and in the temperature range between 1.8 K and 300 K.

3 RESULTS AND DISCCUSION

The paramagnetic-ferromagnetic phase transition is accompanied by a sharp peak in both in phase component $\chi'(T)$ and out of phase component $\chi''(T)$ of AC susceptibility (Fig. 1). The Curie temperatures T_C, determined as a minimum on $d\chi'/dT(T)$ correspond very well with results obtained for DC susceptibility. The sharp peak in $\chi''(T)$ is only weakly frequency dependent and the position of the peak does not change significantly with the frequency.

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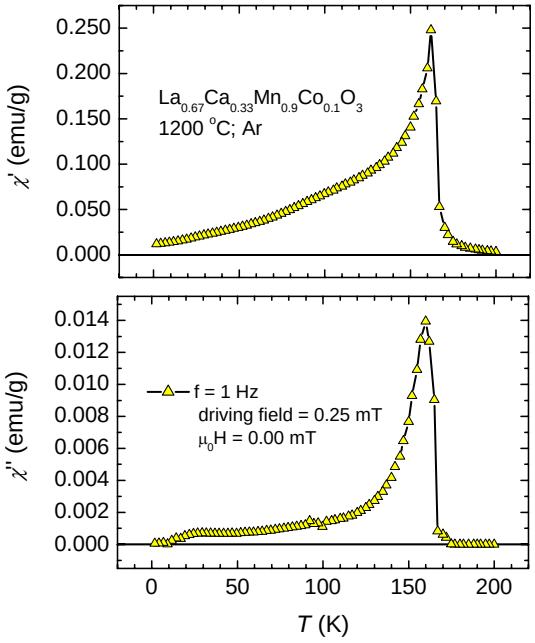

Fig. 1. The temperature dependence of $\chi'(T)$ and $\chi''(T)$; the earth-magnetic field was compensated ($\mu_0 H$=0).

Variation of the magnetization with temperature was studied in magnetic fields with induction $\mu_0 H$ = 0 (the actual field was less than 0.01 mT, the earth-magnetic field was compensated) 1 mT and 5 mT. All samples underwent a paramagnetic (PM) to ferromagnetic (FM) transition. The paramagnetic-ferromagnetic phase transition is very sharp (Fig. 2). The Curie temperature T_C was determined as a minimum on $d\mu/dT(T)$ dependence for measurements at $\mu_0 H$ = 0. Substitution of Mn by Co leads to a monotonous decrease in T_C and to a broadening of the magnetic transition. The magnetic pole inversion at the compensation temperature T_{comp} was observed for ZFC regime (Fig. 2 and Fig. 3). The hysteretic behaviour between magnetization measurements in ZFC and FC regimes in low magnetic fields is typical feature of $La_{0.67}Ca_{0.33}(Mn_{1-x}Co_x)O_3$ materials and is more pronounced with increasing Co substitution (Fig. 3). The $\mu(T)$ curves measured in ZFC regime start to deviate from the $\mu(T)$ curve measured in FC regime at the bifurcation temperature T_b, which is very close to T_C. The region of the irreversible magnetization processes is enlarged with Co-substitution. This behaviour is similar to the one observed in magnetic hysteresis loops (Fig. 5). The field dependence of the bifurcation temperature T_b is weak.

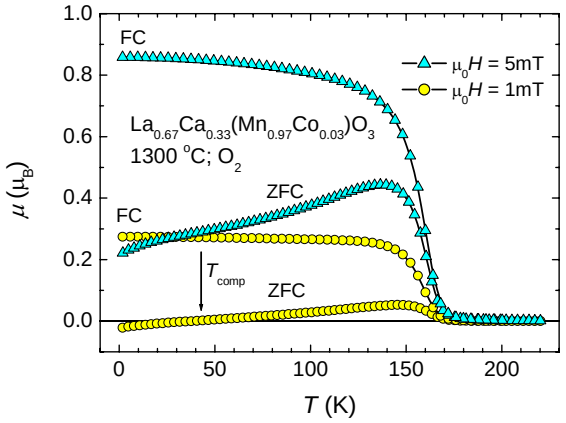

Fig. 3. The hysteretic behavior between magnetization measurements in ZFC and FC regimes

High temperature magnetic susceptibility χ follows the Curie Weiss law $\chi = C/(T - \Theta)$ for all samples and temperatures which are at least 60 K higher than T_C (Fig. 4). C is the Curie constant and Θ is the Curie-Weiss temperature. The value of Θ is usually larger than the value of T_C (Θ = 218 K and T_C = 203 K for x = 0.03 sintered in Ar). Both temperatures decrease with Co – substitution and the difference Θ - T_C increases with Co – substitution. This indicates the presence of magnetic inhomogeneities. The typical figure of $1/\chi(T)$ dependence is shown in Fig. 4.

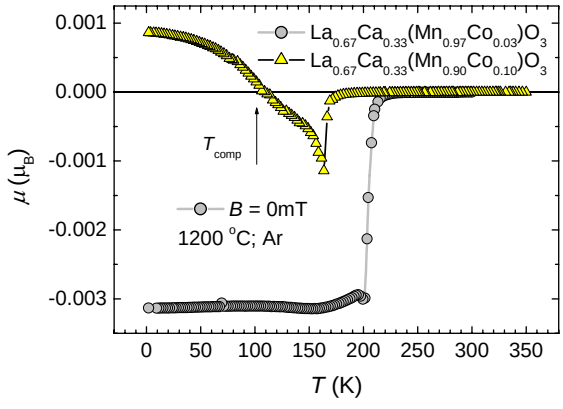

Fig. 2. Variation of the magnetization with temperature in zero magnetic field

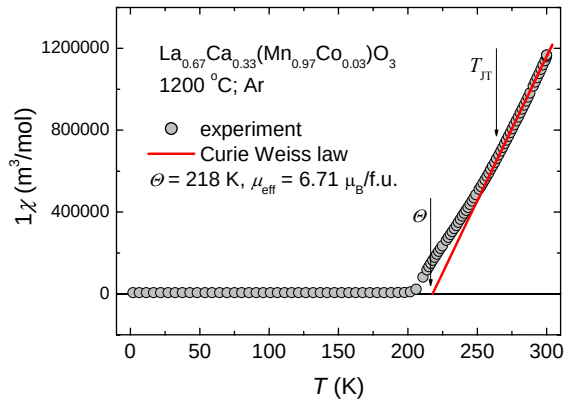

Fig. 4. The typical $1/\chi(T)$ dependence for low value of x

The small maximum above Θ may indicate short range magnetic ordering in the PM state. At a certain temperature T_{JT} the slope of $1/\chi(T)$ dependence changes, indicating the Jahn-Teller transition [5].
The temperature of the Jahn-Teller transition T_{JT} decreases with Co – doping.

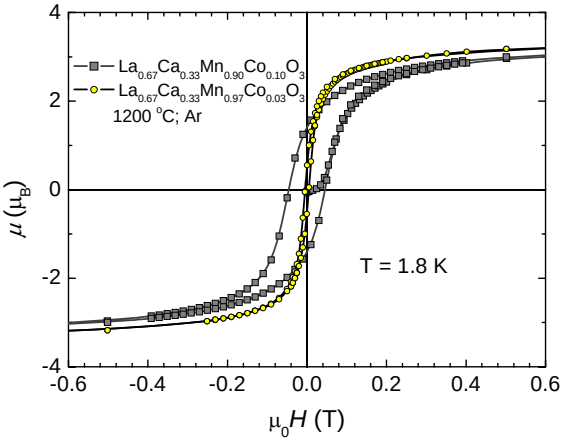

Fig. 5. Variation of the magnetization loops with concentration of Co

The initial magnetization increases first linearly with the rising magnetic field, then increases very steeply and in fields with induction of about $\mu_0 H$ = 0.2 T starts to saturate (Fig. 5). Depending on the Co - substitution the magnetization saturates between $\mu_0 H$ = 1 T and $\mu_0 H$ = 3 T and nearly complete saturation is reached in the field with induction of about $\mu_0 H$ = 5 T. Saturation occurs at higher magnetic fields as the Co amount increases. The area of the hysteresis loops, the remanent magnetization μ_{rem} and the coercive field H_c increase with Co-doping. It seems that the anisotropy of the system increases with Co – doping, which may be related to the strong magnetic anisotropy of the Co ion itself.

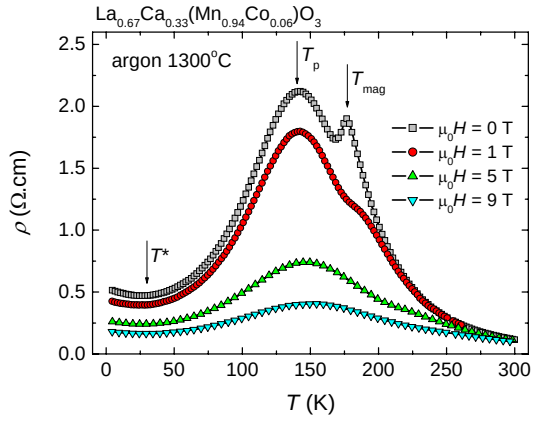

Fig. 6. Variation of electrical resistivity with magnetic field for sample sintered in Ar

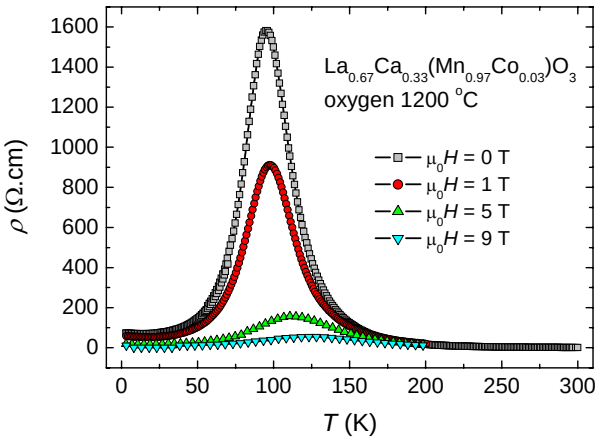

Fig. 7. Variation of electrical resistivity with magnetic field for sample sintered in O_2

Very typical variation of the electrical resistivity $\rho(T)$ at different magnetic fields and for different samples sintered either in Ar or in O_2 are shown in Fig. 6, Fig. 7 and Fig. 8. Maxima in the resistivity appear at T_{max} close to T_C for samples with x = 0.03 and 0.06 sintered in Ar (Fig. 6). For all remaining compounds only a maximum or local maximum at T_p corresponding to the insulator – metal transition (I – M) was observed (Fig. 6 and Fig. 7). The re-entrant metal – insulator (M – I) represented by a minimum at T^* is characteristic feature of all samples (Fig. 6). Sharp increase of resistivity at low temperature is characteristic feature for samples with x = 0.1 and 0.15 (Fig. 8). These samples have an insulator character at low temperatures. Two characteristic temperatures T_p decrease with Co – doping from 240 K to about 75 K for Ar-sintered samples and from 140 K to about 60 for O_2-sintered samples. Peaks at T_p are much narrow for O_2-sintered samples. On the other hand the re-entrant temperature T^* increases with Co – doping. The applied magnetic field smears out the anomalies at T_C and T_p and increases the value of these temperatures. The re-entrant temperature T^* is reduced by the applied magnetic field.

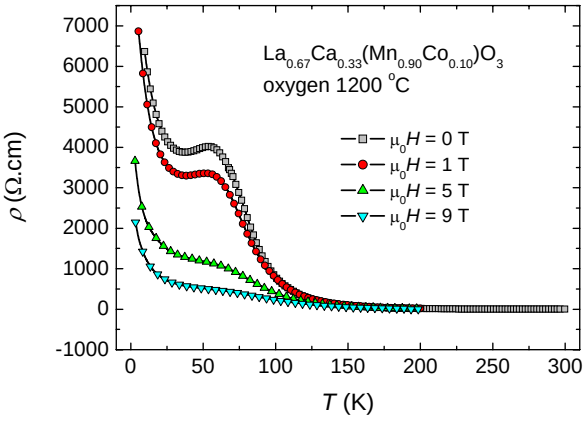

Fig. 8. Variation of resistivity with magnetic field

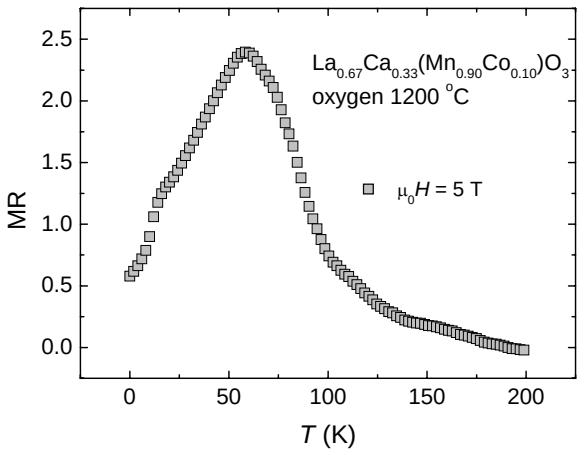

Fig. 9. Variation of magneto-resistance with temperature

The temperature dependence of magneto-resistance (MR), defined as $\Delta\rho/\rho_H = (\rho_0 - \rho_H)/\rho_H$ is plotted in Fig. 8; ρ_0 is the resistivity measured at $\mu_0 H = 0$ and ρ_H is resistivity measured at $\mu_0 H = 5$ T, [5]. A large magnetoresistance (MR) peak is observed for all compounds at the magnetic phase transition. The MR increases is still very high at $T = 1.8$ K Fig. 8.

4 CONCLUSIONS

The ferromagnetic character of the parent compound still remains after Co-doping for whole concentration range. This is mainly due to the double exchange mechanism (DE) that arises from the ratio of Mn^{3+} and Mn^{4+}. All compounds undergo a paramagnetic-ferromagnetic phase transition. With respect to un-doped composition, the Curie temperature T_C, the paramagnetic Curie temperature Θ, the effective magnetic moment μ_{eff} and the saturated magnetization μ_s decrease with increasing Co-doping. The decrease in the magnetic characteristics indicates a dilution effect by Co^{3+} ions, which are mostly in the low spin state with $S = 0$. Moreover, the Co^{3+} ion will also fix the nearest neighbour spins, reducing mainly the population of hoping electrons and available hoping sites. Double exchange (DE) is then progressively suppressed, weakening the ferromagnetism and metallic behaviour of the samples. Hysteretic behaviour between ZFC mode and the FC mode is a typical feature of all compounds. The ferromagnetic transition is accompanied by an anomaly in electrical resistance for all compounds. The metal - insulator transitions at T_p coincide with the relevant Curie temperatures and only one peak at T_p was observed for all samples sintered in O_2 and samples sintered in Ar with x = 0.10 and 0.15. The peak in resistivity at T_p is much broader for samples sintered in Ar. The short range magnetic ordering and the magnetic correlations existing on the scale of the hoping distance (circa 1 nm) have to be consider to understand the maxima in the $\rho(T)$ at I-M transitions. The resistivity is also affected by changes in DE induced by Co-doping. Besides of the DE interaction and the observed weakening in the ferromagnetic character of the samples there is also a transition from conductive to insulating behaviour at low temperatures. The intermediate state below this re-entrant transition is characterized not only by the tunnelling inter-grain mechanism but also the observed enhancement of resistivity arises from an effective Coulomb barrier of electrostatic origin. The high-temperature I-M transition at T_p, observed for all compounds decreases with Co-doping and the re-entrant temperature T^*, observed at low temperatures, increases with Co-doping. All characteristic features of $\rho(T)$ are strongly magnetic field dependent confirming magnetic origin of all anomalies in the system. The applied magnetic field smears out the anomaly at T_C, increases both T_p and T_C but on the other hand decreases T^*. All studied samples show large magnetoresistance, with maximum located at T_p.

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