Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

Magnetic and Transport Properties of $La_{0.67}Pb_{0.33}(Mn_{1-x}Co_x)O_3$

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Detailed studies of temperature dependences of magnetization, AC susceptibility and electrical resistance were performed on $La_{0.67}Pb_{0.33}(Mn_{1-x}Co_x)O_3$ ceramics with $x = 0.01$ and 0.1. Typical features of both compounds are the hysteretic behavior between the zero-field-cooled magnetization regime and the field-cooled magnetization regime, a very weak field dependence of a maximum in zero-field-cooled magnetization and practically no frequency dependence of the peak in AC susceptibility $\chi''(T)$. Anomalies in the electrical resistance connected with the ferromagnetic transition at T_C, the insulator-metal transitions at T_p and the re-entrant metal–isolator transition at T^* are field dependent pointing to magnetic origin of these transitions. Colossal magnetoresistance was observed in both compounds.

PACS numbers: 71.30.+h, 72.80.Ga, 75.20.Hr, 75.30.Et, 75.30.Vn

1. Introduction

The mixed-valence perovskite manganese oxides have been studied for almost 60 years. Recent work has been driven by a desire to understand and exploit the large negative magnetoresistance effect [1]. Pb-doped lanthanum manganates were first reported during a study of ionic ferromagnets of the general composition $(La_{1-x}M_x)MnO_3$, where M was a divalent cation, either Ca, Sr, Ba Cd or Pb [2]. A mixed valence of Mn^{3+}/Mn^{4+} is needed for both metallic behavior and ferromagnetism in these materials [3]. Pb-doped lanthanum manganates with partial substitution of Mn by transition metal cation such as Fe, Co or Ni were investigated [3–5]. Our recent study [6] revealed that $La_{0.67}Pb_{0.33}(Mn_{1-x}Co_x)O_{3-\delta}$ ceramics with $x \leq 0.15$ crystallize in rhombohedral crystal structure (space group $R\bar{3}c$). All compounds undergo a paramagnetic–ferromagnetic phase transition between 225 K and 335 K. The Curie temperature T_C, the effective magnetic moment μ_{eff}, and the saturated magnetization μ_s decrease with increasing Co-doping. The

ferromagnetic transition is accompanied by an anomaly in the electrical resistance. The high-temperature insulator–metal (I–M) transition at T_{p} decreased with Co-doping but the re-entrant temperature T^*, observed at low temperatures, increases with Co-doping. The metal–insulator transitions do not coincide with the relevant Curie temperatures. A large magnetoresistance (MR) peak of about 15% was observed for all compounds at T_{C} ($\mu_0 H = 1$ T). Here we discuss possible spin-glass and cluster-glass behavior. We extended magnetoresistance measurements to magnetic field with induction of 9 T.

2. Experimental

The preparation of the ceramic samples followed the malic acid gel method and in details is described in [6]. Details of the crystal structure and characterization of both samples were published in [6]. Magnetization and AC susceptibility measurements were performed in magnetic fields up to 5 T and in the temperature range between 1.8 K and 380 K by a commercial SQUID magnetometer (MPMS - Quantum Design). Electrical resistance measurements were carried out on PPMS equipment (Quantum Design) using the AC-transport method in magnetic fields up to 9 T and in the temperature range between 1.8 K and 360 K.

3. Results and discussions

Figure 1 shows the temperature dependence of the magnetization M for both compounds measured in the zero-field-cooled (ZFC) regime and the field-cooled (FC) regime at different magnetic fields. Both compounds undergo paramagnetic–ferromagnetic phase transition. The ferromagnetic character of the undoped compound still remains after Co-doping [6]. This is mainly due to the double-exchange (DE) mechanism that arises from the ratio of Mn^{3+} to Mn^{4+}. Magnetization in the ZFC regime for $x = 0.01$ below T_{C} remains at first constant and then at T_{AF} decreases with decreasing temperature. Below this temperature the strength of the DE interaction between Mn^{3+} and Mn^{4+} ions, mediated by Mn–O–Mn bonds, is reduced and the superexchange antiferromagnetic interaction is dominant. We assumed that trivalent Co replaces trivalent Mn sites. Co-doping induces antiferromagnetic coupling due to the reduction of DE interaction, and/or a dilution

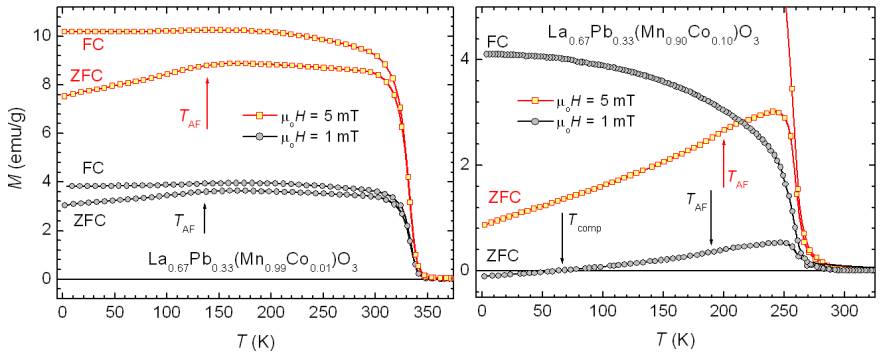

Fig. 1. ZFC and FC magnetization measured in two different magnetic fields.

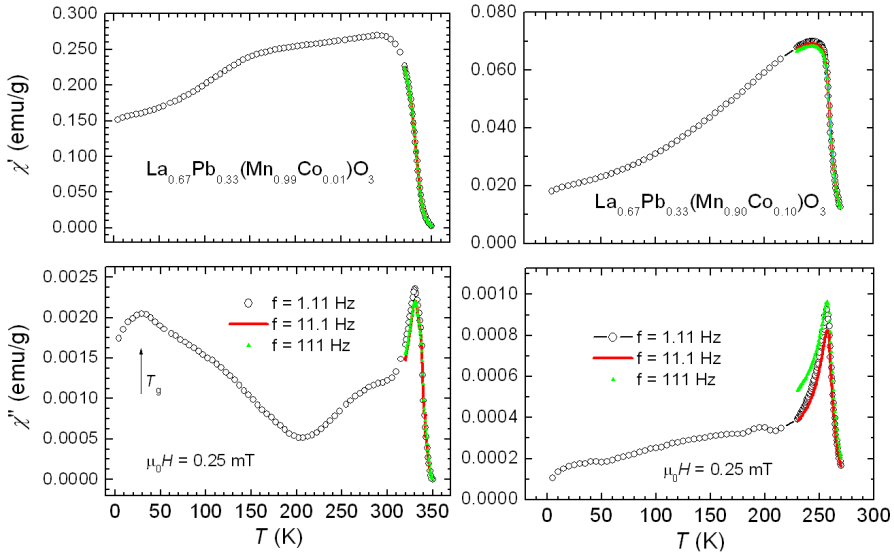

Fig. 2. Temperature variation of AC susceptibility measured for both compounds.

effect by Co^{3+} ions, which are mainly in the low-spin state with $S = 0$ [6]. As a consequence T_C is reduced and T_{AF} rises with doping (see Fig. 1). Similarly as for $x = 0.15$ [6] compensation temperature T_{comp} was observed for material with $x = 0.10$ in the ZFC regime. The hysteretic behavior between ZFC and FC regimes in low magnetic fields is a typical feature of this system [6]. Magnetization bifurcates at the temperature of irreversibility T_{irr} which is very close to T_C. For the compound with $x = 0.01$ the FC magnetic curves show a nearly constant value of magnetization below T_{irr} (Fig. 1). Such behavior is typical of canonical spin glass systems. On the other hand, FC magnetization continues to increase strongly below T_{irr} for $x = 0.10$, a typical feature of cluster glass systems. A small cusp below T_C which is stronger for $x = 0.10$ is field independent. The in-phase component $\chi'(T)$ of the AC susceptibility follows $M(T)$ data and T_{AF} is seen in Fig. 2. The Curie temperatures T_C determined as a minimum on $d\chi/dT(T)$ correspond very well with the results published for DC susceptibility in [6]. The characteristic feature of out-of-phase component $\chi''(T)$ of AC susceptibility is a sharp peak below T_C which is only weakly frequency dependent and the position of the peak does not change with frequency. $\chi''(T)$ for $x = 0.01$ at first decreases, showing a shoulder, a minimum, and a peak at T_g, which may indicate the freezing temperature.

The transition at T_C is accompanied by an anomaly in the electrical resistance $\rho(T)$ (Fig. 3a,b). Anomalies connected with the insulator–metal transitions at T_p and the re-entrant transition at T^* become stronger with Co-doping [6]. Sensitivity of the anomalies at T_p and T^* in $\rho(T)$ on magnetic field indicates their magnetic origin. The applied field smears out the anomalies [6]. The difference

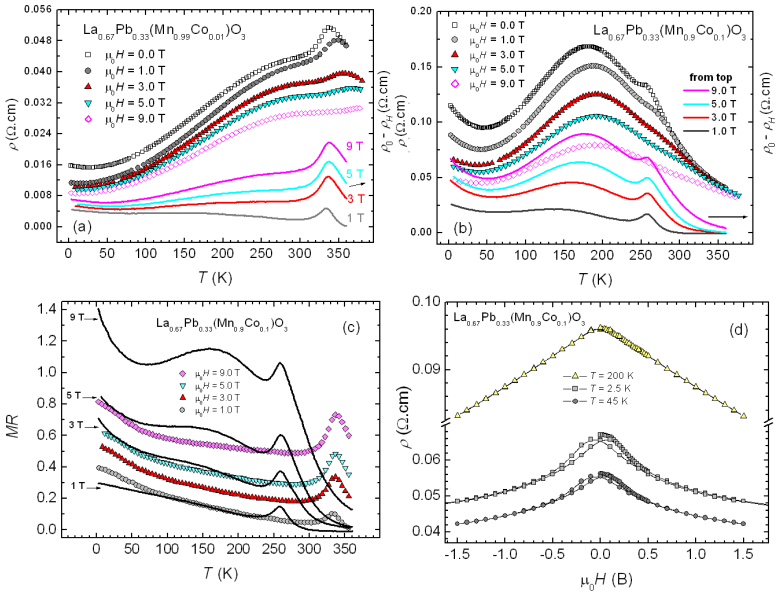

Fig. 3. Variation of electrical resistance with magnetic field: temperature dependence (a) and (b); magnetoresistance (c); hysteresis behavior at different temperatures (d).

$\rho_0 - \rho_H$ is large not only at T_C but at T_p and below T^*. The effect becomes stronger with Co-doping [6]. Similar effects are observed for magnetoresistance $MR = \Delta\rho/\rho_H = (\rho_0 - \rho_H)/\rho_H$ (Fig. 3c). The low-field magnetoresistance shows a butterfly curve at low temperature with the resistance greater for the virgin state. The hysteresis loop is reversible with the peak resistance corresponding to the coercive field (Fig. 3d).

Acknowledgments

This work was supported by the Projects SK-05/06-KE-005 (ASO), APVT-51-031704 and VEGA 2/7184/27.

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