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Magnetic Properties of $La_{0.9}Ag_{0.1}(Mn_{1-x}Co_x)O_3$ under Pressure

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Abstract. In our paper we report on magnetic properties of $La_{0.90}Ag_{0.10}(Co_xMn_{1-x})O_3$ ferromagnetic ceramics (x = 0.00 and0.03) which were studied in pressures up to 0.9 GPa. Magnetic transition at the Curie temperature T_C is accompanied with metal insulator transition with a maximum at T^* which is shifted to lower temperature with applied magnetic field. The Curie temperature is decreasing with substitution of Co for Mn and is ranging from 178 K to 126.5 K. Hydrostatic pressure increases T_C for sample with x = 0.03 nearly linearly with the pressure coefficient $dT_C/dp = 5.7$ K/GPa. Hysteresis loop is affected marginally; μ_s increases and H_c decreases with pressure.

1 Introduction

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 with the general composition $La_{1-x}M_xMnO_3$, where M was a divalent cation, e.g. Ca^{2+}, Sr^{2+}, Ba^{2+} Cd^{2+} or Pb^{2+} [1]. The compound $La_{1-x}Ca_xMnO_3$ is a metallic ferromagnet for $0.23<x<0.45$; for all other calcium concentrations x, the ground state is insulating [2, 3]. Both, the mixed valence state Mn^{3+}/ Mn^{4+} and the double exchange (DE) interaction are needed for metallic behaviour and ferromagnetism in these materials [2]. Replacing the divalent alkali-earth metals by monovalent elements, such as Na, K and Li, also leads to similar phenomena in manganites. Recently substitution of Ag for La in $LaMnO_3$ leads to another series of novel oxides exhibiting ferromagnetic metal to paramagnetic insulators transition with high CMR effect at room temperature [4-15]. In our paper we study magnetic properties of $La_{0.90}Ag_{0.10}(Co_xMn_{1-x})O_3$ ferromagnetic ceramics at ambient pressure and high hydrostatic pressure.

2 Experimental

The preparation of the ceramic $La_{0.90}Ag_{0.10}(Mn_{1-x}Co_x)O_{3-\delta}$ (x = 0.0 and 0.03) followed the malic acid gel method. The solution was slowly evaporated until a gel was formed. The gels were ground, dried at 150 °C in vacuum and then calcinated at 800 °C in flowing air. The powders were compacted into discs of about 10 mm diameter and a thickness of 1 mm with a pressure of 50 bar and sintered at 1200 °C in O_2 atmosphere for 10 hours. The microstructure of the samples was examined by means of scanning electron microscopy. Crystallites with diameters of about 2 μm, partly melted on the edges and connected to larger agglomerates can be seen in electron microscopy (Fig.1.). EDAX analysis revealed Ag particles randomly spread in ceramic. The number of particles is small and Ag - particles do not effect magnetic properties of samples. X-ray powder diffractions were measured using the X'pert Pro (Panalytical) diffractometer with Ni-filtered Cu K_α radiation (40 kV, 45 mA). X-ray diffraction revealed that sample consists of a single phase which adopts rhombhoedral crystal structure (space group $R\bar{3}c$) with lattice parameters $a = 0.5514(3)$ nm, $c = 1.3338(7)$ nm for x = 0.0 and $a = 0.5515(6)$ nm, $c = 1.3334$ nm for x = 0.03 (Fig.2.). Magnetization measurements were performed by a SQUID magnetometer MPMS XL−5. In the case of high pressure measurements the sample was placed in a pressure cell during all magnetization measurements. A piston cylinder type of the CuBe pressure cell was filled up by a mixture of mineral oils serving as hydrostatic pressure transmitting medium and operating up to 1.2 GPa. Actual pressure was determined in-situ from the pressure dependence of the superconducting transition temperature $T_c(p)$ of an inserted high-purity lead sample. Pressure in the clamped CuBe cell increases with increasing temperature and a correction on actual pressure at the actual temperature was made. The pressure CuBe cell is permanently present in all detecting coils of the SQUID magnetometer and hence, it practically does not

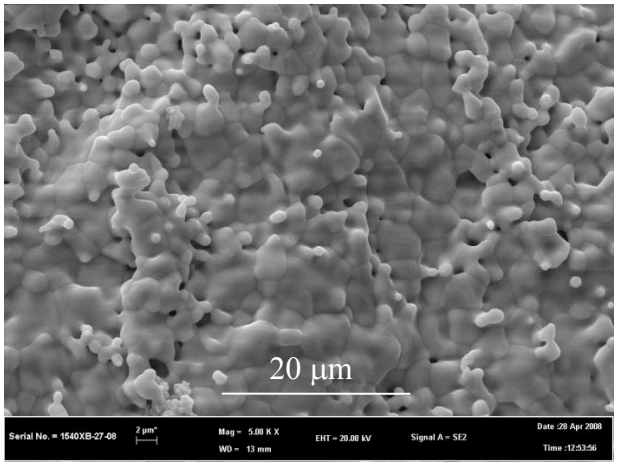

Fig. 1. Scanning electron micrograph of a $La_{0.90}Ag_{0.10}MnO_3$ sample sintered at 1200°C in O_2.

contribute to overall magnetization of the studied samples. Experimental data presented in our paper were not corrected for a signal of the pressure cell. The pressure was changed at room temperature only and the experiments were started at the highest pressure that was then gradually decreased in two or three steps. All pressure induced changes of magnetization were reversible. Electrical resistance measurements were performed by the four probe method in the PPMS equipment.

3 Results and discussion

Temperature dependence of resistivity which is shown in Fig.3 clearly displays the insulator metal transition at about $T^* = 121$ K. The insulator metal transition appears near the magnetic phase transition. The insulator metal transition is characteristic feature of many ferromagnetic manganites $La_{1-x}M_xMnO_3$ with perovskite like crystal structure (M is a divalent cation). Applied magnetic field

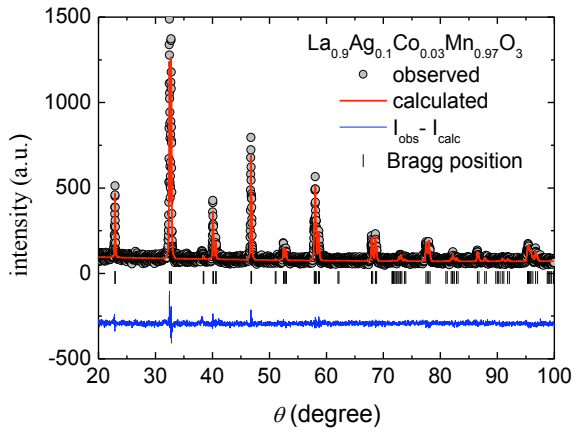

Fig. 2. X-ray powder diffraction pattern from $La_{0.90}Ag_{0.10}Co_{0.03}Mn_{0.97}O_3$ sample sintered at 1200°C in O_2. The measured points are indicated by circles, calculated by the overlaying red line. The lower curve shows the difference between the observed and calculated diffraction patterns.

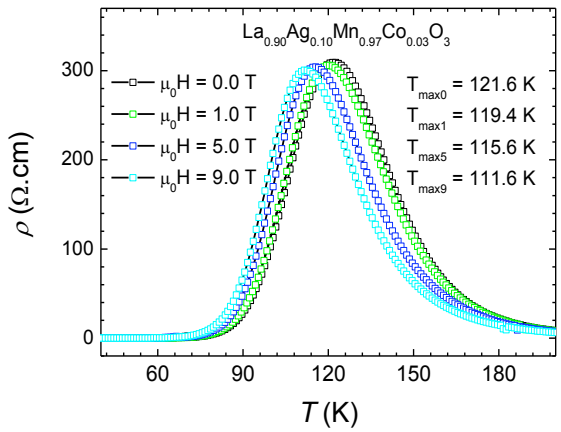

Fig.3. Temperature dependence of the resistivity of $La_{0.90}Ag_{0.10}Co_{0.03}Mn_{0.97}O_3$ ceramic at various applied magnetic field.

shifts T^* to lower temperature but the shape of resistivity maximum is not affected by magnetic field up to 9 T. This behaviour is unusual for manganites where colossal magnetoresistance appears very frequently.

Temperature dependence of magnetization which was measured in zero field cooled (ZFC) and field cooled (FC) is shown in Fig.4 for parent compound. Magnetic phase transition is accompanied by an increase of magnetization. Hysteresis behavior between magnetization measured in ZFC and FC regimes is typical feature of both samples. The $M(T)$ curves measured in ZFC regime start to deviate from the $M(T)$ curve measured in FC regime at the bifurcation temperature T_b, which is close to magnetic phase transition. Both samples undergo paramagnetic to ferromagnetic phase transition at the Curie temperature T_C which was determined as a minimum on $d\mu/dT(T)$ dependence. Substitution of Co for Mn reduces T_C from 178 K to 126.5 K for x = 0.00 and x = 0.03, respectively.

High temperature magnetic susceptibility χ follows the Curie-Weiss law $\chi = C/(T - \theta)$ for both samples in temperature region high enough above T_C (C is the Curie constant and θ is paramagnetic Curie-Weiss temperature)

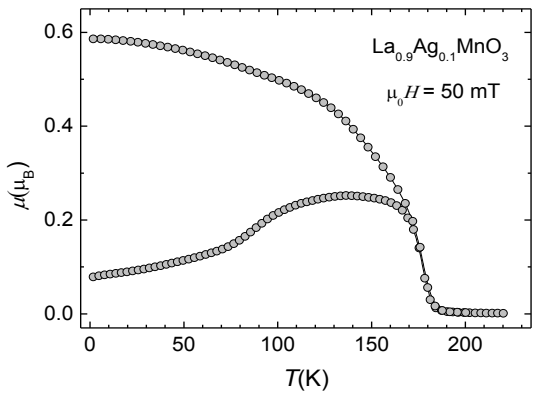

Fig.4. Temperature dependence of the magnetization of $La_{0.90}Ag_{0.10}MnO_3$ ceramic was measured in ZFC and FC regimes.

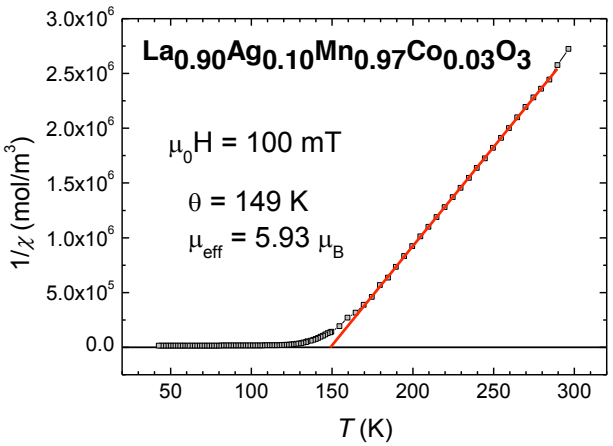

Fig.5. Temperature dependence of the inverse magnetic susceptibility for $La_{0.90}Ag_{0.10}Co_{0.03}Mn_{0.97}O_3$. The solid line represents fit to the Curie–Weiss law.

as it is demonstrated for sample with x = 0.03 (Fig.5). The paramagnetic Curie temperature decreases with substitution from θ = 181.5 K to 149 K and effective magnetic moment μ_{eff} is reduced from 6.56μ_B to 5.93μ_B. It is expected that in given electric crystalline field the spin of Co is zero and substitution of Co for Mn has a dilution effect; the number of Mn^{4+} ions is smaller and double exchange which is dominantly responsible for ferromagnetic ordering is weaker. The value of μ_{eff} is very high in comparison with magnetic moment of Mn^{3+} (4.90) or Mn^{4+}(3.87 μ_B) and at present we do not have any explanation for this fact.

Fig.6. displays temperature dependences of magnetization measured in ZFC and FC regimes for sample with x = 0.03 under different pressures. At ambient pressure, the sample undergoes the transition from paramagnetic to ferromagnetic state at T_C = 126.5 K. Under hydrostatic pressure, T_C increases almost linearly with the slope of a linear fit dT_C/dp = +5.7 K/GPa (Fig.7.). This pressure parameter is small in comparison

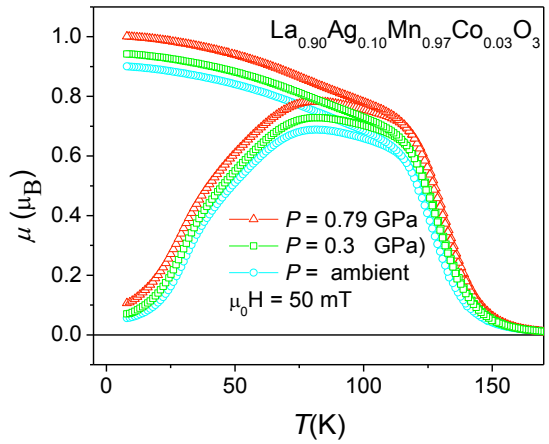

Fig.6. Temperature dependence of the magnetization which was measured in FC regime and in ZFC regime on $La_{0.90}Ag_{0.10}Co_{0.03}Mn_{0.97}O_3$ is shown for different value of hydrostatic pressure.

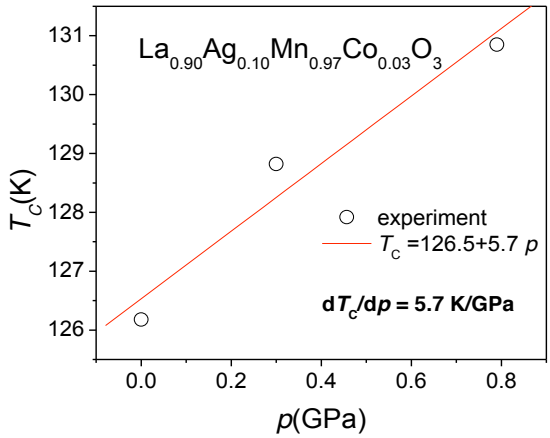

Fig. 7. The Curie temperature T_C of ceramic with x = 0.03 is shown as a function of pressure.

to the same parameters obtained usually on manganites which can reach value of about dT_C/dp = +23.4 K/GPa as it was determined for $La_{0.67}Ca_{0.33}Co_{0.03}Mn_{0.97}O_3$ ceramic prepared by the same technique [16]. The increase of T_C is usually attributed to the pressure induced increase of the electronic band width W due to increase of the bonding angle and reduction of the bond length of Mn-O-Mn [17, 18]. Magnetization μ measured in both ZFC and FC regimes increases with applied pressure. Effect of pressure on saturated magnetization μ_s is small (Fig.8). Hysteresis loops shows a typical ferromagnetic state but magnetization does not saturate even at 3 T. Applied pressure reduces a coercivity force at about 30% and increases μ_s at about 5 % per 1 GPa.

In conclusion, $La_{0.90}Ag_{0.10}(Mn_{1-x}Co_x)O_3$ ferromagnetic ceramics (x = 0.0 and 0.03) were synthetized by a sol gel method. The Curie temperature ranging from 178 K to 126.5 K is decreasing with substitution of Co for Mn. The Curie temperature T_C increases almost linearly with applied pressure with the slope of a linear fit dT_C/dp = +5.7 K/GPa and the coercive force decreases at about 30% per GPa.

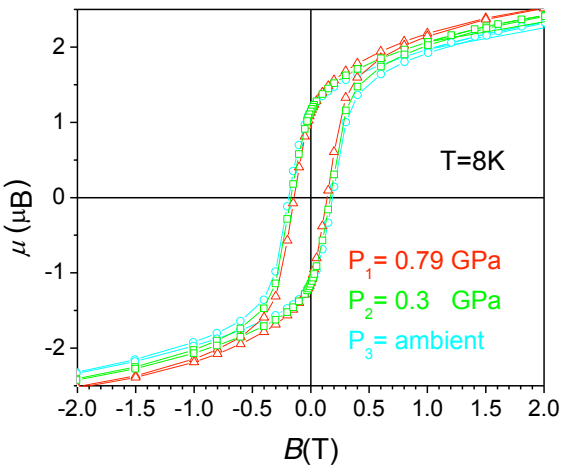

Fig.8. Hysteresis loops of $La_{0.90}Ag_{0.10}Mn_{0.97}Co_{0.03}O_3$ ceramic were measured at 8 K for three for different pressures.

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