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Journal of Magnetism and Magnetic Materials 260 (2003) 375–379

Journal of
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Double peak behavior of resistivity curves in Cd doped LaMnO_3 perovskite systems

G. Narsinga Rao, Saibal Roy¹, R.C. Yang, J.W. Chen**Department of Physics, National Taiwan University, Taipei 10617, Taiwan, ROC*

Received 12 August 2002; received in revised form 7 October 2002

Abstract

The effect of Cd doping on transport, magnetotransport, and magnetic properties has been investigated in the perovskite $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) systems. The $\rho(T)$ curves exhibit a sharp metal insulator transition (T_{p1}), which is close to paramagnetic to ferromagnetic transition (T_{c}) obtained from $M - T$ curves for all samples. In addition, $\rho(T)$ curves for Cd doped samples exhibit another broad transition (T_{p2}) below T_{p1} . This transition becomes more prominent and the transition temperature (T_{p2}) shifts to lower temperature with increasing Cd content. Such double peak behavior in the $\rho(T)$ curve is attributed to the phase separation between the ferromagnetic metallic phases and the ferromagnetic insulating phases induced by the electronic inhomogeneity in the samples.

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PACS: 75.30.Vn; 71.30.+h; 75.30.Kz

Keywords: A. Magnetically ordered materials; D. Electric transport; D. Magnetoresistance

1. Introduction

The discovery of colossal magnetoresistance (CMR) in perovskite manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln is a trivalent rare-earth ions and A is a divalent alkaline-earth metal ions) has attracted considerable scientific and technological interest due to their exotic electrical and magnetic properties [1,2]. Most of these interesting physical properties of the manganites are correlated with the double exchange (DE) mechanism [3], i.e. the

hopping of e_g electrons between spin aligned Mn^{3+} and Mn^{4+} ions through oxygen ions. Recently, a number of groups [4,5] have presented arguments to show that the double exchange model alone is not sufficient to explain the CMR effect of the manganites. They suggested that a strong spin-phonon interaction arises from the deformation of the MnO_6 octahedra due to Jahn-Teller effect, which plays an important role in the localization of carriers and the origin of CMR. The lattice distortion not only influences the effective transfer integral of the e_g electrons but also the super-exchange interaction between manganese ions, as well as the magnetic structure of the compounds. Different local distortions of the lattice around different ions could result in

*Corresponding author. Tel.: +886-2-33665172; fax: +886-2-23639984.

E-mail address: jwchen@phys.ntu.edu.tw (J.W. Chen).

¹On leave from Datar Switchgear Ltd., Nashik, India.

magnetic inhomogeneity in the compounds and give rise to an intriguing magnetic structure and magnetoresistance behaviors [6].

One of the main features of doped rare-earth manganites is the electronic phase separation [7] scenario. This phenomenon improves the DE theory by employing the charge inhomogeneity induced by Mn oxides, which explains the complicated and fascinating CMR behavior well below and above the Curie temperature T_c . The origin of the ferromagnetic insulating (FMI) to ferromagnetic conducting (FMC) phase transition has been very recently verified by NMR technique in the low doping regime of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [8] and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [9,10]. The coexistence of both phases were also observed at low temperatures [10]. Since cadmium is also a divalent transition metal and its ionic radius is comparable with that of Ca^{2+} , study of Cd doped LaMnO_3 samples would offer a complementary understanding of the magnetic and electronic properties of the perovskite system, which is of significance for achieving a complete understanding of CMR effects. In this paper, we report effect of Cd doping on transport and magnetic properties of the polycrystalline LaMnO_3 samples.

2. Experimental

The polycrystalline $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ samples have been prepared by standard solid state reaction method using high purity powders of La_2O_3 , CdO and MnCO_3 (99.99%, Johnson Mathews) taken in proper stoichiometric ratio. Powders were ground and calcined at 900°C for 24 hours in air. The calcined powders were ground, pelletized and sintered at 1200°C for 48 h in air with an intermediate regrinding. The formation of perovskite single phase of the samples has been confirmed by powder X-ray diffraction pattern using Philips PW-1817 with Cu-K_α radiation. The composition of each of the samples has been reestimated using EDAX analysis, which shows the presence of relatively less cadmium atomic percentage than the initial stoichiometric ratio taken for all the samples. The DC resistance and magnetoresistance have been measured by stan-

dard four probe technique using close cycle cryostat from 10 to 300 K (CTI Cryogenics, USA) placed in a conventional water cooled electromagnet with a field from -0.88 to $+0.88$ T. The field cooled (FC) and zero field cooled (ZFC) magnetizations have been measured in commercial SQUID magnetometer (CONDUCTUS, USA) from 2 to 300 K with a field $H = 10$ mT.

3. Results and discussion

Fig. 1 shows powder X-ray diffraction patterns of the polycrystalline $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) samples. The XRD patterns of the samples reveal that the prepared samples are of single phase rhombohedral structure [11] with a space group $R\bar{3}c$.

Fig. 1. Powder X-ray diffraction patterns of polycrystalline $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) samples.

Fig. 2. The variation of resistivity in zero field and $H = 8$ kOe with respect to temperature and Cd content.

Fig. 2 shows the resistivity as a function of temperature for the $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ samples below room temperature. The $\rho(T)$ curve for $x = 0$ exhibits a sharp metal insulator ($M-I$) transition at 250 K (T_{p1}). The value of T_{p1} shifts monotonically to a lower temperature with an increasing x content to a value of 226 K for $x = 0.5$. In addition, $\rho(T)$ curves for the Cd doped samples exhibit another broad transition (T_{p2}) below T_{p1} . With an increasing content x , this transition becomes more prominent and the transition temperature (T_{p2}) shifts to a lower temperature as well. At low temperature, $\rho(T)$ curves for all samples showed an upturn in resistivity (T_{p3}). With increasing magnetic field the transition temperature values of T_{p1} and T_{p2} shift to high temperature, while T_{p3} shifts to lower temperature.

The magnetoresistance for the samples with $x = 0, 0.1, 0.3$ and 0.5 shows sharp drop at T_{p1} and

Fig. 3. The temperature variation of (a) MR ratio at 8 kOe for $x = 0, 0.1, 0.3$ and 0.5 . (b) Magnetization (FC & ZFC) at $H = 10$ mT for $x = 0, 0.3$ and 0.5 samples.

nearly a constant value for a field of 8 kOe over a wide temperature range between 10 and 200 K as shown in Fig. 3(a). Fig. 3(b) shows a variation of magnetization (FC & ZFC) with respect to temperature with an applied field $H = 10$ mT for the samples with $x = 0, 0.3$ and 0.5 . The $M-T$ curve of $x = 0$ exhibits paramagnetic to ferromagnetic transition at 258 K (T_c). The transition temperature shifts to low temperature and a divergence between FC and ZFC curves enhances below T_c with an increasing Cd content.

The MR ratios with respect to magnetic field (-0.88 to $+0.88$ T) at 10 K for all the samples are plotted in Fig. 4(a). At $T = 10$ K, a sharp variation of $\sim 20\%$ in MR is observed at low fields (below 0.1 T) for all the samples. When the field exceeds 0.1 T, the MR ratio of all the samples decreases linearly as the slope of the MR curve decreases

Fig. 4. The MR ratio with magnetic field (a) for all the samples at 10 K (b) for sample $x = 0.3$ at different peak temperatures.

with an increasing Cd content. For a sample of $x = 0.3$, the field dependent MR curves at T_{p1} , T_{p2} and 10 K is typical to all other compositions, are depicted in Fig. 4(b). At low fields, the MR ratio increases sharply at 10 K and T_{p2} , whereas at T_{p1} the MR ratio varies linearly throughout the field.

The $\rho(T)$ curve for samples $x = 0$ shows a metal insulator transition (T_{p1}) at 250 K, which is close to the Curie temperature T_c (258 K), obtained from $M - T$ curve (Fig. 3(b)). The observed insulator metal and para to ferromagnetic phase transitions are due to double exchange related transport mechanism. Increasing $M - I$ transition temperature in a magnetic field could substantiate this. With an increased Cd content, the $M - I$ transition and the Curie temperature shift to lower temperature. Due to partial substitution of larger La ions by smaller Cd ions, a reduction of T_{p1} and T_c can be understood as an increase of Mn–O–Mn bond bending with a decrease of average A site

ionic radius $\langle r_A \rangle$. This substitution causes a narrow band width and decreases the mobility of e_g electrons, producing weaker double exchange interaction [12]. In addition, $\rho(T)$ curves for Cd doped samples exhibit an additional bump (T_{p2}) below T_{p1} , similar to that have been observed in alkaline earth metal doped and alkali metal doped samples of LaMnO_3 [13–15]. The double peak behavior of $\rho(T)$ curves for Cd doped samples can be explained in terms of electronic phase separation [7] between ferromagnetic metal and ferromagnetic insulator. The La ions partially replaced by Cd ions in LaMnO_3 will produce more Mn^{4+} as well as a valence difference. This favors electronic inhomogeneity and induces possible phase or domain separation [15], which are due to formation of rich Mn^{4+} regions and rich Mn^{3+} regions. This electronic inhomogeneity will produce antiferromagnetic insulating (AFI) phases, FMI phases and ferromagnetic metallic (FMM) phases. When the system transferred from the paramagnetic to ferromagnetic phase with decreasing temperature, the $\rho(T)$ curves for Cd doped samples do not fully show the metallic state, as the FMM phases are disconnected due to the existence of the FMI phases among them. If the temperature is further lowered below T_c , the FMI region decreases with an effective increase of percolation path between FMM phases, which leads to broad transition (T_{p2}). In addition, the exact doping level of Cd is lower than that in nominal compositions, which creates more vacancies at A site. The A site vacancies developed trapped mobile electrons, which lead to partial FMM phases transformed to additional FMI phases. Therefore, when the nominal Cd content increases, the volume fraction of FMI domains increases with an effective disconnection of FMM phases, which can be evidenced by an increase of resistivity and the shift of the broad transition to lower temperature (Fig. 2). In a magnetic field, the existing FMI phases transformed to the FMM phases, results in both the T_{p2} shift to high temperature (Fig. 2) and the high MR at low applied magnetic fields (Fig. 3(a)).

From Fig. 3(b), it is clear that the FC curve does not coincide with ZFC curves below T_c . This large discrepancy between FC and ZFC

magnetization curves is due to spin fluctuations resulting in spatial magnetic disorder. This plays a key role in electron localization and lead to high resistivity at low temperature (Fig. 2). Under an applied magnetic field the spatial magnetic disorder is reduced, which favors the electron delocalization and consequently results in a significant drop of the low temperature resistivity.

A sharp increase of MR occurs in a fields below 0.1 T for all the samples at 10 K (Fig. 4(a)) and at T_{p2} for Cd doped samples (Fig. 4(b)), which is attributed to the spin polarized tunneling between two ferromagnetic metallic grains through a ferromagnetic insulating region [16]. When the field exceeds 0.1 T, the MR of all the samples decreases linearly with the field, which is due to the suppression of intra ferromagnetic grain spin fluctuations, whereas at T_{p1} the MR ratio varies linearly with field due to entirely double exchange related magnetic transport, i.e. suppression of spin fluctuation only.

4. Conclusion

In summary, the transport and magnetic properties of polycrystalline $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) samples have been investigated. The $\rho(T)$ curve for $x = 0$ exhibits a sharp metal insulator transition and a paramagnetic to ferromagnetic transition obtained from $M - T$ curve. In Cd doped samples, double $M - I$ transitions with a single para to ferromagnetic transition are observed. The coexistence of ferromagnetic metallic phases and ferromagnetic insulating phases induced by electronic inhomogeneity account for an unusual double peak behavior in Cd doped samples.

Acknowledgements

National Science Council of ROC has supported this work under grant No. NSC 90-2112-M-002-042.

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