The comparison of crystallographic and magnetic properties between $La_{1-x}Pb_xMnO_3$ and $La_{1-x}Pb_xCoO_3$ systems

Y. L. Hsieh, M. F. Tai [1]

Dept. of Physics, National Chung Cheng University, Ming-Hsiung, Chia-Yi 621, Taiwan

Abstract

We studied the incorporation effects of Pb atom onto the La site on the crystallographic structure in both mixed-valence transition oxides $La_{1-x}Pb_xMnO_3$ and $La_{1-x}Pb_xCoO_3$ with $x = 0$ - 0.5 by using high-power powder X-ray differaction. In addition, the magnetic and electrical transport properties were determined by *dc* magnetic and $I-V$ measurements, respectively. Rietveld structural analysis showed that all compounds crystallized in a rhombohedral structure with a $R\bar{3}c$ space group, however, the magnetic properties are very different. In the Pb-doped manganites we observed strong long-range ordering ferromagnetism. Conversely, only quite weak magnetism in low temperatures was observed in the Pb-doped cobaltates. Nevertheless, the universal behaviors were demonstrated after normalized magnetizations versus field.

Key words: $La_{1-x}Pb_xMnO_3$; $La_{1-x}Pb_xCoO_3$; magnetic properties; scaling behavior; universality

Since the discoveries of the colossal magnetoresistance (CMR) effect in manganites and cobaltates, and high temperature superconductivity in cuprates [1, 2], many studies have focused on the rich physical properties in the perovskite-like $(R_{1-x}A_x)TO_3$ compounds (R = a trivalent rare earth element, A = a divalent alkali metal, T = a 3d transition metal). Many anomalous phenomena showed huge varieties of different physical properties, including high negative magnetoresistance ratio, metal-insulator transitions and anomalous lattice expansions *etc*. These phenomena are due to close interactions of comparable magnitude (all of order 1 eV) and the strong correlations between doped holes and local spins in the $(R,A)TO_3$ oxides. We sought to investigate these rich physical properties through the Pb-doping related system. In this study, we report the correlation of crystal structures, magnetic properties, and the scaling behaviors for both $(La_{1-x}Pb_x)MnO_3$ and $(La_{1-x}Pb_x)CoO_3$ series with x = 0 - 0.5.

Samples with nominal compositions $(La_{1-x}Pb_x)TO_3$ with T = Mn, Co and x = 0-0.5 were prepared by a standard powder solid-state reaction technique. The X-ray diffraction patterns were collected at room temperature using a Rigaku Rotaflex RTP500RC powder X-ray diffractometer. The major structural phase in our samples crystallized into the rhombohedral (trigonal) $R\bar{3}c$ space group with $a \sim 0.550$ nm and $c \sim 1.33$ nm for manganites; and $a \sim 0.544$ nm and $c \sim 1.31$ nm for cobaltates. We detected very few impurity of PbO_2 oxide in the Mn-based compounds. However, we found the mainly impurity phases of the Co-based oxides are CoO and Co_2O_3 oxides. We further refined the detailed crystallographic parameters by the Rieveld structural analysis [3-5]. The Rietveld refinement results show that the compositions of all cations are in good agreement with their stoichiometric amounts.

The various *dc* magnetic measurements in 2 K$< T <$ 305 K and in $H < 5$ T was carried out by an Oxford MagLab^{AC} 2000 magnetometer. We collected data based on the zero-field cooling and field-cooling magnetizations verus temperature in various *dc* fields and *dc* magnetization as a function of field at $T = 5$ K and

[1] E-mail: phymft@ccunix.ccu.edu.tw

Table 1. Some magnetic data in both systems

	$La_{1-x}Pb_xMnO_3$			
x	$T_C(K)$	$M_{5K,5T}(\mu_B)$	θ_p (K)	$\mu_{eff,PM}(\mu_B)$
0.0	198.6	3.25	204.8	6.49
0.1	247.5	3.43	246.2	6.11
0.2	260.3	3.37	275.4	6.25
0.3	>300	3.01	341.2	5.20
0.4	>300	3.14	347.3	5.43
0.5	>300	3.11	353.8	5.34
	$La_{1-x}Pb_xCoO_3$			
x	$T_C(K)$	$M_{5K,5T}(\mu_B)$	θ_p (K)	$\mu_{eff,PM}(\mu_B)$
0.0	12.8	0.045	-136.3	2.97
0.1	3.28	0.094	-145.3	3.24
0.2	7.37	0.168	-83.50	3.02
0.3	6.47	0.185	-116.0	3.31
0.4	8.82	0.178	-165.0	3.56
0.5	8.82	0.132	-74.90	2.82

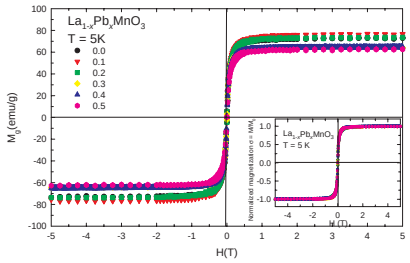

Fig. 1. $M-H$ curves of $(La_{1-x}Pb_x)MnO_3$ oxides at $T = 5$ K. Inset: The normalized magnetization, M/M_0, as a function of H at $T = 5$ K.

room temperature. Some related magnetic physical quantities, which were obtained from these magnetic data, are listed in Table 1. For manganites, the mixed valences of Mn ion induced by the Pb-doping can lead to the strong long-range ferromagnetic order. The metallic state in low temperature is arising from double-exchange interaction of the Mn^{3+}-O-Mn^{4+} bonds. The low-temperature saturation magnetization of 3.0 - 3.4 μ_B per Mn site is slightly smaller than the expected value from complete spin-alignment of the Mn ions (3.5 μ_B/Mn). However, the Pb-doping cobaltates exhibit quite weak magnetic order with low-temperature effective magnetic moments per Co site, which are smaller than 0.2 μ_B in insulating state and spin-glass behaviors.

Fig.1 and 2 show *dc* magnetization as a function of field, $M(H)$, at $T = 5$ K of all samples in each system. The normalized magnetization, M/M_0 (M_0 is the magnetization at $T = 5$ K and $H = 5$ T), presents the same variations with applied field for all samples of each series. These plots are shown in the insets of both figures. The six $M(H)$ loops in the Mn/Co system all collapse into an universal curve. Thus, our results demonstrate universal behaviors of magnetization exhibit in both systems. We conclude that the Pb-doped samples obey the same magnetic mechanisms and the variation tendency in each system [3-5].

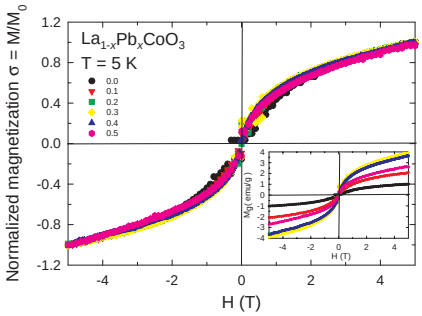

Fig. 2. The normalized magnetization, M/M_0, of $(La_{1-x}Pb_x)CoO_3$ oxides as a function of H at $T = 5$ K.Inset: $M-H$ curves at $T = 5$ K.

The spin glass behaviors in our Pb-doping cobaltates are observed in a wider H-T range than those in manganites. The differences in magnetic properties between both systems can attribute from the competition of the exchange energy, U_{ex}, of spin-up and spin-down orbits and the crystal splitting energy, Δ_{cf} ,between the t_{2g} and e_g orbits. The intra-atomic correlation which give rise to the Hund first rule (max. S) is represented on a one-electron energy diagram by introducing an energy splitting U_{ex}. For manganeses U_{ex} is greater than the crystal spitting energy. As a result manganese ions generally have a high-spin electronic configuration and supply a higher spin moments per Mn ions. Some studies suggested that the exchange energy and crystal splitting energy provided by the trivalent Co ions are quite similar in magnitude on the perovskite-structure of Co-based oxides. This leads to the breakdown of the Hund's rule. We propose the Co^{3+} ions generally are in a low-spin configuration state ($3d^6$,$t^6{}_{2g}e^0{}_g$) with S = 0 at low temperature. In conclusion, our result explains why low effective magnetic moment per Co ion is in the Co-based samples.

References

[1] J. M. D. Coey *et al.*, Adv. Phys. 48 (1999) 167.

[2] S. Yamaguchi *et al.*, Phys. Rev. B 58 (1998) 6862.

[3] T. S. Huang *et al.*, Mater. Res. Soc. Symp. Proc. series 674 (2001) U3.4.1-6.

[4] C. H. Chen *et al.*, Mater. Res. Soc. Symp. Proc. series 674 (2001) U3.8.1-7.

[5] T. S. Huang *et al.*, J. Magn. Mag. Mater. 239 (2002) 97.