Vol 12 No 7, July 2003
1009-1963/2003/12(07)/0789-03

Chinese Physics

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Magnetic properties of $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ materials*

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(Received 26 December 2002; revised manuscript received 8 April 2003)

The structure and magnetic properties of $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ ($0 \leq x \leq 0.4$) manganites were systematically investigated. Significant changes in Curie temperature and metal-insulator (MI) transition temperature of the samples were observed. All samples exhibited a transition from paramagnetic semiconducting to ferromagnetic metallic state. Curie temperature T_C and the MI transition temperature T_p increased with increasing Sr content. We attributed these behaviours to the enhancing of both the double exchange mechanism and the Jahn–Teller electron–phonon coupling.

Keywords: structure, magnetic properties, double exchange interaction, transition temperature T_p, Jahn–Teller distortion, neutron diffraction.

PACC: 7530V, 7530E

1. Introduction

Recent discovery of colossal magnetoresistance in La-Ca-Mn-O perovskites has sparked a great deal of efforts to understand the unusual electronic and magnetic properties of these materials.[1] The most commonly studied materials are manganites $R_{1-x}A_xMnO_3$ (R=La, Nd, etc., A=Pb, Ca, Sr, etc). The transition from paramagnetism to ferromagnetism, understood within the framework of the double exchange theory,[2] is a generic behaviour. The doped manganites show much more multifarious properties in the heavily doped region ($x \geq 0.5$). The synthesis of different compounds $Ln_{0.5}(Ca,A)_{0.5}MnO_3$ with Ln(Ln=La, Pr, Nd, etc.) and A(A=Sr, Pb, etc.) has been carried out according to the standard experimental method previously described for these materials.[3–7] Recently, Sun and co-workers[8–11] studied the Mn-site doping effects in $La_{0.7}Ca_{0.3}(Mn,A)O_3$ (A=Fe, Ge, Ti, Sn, etc). Caignaert *et al*[12] have performed the neutron diffraction measurement on $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ and found that these compounds exhibit different magnetic transition. Our results show that the strong Jahn–Teller distortion plays an important role in magnetic and MI transitions. In this paper, we investigate the magnetic and transport properties of $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ (x=0.0–0.4) compounds.

2. Experimental methods

Polycrystalline samples $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ (NPSM, x=0.0, 0.1, 0.2, 0.4) were prepared by the conventional solid-state reaction method. The well-mixed Nd_2O_3, $MnCO_3$, PbO, $SrCO_3$ powders (with purities higher than 99.99%) with a stoichiometric composition were first calcinated at 750°C for 12h in air. The samples were reground, pressed into pellets, and sintered two times at 1050°C–1180°C ($0 \leq x \leq 0.4$) for 24h in a mixing atmosphere (70% Ar and 30% O_2) with intermediate grinding and pressings, then furnace cooled to room temperature. A Rigaku x-ray diffractometer with a rotating anode and Cu $K\alpha$ radiation was used to examine the phase purity and the crystal structure for these series. The magnetization measurements were performed by a commercial superconductor quantum interference device magnetometer. The electric resistance was measured by means of the standard four-probe technique.

*Project supported by the "Hundred Talents Program" of Chinese Academy of Sciences, the National Natural Science Foundation of China (Grant No 50272082) and the State Key Development Program for Basic Research of China (Grant No 2001 CB610605).

3. Results and discussion

All samples are single phase detected by x-ray diffraction (XRD). Figure 1 shows the typical powder XRD pattern for the selected NPSM series. The XRD patterns can be indexed in an orthorhombic distorted perovskite structure with space group Pbnm. The lattice parameters are listed in Table 1.

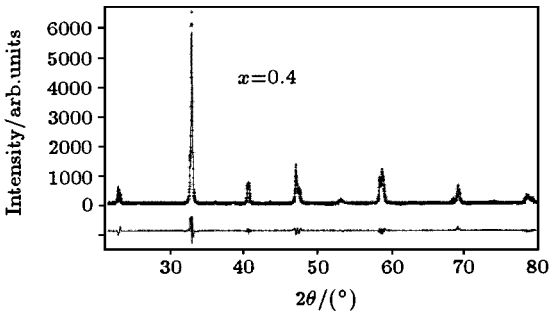


Fig.1. Typical powder XRD pattern for selected NPSM series.

Table 1. Structure parameters of $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ deduced from the Rietveld refinement of powder XRD data.

x	a/nm	b/nm	c/nm	R_p/%	R_{wp}/%	χ^2
0.0	0.5494(9)	0.5460(2)	0.7704(6)	24.4	32.3	2.148
0.1	0.5480(7)	0.5499(7)	0.7696(1)	11.7	16.9	4.135
0.2	0.5476(9)	0.5438(4)	0.7678(3)	14.9	19.3	4.606
0.4	0.5469(3)	0.5429(3)	0.7644(3)	13.2	18.0	2.566

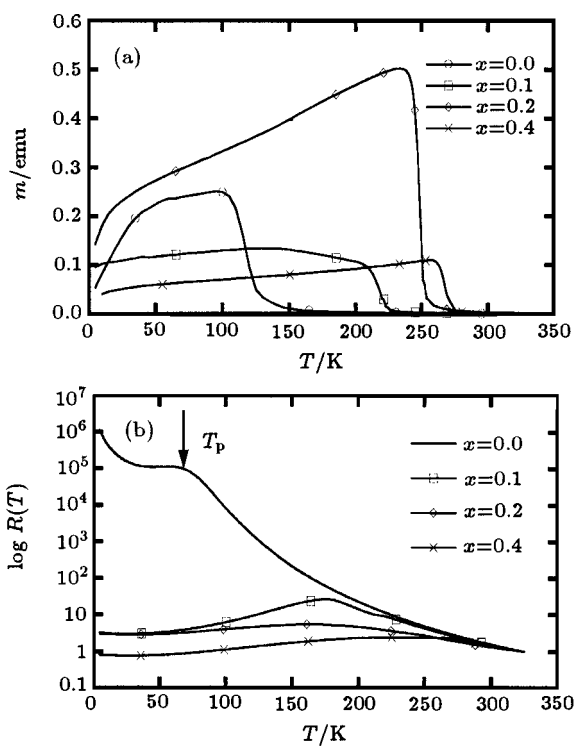


Fig.2. Temperature dependence of the magnetization M in a 0.01T field (a), and the electric resistance log $R(T)$ in a zero magnetic field (b), for $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ with x=0, 0.1, 0.2, and 0.4.

The cell volume V contracts from 0.231nm^3 to 0.227nm^3 as x increases from 0 to 0.4. This is consistent with the ionic radius change of Sr^{2+}(0.144nm) to Pb^{2+}(0.149nm). Figure 2 shows the magnetization (Fig.2(a)) and electric resistance (Fig.2(b)) of NPSM as a function of temperature. The M-T curves of the samples show the Curie temperature T_C increasing with x from 127K (x=0.0) to 273K (x=0.4) and the changing rate is 31K per 1% Sr substitution. The R-T curves exhibit a resistive behaviour of activation character observed at high temperatures. Two phases, i.e., a paramagnetic semiconductor phase and a ferromagnetic metal phase are identified from Fig.2. Upon Sr doping, all samples ($x \geq 0.1$) exhibit a transition from paramagnetic semiconductor state to ferromagnetic metallic state and T_p increases from 71 to 225 K. The value of resistive peak drops rapidly. We suggest a possible explanation of above phenomena as follows. In $A_{1-x}B_xMnO_3$, it is believed that the essential interactions come from two different parts: double exchange and Jahn–Teller electron–phonon coupling. Recently many experiments[13–15] have confirmed the existence of lattice distortion and the formation of polaron in doped Lanthanum manganites. In addition, we have achieved the neutron diffraction for the $Nd_{0.5}Pb_{0.1}Sr_{0.4}MnO_3$ (x=0.4) at room temperature.

The most important feature is associated with the geometry of the MnO_6 octahedra, which has two different bond lengths of the Mn-O_2 (i.e. 0.1907(2)nm×2 and 0.1935(7)nm×2) and two equal bond lengths of the Mn-O_1 (0.1934(3)nm×2) as well as the bond an-

gle of Mn-O_1-Mn (158.35°) and Mn-O_2-Mn (171.21°). Caignaert *et al*[16] reported the results of neutron diffraction on $Nd_{0.5}Sr_{0.5}MnO_3$. The results showed that there are two equal bond lengths Mn-O_1 (0.1927(2)nm) and four equatorial larger ones of 0.1937(1)nm(Mn-O_2). By comparison, we found that the distortion of MnO_6 octahedra, i.e. in the *ab* plane of the MnO_6 octahedra is slightly contracted and the bond angle of Mn-O_2-Mn changes from 167.90° to 171.21°. The distortion of MnO_6 octahedra leads to the structural distortion in the $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ ($x < 0.5$) samples and the structural distortion changes slightly with the different ratio of Sr to Pb also. This phenomenon can be ascribed to the Jahn–Teller effect of the $Nd_{0.5}Sr_{0.5}MnO_3$[16] sample. Figure 2(b) shows that not only the charge ordering character disappears but also all samples exhibit a transition from a ferromagnetic metal state to a paramagnetic semiconductor state as temperature increases. It is obvious that the strong Jahn–Teller electron–phonon coupling plays an important role. The strong crystal structural distortion results in current carrier localization by electron–phonon coupling. The competition between the localization of the electron–phonon coupling and the double exchange interaction shows up paramagnetic semiconductor state in $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ samples at temperatures above T_p. At temperatures below T_p, the double exchange becomes dominant. A large number of doping ions contribute to the motion of charge carries. Thereby the system is in a ferromagnetic metallic state. In addition, the T_c and T_p increase with increasing Sr content. These behaviours are attributed to the enhancing double exchange. We found that our results are different from that suggested by Hwang *et al.*[3] So we carried out the chemical analysis on two types of our samples (x=0.1 and 0.4). It shows a loss of lead content (e.g. at x=0.4, the ideal atom ratio is Pb:Sr=2.5:10, while the actual ratio is Pb:Sr=1:10) and the loss factor increases slightly as x increases. One of the important causes bringing about the different results is the loss of Pb. This changes the composition of the samples from their stoichiometry and thus enhances the importance of double exchange interaction. Hence T_c increases and the value of resistive peak drops rapidly.

4. Conclusion

In summary, we have investigated the magnetic and transport properties of $Nd_{0.5}Pb_{0.5-x}Sr_xMnO_3$ (x=0.0, 0.1, 0.2 0.4). These compounds exhibit a transition from a ferromagnetic metallic state to a paramagnetic semi-conducting state. T_c obviously increases and the peak in the resistivity decreases as x increases. At room temperature XRD shows that the space groups of all samples are Pbnm.

Acknowledgments

Thanks will go to T. S. Ning and S. Y. Fan for their help in measurements.

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