X-ray absorption spectroscopy and photoemission study of Bi-doped LaMnO₃

H G Zhang¹, Y T Li², X G Dong¹, Q T Hou¹, Y C Huang¹, H Liu¹ and Q Li¹
¹ Physics Department, Southeast University, Nanjing, 211189, P. R. China
² College of Science, Nanjing University of Post and Telecommunications, Nanjing, 210046, P. R. China
E-mail: qli@seu.edu.cn

Abstract. The magnetic property of Bi-doped LaMnO₃ was studied from perspective of valence state and local distortion given by XPS and XAFS. An isotrivalent Mn³⁺ is proved to be existed in samples by XPS due to trivalent Bi³⁺ ions doped LaMnO₃. Compared to the traditional ferromagnetic-paramagnetic phase transition with double exchange interaction between mixed valence states, this phase transition in our samples with isotrivalent Mn ions is understood by superexchange interaction in the way of Mn K-edge XAFS. A net ferromagnetic moment exists when the Mn-O-Mn bond angle deviates from 180º. The regular pattern of magnetization with doping concentration is related to the disorder degree of Mn-O and Mn-Mn pairs.

1. Introduction
To pervoskite manganites with colossal magnetoresistance (CMR), the occurrence of ferromagnetic (FM)-paramagnetic (PM) phase transition is generally understood by double exchange (DE) interaction [1], although DE interaction alone can not account for the large magnitude of magnetoresistance [2]. In the DE model, Mn ions should be in mixed-valence states. The ferromagnetic transition with metallic transition can be explained by DE interaction between Mn³⁺ (t²₃e¹₂g) and Mn⁴⁺ (t²₂g) via oxygen ions due to the Hund coupling. In fact, the DE interaction is also operative in the electron-doped colossal magnetoresistive manganites with Mn⁵⁺ (t²₂g) /Mn³⁺ (t²₂g) mixed-valence states [3].

As is known, LaMnO₃ parent compound is an antiferromagnetic (AFM) insulator. Divalent cations or tetravalent ions doped at La-site can induce the mixed-valence states of transition metal Mn ions. However, trivalent ions (like Dy³⁺, Bi³⁺) doped LaMnO₃ samples also exhibit FM-PM phase transition with negative magnetoresistance [4]. It is known that the chemical valence of Mn ions in trivalent ions doped LaMnO₃ samples generally shows consistency with that of their parent compound due to the charge neutrality of the whole system. If so, does the FM-PM phase transition in this system also originate from the mixed-valence states, like in compounds with divalent cations or tetravalent ions doping at La-site? In order to understand the change of magnetic properties in trivalent ions doped LaMnO₃, it is essential to investigate the electronic structure of this system, especially the electronic structure of Mn ions and doping ions.

In this paper, the valence states of Mn ions and related magnetic properties in the trivalent Bi³⁺ ions doped LaMnO₃ samples are investigated by x-ray photoemission (XPS) and extended x-ray absorption fine structure (EXAFS). An isotrivalent Mn³⁺ is proved to exist in samples. By studying
EXAFS of Mn K-edge, traditional FM-PM phase transition in Bi-doped LaMnO₃ with isotrivalent Mn ions is understood by superexchange interaction, compared to that with double exchange interaction between mixed valence states. A net ferromagnetic moment exists when the Mn-O-Mn bond angle deviates from 180°. And the regular pattern of magnetization with doping concentration is related to the disorder degree of Mn-O and Mn-Mn pairs.

2. Experimental
The compounds La₁₋ₓBiₓMnO₃ (x=0.2, 0.25, 0.3, 0.4) were prepared by solid state method. The high-purity oxides with stoichiometric ratio La₂O₃, Bi₂O₃, MnO₂ were mixed together, and the mixtures are thoroughly ground within petroleum ether. Three times were calcined at 900 °C, 950 °C, 1050 °C in ambient atmosphere for 10 hours, respectively. The structural characterization was carried out by X-ray diffraction (XRD) with Cu-Kα at room temperature. XPS spectrum of Mn 2p core level with photon energy hν=1486.7 eV and EXAFS of Mn K-edge were performed at National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC). Its binding energy position was calibrated by C 1s binding energy of 284.6 eV.

3. Results and Discussion
Fig.1 shows the XRD patterns of La₁₋ₓBiₓMnO₃ (x=0.2, 0.25, 0.3, 0.4) samples at room temperature. It is suggested that the well-single phase samples have been synthesized and all the samples can be indexed as rhombohedral structure, which are same as results in literature [4]. A shift of diffraction angle (inset of Fig.1) is observed. Except sample with x=0.4, diffraction angle for another three samples shifts to higher angle with the increasing of doping concentration, which means the contraction of lattice. It is due to the increasing of doping Bi³⁺ (r=0.096nm) with lower ions radius compared to La³⁺ (r=0.106nm) ions. However, when the concentration x increases to 0.4, the unusual behavior of XRD peaks indicates the crystal structure may begin to transform, which can be seen from that the doublet peak (1,0,-1) and (2,0,1) tend to merge to a single peak.

To the valence states of Mn ions, the XPS spectra of Mn 2p core level are shown in Fig. 2. Two obviously intense peaks at near 653.2 eV and 641.7 eV are observed, which is the Mn 2p₁/₂ and 2p₃/₂ states. The 11.5 eV difference between the two states is owing to the spin-orbital splitting. It can be seen from the Figure that there is no obvious change of binding energy for Mn 2p₁/₂ and 2p₃/₂ levels with doping concentration. The value of binding energy of Mn 2p₃/₂ peak for our samples is 641.7 eV,
which is consistent with that of parent compound LaMnO$_3$ [5]. It demonstrates that the electronic state of Mn ions is proved to maintain trivalent after trivalent Bi$^{3+}$ ions are doped in LaMnO$_3$.

Now that the valence state of Mn ions with trivalent in prepared samples is determined, it is necessary to check the magnetic property of those sample that whether they show FM-PM phase transition without existence of double exchange interaction between Mn$^{3+}$-O-Mn$^{4+}$. The magnetization as a function of temperature ($M-T$ curve) presented in Fig. 3 exhibits the traditional transition from FM to PM phase. The transition temperature $T_C$ is obtained from the maximum of $dM/dT$. The value of $T_C$ is 139.1, 110.0, 122.3, and 71.1 K for $x$=0.20, 0.25, 0.30, 0.40 respectively. The magnitude of magnetization at low temperature is 5.47, 6.61, 6.31, 3.24 emu/g with increasing of doping concentration respectively. From the tendency of magnetic variation, the singularity for $x$=0.25 is displayed.

To the FM to PM phase transition, the DE interaction between Mn$^{3+}$ and Mn$^{4+}$ is usually taken into main consideration. However, under the existence of only isovalent Mn$^{3+}$ ions in our system, the transition to ferromagnetism at low temperature does never be explained by DE again due to the absent of Mn$^{4+}$ ions, but can be understood by super-exchange AFM interaction among Mn$^{3+}$ ions. Although superexchange between Mn$^{3+}$ ions via O$^{2-}$ ions exhibits AFM ordering when Mn$^{3+}$-O-Mn$^{3+}$ bond angle is 180$^\circ$ based on Goodenough’s predictions [6], A FM ordering can be obtained when bond angle of Mn$^{3+}$-O-Mn$^{3+}$ is bended to lower than 180$^\circ$ with higher lattice distortion. A net FM moment exists when spins antiparallel to each other with a small canting angle. Thus, a larger distortion in the samples would be shown up. The local structural distortion was studied by the following data of EXAFS.

As to understand the tendency of magnetic properties with doping concentration, the local structure around Mn atoms is thus investigated. As literature reported [7-8], high disorder degree of Mn-O distribution ($\sigma^2$) is related to the low magnetization. Thus, the radial structure function distribution curve is obtained from extend XAFS after background subtraction, normalization, Fourier transform, which is shown in Fig. 4. The first peak near 0.14 nm is the first shell information manifesting the distribution of Mn-O bond, and the second shell coordination peak near 0.3 nm results mainly from contribution of Mn-Mn, and Mn-La/Bi bonds. The regular pattern of the intensity for the first peak and second peak is plotted in Fig. 5.

It can be seen that the change tendency of the intensity in first shell with doping concentration is basically same as that of magnetization, except for sample $x=0.4$, while that of the second shell is just completely opposite. It is reported that a low degree disorder of Mn-O bond distribution is favorable for the FM interaction via DE interaction [8], because DE interaction happens through Mn-O bonds. Thus, so does the superexchange interaction between Mn$^{3+}$ ions via O$^{2-}$ ions, like that happened for DE interaction [8]. Thus, sample $x=0.2$ with a low disorder degree of Mn-O shows a large magnetization. To the singularity of $x=0.4$, the disorder degree of second shell should be taken into consideration. In fact, the Mn-O-Mn bond angle of near 180$^\circ$ with low degree of disorder is generally to be formed in
the perovskite manganite structure. Thus, the degree of disorder in the second shell means the bending degree (deviate from 180°) of Mn-O-Mn bond angle or the amount of such bond bending. It is correspondingly understood that sample $x=0.25$ displaying higher magnetization is due to the higher bending degree of Mn-O-Mn bond angle or more bending bonds caused by disorder degree of Mn-Mn pairs, which is apt to give rise to ferromagnetic ordering by superexchange interaction. Although the low degree disorder of Mn-O is exhibited for sample $x=0.4$, the low degree disorder of Mn-Mn pairs as a fundamental to ferromagnetic superexchange determines the low magnetization at low temperature.

Figure 5. Doping concentration dependence of magnetization at low temperature (a), intensity of the first peak (b) and second peak (c) in radial structure function (from Figure 4).

4. Conclusion
In the paper, an isotrivalent Mn$^{3+}$ in the trivalent Bi$^{3+}$ ions doped LaMnO$_3$ samples is proved to exist by XPS. Compared to the traditional FM-PM phase transition with DE interaction between mixed valence states, this phase transition in Bi-doped LaMnO$_3$ with isotrivalent Mn ions is understood by superexchange interaction in the way of Mn $K$-edge XAFS. A net FM moment exists when the Mn-O-Mn bond angle deviates from 180°. The regular pattern of magnetization with doping concentration is related to the disorder degree of Mn-O and Mn-Mn pairs.

References
[1] Zener C 1951 Phys. Rev. 82 403
[2] Millis A J et al 1995 Phys. Rev. Lett. 74 5144
[3] Han S W et al 2004 Phys. Rev. B 69 104406
[4] Zhao Y D et al 2004 J. Magn. Magn. Mater. 280 404
[5] Matsuno J et al 2002 Europhys. Lett. 59(2) 252
[6] Goodenough J B 1963 Magnetism and the Chemical Bond (Inter-science, New York)
[7] Downward L et al 2005 Physica Scripta. T115 629
[8] Jiang Y et al 2007 Phys. Rev. B 76 224428