Anomalous Structural Change of Layered Perovskite Manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$

Aihua Wang[1,2], Tao Liu[3], Yang Liu[4], Guohui Cao[1,4], Cheng Dong[5], Ning Chen[1,4], Zhaosheng Feng[6] and Yang Li[*,1,7]

[1]*Department of Physics, Beijing University of Science and Technology, Beijing 100083, China*

[2]*Department of Physics, Capital Normal University, Beijing 100037, China*

[3]*Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Science, Beijing, 100049, China*

[4]*Department of Material Physics and Chemistry, Beijing University of Science and Technology, Beijing 100083, China*

[5]*Institute of Physics, Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, China*

[6]*Department of Mathematics, University of Texas-Pan American, Edinburg, TX 78541, USA*

[7]*Department of Engineering Science and Materials, University of Puerto Rico at Mayaguez, PR 00681-9044, USA*

Abstract: The temperature-dependent structural changes were investigated by using the X-ray diffraction and the Extended X-ray absorption fine spectroscopy (EXAFS) for layered perovskite manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.33 and 0.4). The anomalous changes of Mn-O bond length and Jahn-Teller (J-T) distortion of MnO_6 octahedron were observed, corresponding to ferromagnetic transition temperature (~ 120 K). Around the temperature of 2D short-range magnetic ordering (~ 235 K), there occurs an anomaly of the Jahn-Teller distortions of MnO_6. These results indicate that magnetic properties of perovskite manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ depend heavily on their microstructure change. The orbital state occupancy is involved in the observed Mn-O bond change.

PACS: 75.30.-m, 72.15.Gd, Vn, 61.10.Ht

Keywords: Jahn-Teller distortion, layered perovskite manganites, EXAFS.

INTRODUCTION

Perovskite manganites $Ln_{1-x}A_xMnO_3$ (*Ln*=La, Nd, Pr; *A*=Ca, Sr, Ba, Pb) have attracted much attention [1] since the discovery of a colossal magnetoresistance (CMR) effect [2, 3]. The CMR effect of metallic manganites around ferromagnetic transition was generally explained by the double-exchange (DE) model [4]. After investigating magnetic properties of CMR manganites, however, Millis *et al.*, pointed out that some striking characteristics exhibited by perovskite manganites could not be simply explained by the DE model completely [5]. For instance, the ferromagnetic transition temperature (T_C) calculated theoretically under the DE model is much higher than the observed value in experiment. Moreover, the resistivity above T_C predicted by the double-exchange theory is significantly smaller than the experimental values by several orders of magnitude. In order to explain this discrepancy, Millis suggested that the electron-phonon interaction induced by the Jahn-Teller (J-T) effect should be taken into account (see ref. [5]). Such electron-phonon interaction would cause the localization of carrier electrons and further reduction of T_C. Under this model, the theoretical T_C is even close to the observed value in experiment. Apparently, the study on the J-T effect induced by change of local lattice structure is significant in these manganese materials.

It has been widely accepted that the MnO_6 octahedron, as the basic structural constitution in perovskite manganites, can be distorted and modified by substitution for rare earth atoms in $Ln_{1-x}A_xMnO_3$ and $Ln_{2-2x}A_{1+2x}Mn_2O_7$. The distortion of MnO_6 depends on elements *A* and doping concentration *x*. Moreover, the dynamic structure studies [6] also show that there is a large difference in temperature-dependent lattice distortion for different doping concentrations of *x* [7, 8]. For the bilayered manganites $Ln_{2-2x}A_{1+2x}Mn_2O_7$, anisotropy in structure determines distinct characteristics in magnetic properties. Measurements of magnetocaloric properties for the Mn-O bilayer perovskite reveal a broad peak of magnetic entropy change around T_C [9]. The layered structure should bias the crystal field and hence lift the degenerate e_g orbital [7]. Clearly, the study of the J-T effect corresponding to the local structure will provide very helpful information for understanding peculiarity of CMR.

For $La_{2-2x}Sr_{1+2x}Mn_2O_7$ system, in the light Sr-doping level, Campbell *et al.* found that a system of strongly interacting electron-lattice polarons exhibited charge and orbital order at sufficiently high polaron concentrations in $La_{1.2}Sr_{1.8}$

*Address correspondence to this author at the Department of Physics, Beijing University of Science and Technology, Beijing 100083, China;
E-mail: ylibp@hotmail.com

1874-186X/09

Mn_2O_7 [10]. In their study, the structure of short-range polaron correlations in the layered colossal magnetoresistive perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ has been determined by a crystallographic analysis of broad satellite maxima observed in diffuse x-ray and neutron-scattering data. The resulting **q** ~(0.3,0,±1) modulation is a longitudinal octahedral-stretch mode.

Hur's group [11] perform measurements of susceptibility and resistivity in order to investigate the charge-ordering behavior in of the layered manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ in a wide doping range ($0.3 \leq x \leq 0.8$). The charge-ordering transitions occur in 200 – 340 K and the re-entrant charge-ordering behaviors are exhibited in a doping range ($0.47 \leq x \leq 0.62$).

In addition Wikins *et al.* investigated $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with heavy Sr-doping level x=0.475 and 0.5 [12]. The x-ray scattering results showed the charge and orbital ordering in the bilayer manganite. By using high-energy x-ray scattering, the structural distortion due to the Jahn-Teller ordering and the charge ordering due to the Mn^{3+}/Mn^{4+} pattern have been measured. Both the x=0.5 and x=0.475 samples are found to display charge and Jahn-Teller order.

In the heavy doping range $0.54 < x < 0.80$, Qiu *et al*. [13] observed the Jahn-Teller distorted MnO_6 octahedra at low temperature by applying atomic pair distribution function (PDF) analysis of neutron powder diffraction data. Their results indicated a gradual change of the local structure with doping rather than an abrupt phase transition as seen in the average structure. The number of J-T distorted octahedral varies smoothly with doping.

The extended X-ray absorption fine spectroscopy (EXAFS) technique which is sensitive to the fine differences in local structure and the short-range ordering [14] is the most desirable to be applied to study the atomic structure of CMR perovskite manganites. The local structure changes with temperature have been investigated for perovskite manganites $La_{2/x}Ca_{1/3}MnO_3$ and $La_{0.75}Ca_{0.25}MnO_3$ [15, 16]. Variations of the Mn-O bond length and the octahedral distortion of MnO_6 occur near their T_C. At low temperatures, six Mn-O bonds of MnO_6 with the same length turn into three pairs of Mn-O bonds with different lengths, as the temperature increases above T_C. These results indicate that the magnetic properties depend on local structure changes in CMR perovskite manganites. Unlike the ABO_3 structure, bilayered CMR manganites show a large anisotropy in structure, which dominates unique magnetic behavior. The Jahn-Teller effect accompanied by local change in structure cannot be simply neglected. It is very significant to study thermal evolution of the local structure of these materials.

In this work, the temperature-dependent local structure of Mn for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.33 and 0.4) was investigated by X-ray diffraction and Mn *K*-edge extended X-ray absorption fine spectroscopy (EXAFS). We selected x = 0.33 and 0.4 samples because their huge CMR signal in these doping concentrations. In addition, for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ system, in the doping range 0.3-0.4, there is no charge ordering (see ref. [11]). Moreover, in this bilayer system, the presence of rock salt blocker layer has the effect of reducing the dimensionality, and in the x=0.4 doped system there exists a paramagnetic-to-ferromagnetic transition at 126 K with huge accompanying change in CMR [11, 17]. In our experiments, we observed an abnormal variation in term of lattice parameter, bond length of Mn-O, and the distortion Δ_{JT} of MnO_6 around ferromagnetic transition temperature. The anomalous behaviors reflect variation of orbital dependent occupancy in the two-dimensional conduction band.

EXPERIMENT

Samples of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x =0.33, 0.4) were synthesized using the solid-state reaction. Powders of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ were prepared by the sol-gel method. The precursors of nitrates $La(NO_3)_3$, $Sr(NO_3)_2$ and $Mn(NO_3)_3$ were mixed according to the nominal composition of $La_{2-2x}Sr_{1+2x}Mn_2O_7$, then dissolved into pure water and an equal weight of citric acids was added. Stirring the mixture for 24 hours then baking at 120˚C until the liquid-like samples became gel. Heated the gel at 700˚C until nitrates were decomposed and citric acids were removed. The powders were ground and pressed into pellets. A subsequent heat treatment was performed at 1380˚C in air for 5 hours, and then cooled down to room temperature. The pellets were ground to fine powders, pressed again into pellets, and then sintered at the same temperature, the same procedure was repeated 4 times in order to obtain the homogeneous samples.

The as-prepared samples were characterized by X-ray diffraction (Rigaku, D_{max}/RC) in the temperature range from 80K to 300K. All patterns show a pure tetragonal $Sr_3Ti_2O_7$-type phase (space group of *I4/mmm*, No. 139) in samples. The lattice parameters were analyzed by the PowderX software package [18]. Structural refinement of the powder X-ray diffraction data was carried out using the GSAS software package. The experimental pattern at room temperature is in agreement with the simulated one for the entire 2θ region. R values for the fit are R_{wp} = 0.03 and R_p = 0.01 for x = 0.33 sample, and R_{wp} = 0.04 and R_p = 0.02 for x = 0.40 sample.

Magnetization versus temperature of samples was measured in the warming run with a field of 100 Oe after cooling down 5K in zero field using a superconducting quantum interference device (SQUID) magnetometer.

EXAFS data was collected on the 1W1B beam line at the Beijing Synchrotron Radiation Facility (BSRF) by using a Si(111) double-crystal monochromator and ion-chamber as detectors. The storage ring was operated at 2.2 GeV and the injection current was between 80 to 100 mA. In the temperature range 80 - 300K, the Mn K-edge data was collected in transmission mode. $La_{2-2x}Sr_{1+2x}Mn_2O_7$ samples were ground into fine powders with 400 mesh. WinXAS software package [16] was used for data analysis.

RESULTS AND DISCUSSIONS

The lattice parameters a and c of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.33 and 0.4) are presented in Fig. (**1a** and **b**) as a function of temperature T. For both samples, a and c gradually decrease with decreasing temperature at a high temperature range (T > 150K). There occurs an anomalous jump or heave

in *a* and *c* around the Curie temperature T_C. In order to contrast directly temperatures of structural anomaly and magnetic transition, temperature dependent magnetization under H=100 Oe is plotted in Fig. (**1c**). The Curie temperature T_C (defined as the temperature of maximum slope in dM/dT) was found to be 118K for x = 0.33 and 125K for x = 0.4, respectively. The temperature width of ferromagnetic transition is about 40K. Comparing with the behavior of single crystals [17, 19], such broadening of magnetic transition for our polycrystalline $La_{2-2x}Sr_{1+2x}Mn_2O_7$ samples is wider than that of the single crystals [20, 21]. We observed an abnormal variation in term of lattice parameter around ferromagnetic transition temperature. The anomalous behaviors reflect variation of orbital dependent occupancy in the two-dimensional conduction band.

As shown in Fig. (**1**), the lower Sr doping sample (x = 0.33) shows a larger lattice parameter *c* and smaller lattice parameter *a*, which implies that two samples have different two-dimensional structural characteristic attributing to Sr doping. In addition, samples with x = 0.33 and x = 0.4 exhibit different anomalous behavior in lattice change around T_C. For the sample of x = 0.33, the maximum of *a* occurs at T = 110 K, and at the same temperature, *c* reaches its minimum. Unlike x = 0.33, lattice parameter *c* of sample x = 0.4 shows a maximum at 110 K. There is no significant change for lattice parameter *c* but a kind of a shoulder appearing at 110 K. Such two samples have different lattice change in trend, which could be accounted for by the different microstructures. As discussed below, the lattice distortions depends on the Sr concentration. Neutron powder diffraction experiments on layered manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.32 \leq x \leq 0.40$) also show that coherent lattice anomalies are observed at the Curie temperature [14]. These behaviors are different from samples with heavy doping level, in which the charge-ordering and antiferromagnetic ordering occur [14]. The magnetocrystalline anisotropy is heavily dependent on the crystallographic structure and composition [7, 22]. It has been widely accepted that the magnetic peculiarity of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ results from structural and magnetic anisotropy [9].

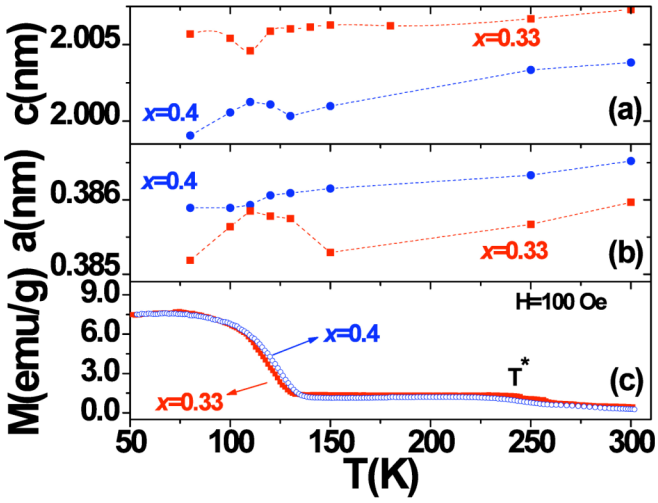

Fig. (1). Lattice parameters *a* and *c* of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.33 and 0.4) versus temperature T in (**a**) and (**b**). In order to compare directly structural and magnetic properties, temperature dependent magnetization in H=100 Oe is plotted in (**c**). The anomalous change of lattice parameters corresponds to ferromagnetic transition temperature.

By comparing with the ABO_3 type perovskite manganites, there are different magnetic characteristics for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with double Mn-O layers. First, T_C (~120 K) of a bilayered manganite is much lower than that of the ABO_3 type manganites with the same doping element and concentration. For instance, T_C is about 300 K for $La_{1-x}Sr_xMnO_3$ (x = 0.3) [22].

As shown in Fig. (**1**), a similar trend of magnetization was observed for the two samples. From room temperature, the magnetization increases slowly with increasing temperature. At about 235 K, there occurs a small plateau of magnetization, which is labeled as T* in Fig. (**1**). The plateau of the *M-T* curves can be explained by the appearance of two dimensional (2D) short-range magnetic ordering in the temperature range between T_C and T* [23, 24]. With decreasing

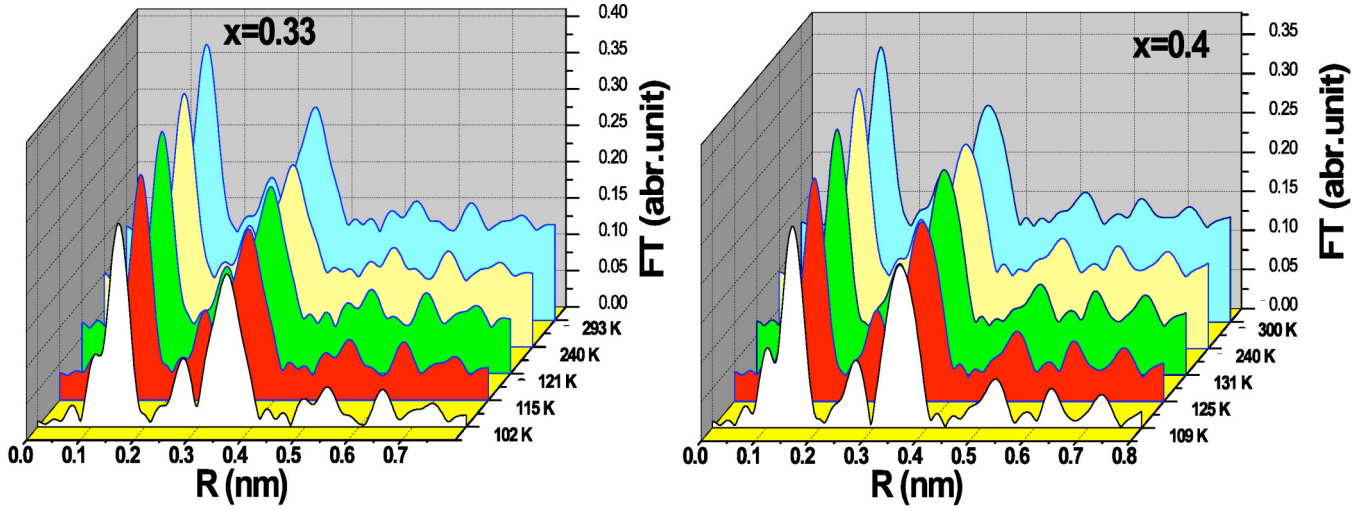

Fig. (2). Magnitude of the Fourier transform, $|FT\ k^3\chi(k)|$ at different temperature for x = 0.33 and x = 0.4 samples.

temperature, three-dimensional long-range magnetic order occurs, leading to a sharp increase of magnetization at T_C. A similar phenomenon was previously observed in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x= 0.3) [23] and (x = 0.3, 0.35, 0.4) [24].

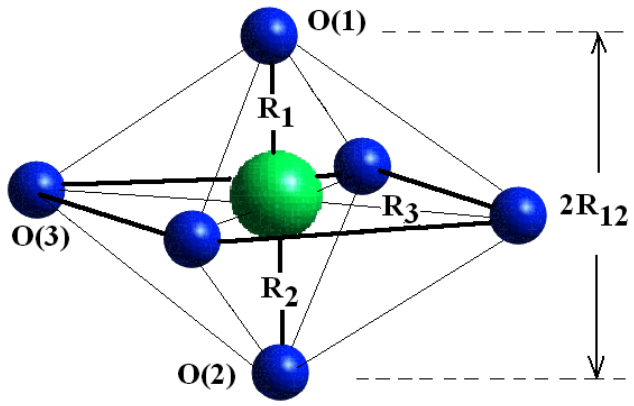

Fig. (3). The local environment of MnO_6 octahedron. A) Mn-O(1) (upper apical oxygen) with bond length R_1, B) Mn-O(2) (bottom apical oxygen) with bond length R_2 along the c axis, and C) a-b planar Mn-O(3) with bond length R_3.

Beside the change in lattice parameters, we are also interested in the change of micro-structure such as the Mn-O bond length around T^*, corresponding to 2D short-range magnetic ordering. In order to investigate change of Mn-O local structure further, Mn K-edge extended X-ray absorption fine spectroscopy (EXAFS) was performed. In our distribution model in fitting procedure, Sr occupies La position. We set an average occupancy of 0.33 and 0.4 respectively. We did not give Sr a preferable site to replace the La atom. The absorption spectra were normalized by the pre-edge fit with a linear function and the post-edge fit with a second polynomial. The EXAFS oscillations $\chi(k)$ were multiplied by a scaling factor k^3, where photoelectron wave vector k ranged from 2.5 to 12.0 Å^{-1}. The radial distribution function of Mn was obtained by the Fourier transform (FT) for $k^3\chi(k)$. Several Fourier transformed spectra at selected temperatures are shown in Fig. (**2**). According to the structural characteristic of $La_{2-2x}Sr_{1+2x}Mn_2O_7$, the first peak at 0.12 - 0.18 nm in Fig. (**2**) corresponds to the first neighbor coordination of Mn, which forms the MnO_6 octahedron as shown in Fig. (**3**). The second broad peak locates about 0.24 - 0.28 nm corresponding to Mn-(La/Sr) and Mn-O-Mn pairs. The third big peak around 0.35 - 0.40 nm are assigned with contribution of the second neighbor O atoms in the a-b plane.

The MnO_6 octahedron as the basic structural constitution in perovskite manganites is shown in Fig. (**3**). Mn has six O atoms as its first neighbors to form three kinds of Mn-O bonds; A) Mn-O(1) (upper apical oxygen) with bond length R_1, B) Mn-O(2) (bottom apical oxygen) with bond length R_2 along the c axis, and C) a-b planar Mn-O(3) with bond length R_3. The EXAFS oscillations $k^3\chi(k)$ from the first coordination shell of Mn-O were filtered out and fit by using scattering amplitudes and phase-shifts extracted from the standard MnO_2. The a-b planar bond length R_3 of Mn-O(3) was fitted with coordination number 4. In order to decrease analysis error for Mn-O bond length along the c axis, the average bond length of R_1 and R_2, i.e. $R_{12}=(R_1+R_2)/2$, was fitted with a fixed coordination number 2.

In Fig. (**4**), the EXAFS analysis display details of local structure change. The temperature dependence of the Mn-O bond length, R_3 and R_{12} are shown in Fig. (**4**). Both samples have a similar Mn-O bond length in the a-b plane. However the x = 0.33 sample as a whole has a larger Mn-O bond length in the direction of c-axis. As shown in Fig. (**4**), both samples show an anomalous change of bond length within the ferromagnetic transition temperature range. It is worth mentioning that bond lengths in the a-b plane and out of the a-b plane exhibit opposite changes for x = 0.33 and x = 0.4.

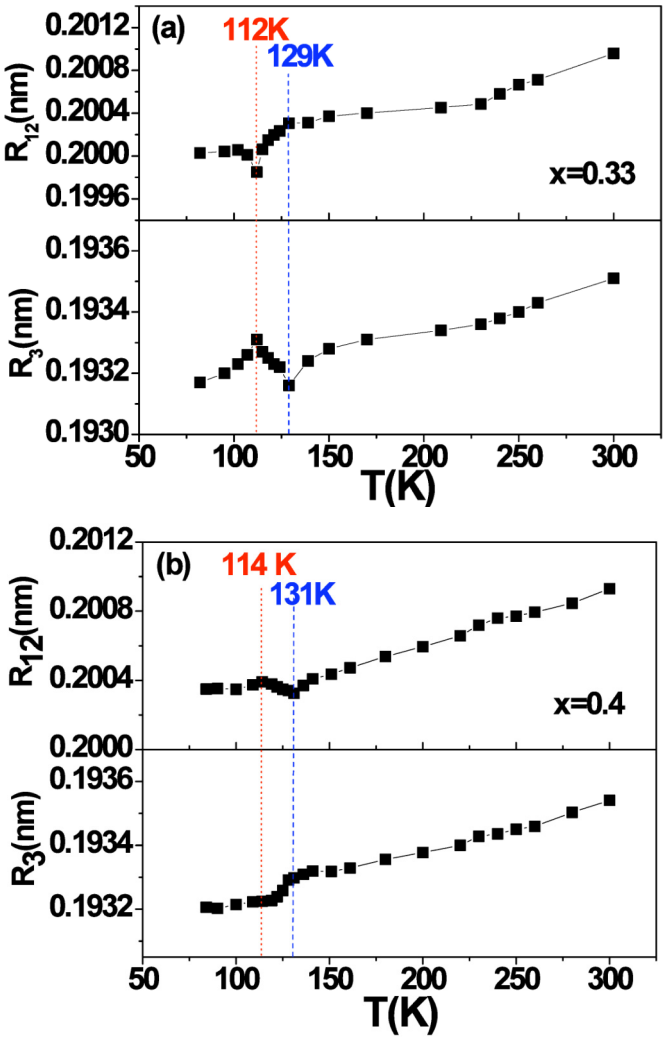

Fig. (4). The temperature dependence of the Mn-O bond length R_3 and R_{12}, (**a**) x = 0.33 and (**b**) x = 0.4. Around T_C the temperature range corresponding to anomalous change of Mn-O is marked by the dotted and dashed lines.

For the sample of x = 0.33, in the a-b plane, R_3 decreases when the temperature decreases, and reaches its minimum at 129K. With further decreasing temperature, R_3 anomalously increases and has a maximum at 112K. This change trend is consistent with the changing of the lattice parameter a as shown in Fig. (**1**). In the same temperature range, R_{12} vertical to the a-b plane exhibits a differently anomalous change; there respectively occurs a minimum at 112 K and a shoulder at 129 K. R_{12} curvilinear trend is very similar to the lattice

parameter *c*. It is clear that lattice change with temperature depends on the change of Mn-O bond length. Within ferromagnetic transition temperature range, the anomalous changes of R_3 and R_{12} results in a distortion of the MnO_6 octahedron. The distortion of MnO_6 behaviors anisotropic. For instance, at 112K, MnO_6 is compressed along the *c*-axis and tensioned in the *a-b* plane.

For the sample of $x = 0.4$, the variation of the two Mn-O bond lengths R_3 and R_{12} are shown in Fig. (**4b**). The temperature corresponding to anomalous change of R_3 and R_{12} shift to a higher temperature by 2K when compared to the sample of $x = 0.33$ due to its higher T_C. In addition, the anomalous trend is different from that of the $x = 0.33$ sample. For example, there is a R_{12} maximum and a smaller R_3 at $T = 114$K. The MnO_6 octahedron distortion was driven by a tension stress along the *c* direction and a compressive stress in the *a-b* plane. The MnO_6 octahedron distortions in two samples (x=0.33 and 0.4) have different directions, which implies Sr doping concentration would play an important role. It has been accepted that the proportion of Mn^{3+}/Mn^{4+} is changed with doping concentration x for bilayered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$. Mn^{4+} component increases when the Sr^{2+} ion concentration x increases. The difference in the anomalous behaviour in their two samples could be attributed to the different concentration ratio of $Mn^{3+}O_6$ *vs* $Mn^{4+}O_6$ octahedra. Clearly, there are more $Mn^{3+}O_6$ octahedrons in sample of the $x = 0.33$, while $Mn^{4+}O_6$ certainly manifold in the sample of $x = 0.4$.

Considering the Mn electronic structure, e_g electron occupancy of conduction band $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ is primarily governed by the doping level x [7]. The lower Sr-doping sample is with a larger out-of-plane Mn-O length and with lower hole concentration x. The different layered structure should bias the crystal field and hence lift the degeneracy of the e_g orbital states [9]. The different lattice distortion can be understood in terms of the e_g orbital state occupancy. Considering the different MnO_6 distortions in samples of $x = 0.33$ and 0.40, the orbital state occupancy of the doped electrons prefer to occupy the $3d_{3z^2-r^2}$ band for $x = 0.33$, while electrons dominantly occupy $3d_{x^2-y^2}$ band for $x = 0.4$.

In addition, as shown in Fig. (**4**) there is a perceptible change of R_3 and R_{12} corresponding to the 2D short-range magnetic ordering temperature T^*, which attributes to a slight MnO_6 octahedron distortion.

In order to highlight the local structure change and to discuss conveniently the Jahn-Teller effect in $La_{2-2x}Sr_{1+2x}Mn_2O_7$, the J-T distortion Δ_{JT} of $x = 0.33$ and $x = 0.4$ samples at different temperatures are shown in Fig. (**5**). The J-T distortion is defined as the ratio of bond length out of the *a-b* plane and in the *a-b* plane, $\Delta_{JT}=(R_1+R_2)/2R_3$ [11]. Both samples show their anomalous behavior in J-T distortion Δ_{JT} around T_C. Particularly the opposite change trend of J-T distortion Δ_{JT} for $x = 0.33$ and 0.4 implies that the e_g orbital state occupancy is involved in the observed Mn-O bond change.

In summary, we performed XRD and EXAFS measurements to investigate the temperature dependence of local structure change in the bilayered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.33$ and $x = 0.4$). We observed an abnormal variation in term of lattice *a* (and *c*), bond length of Mn-O, and the distortion Δ_{JT} of MnO_6 at ferromagnetic transition temperature. Moreover, there is a detectable anomalous change in Mn-O bond length and J-T distortion around 2D short-range ferromagnetic ordering temperature T^*. The different change trend of Mn-O reflects the orbital state occupancy in the 2D conduction band for different Sr doping.

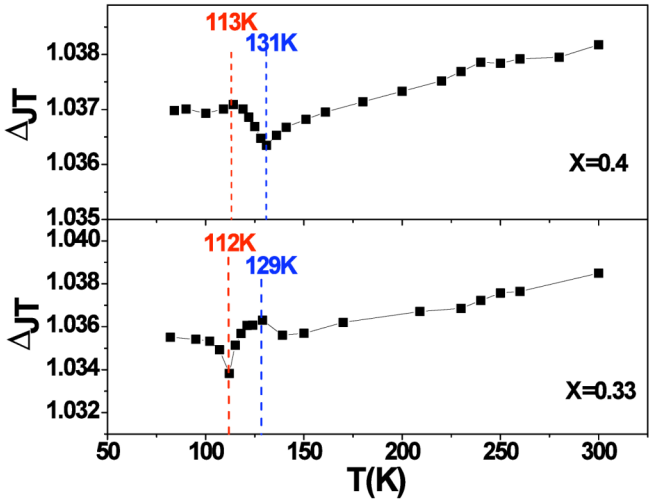

Fig. (5). Temperature dependence of the value of MnO_6 Jahn-Teller distortion Δ_{JT} for $x = 0.33$ and $x = 0.4$ samples.

ACKNOWLEDGEMENTS

This work was supported by the Beijing Natural Science Foundation (Grant No. 1072007), National Natural Science Foundation of China (Grant No.50372005) and National Science Foundation (Grant No. DMR-0821284).

REFERENCES

[1] von Helmolt R, Wecker J, Holzapfel B, Schultz L, Samwer K. Giant negative magnetoresistance in perovskitelike $La_{2/3}Ba_{1/3}MnO_x$ ferromagnetic films. Phys Rev Lett 1993; 71: 2331-4.

[2] Jin S, Tiefel TH, McCormack M, Fastnact RA, Ramesh R, Chen LH. Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O Films. Science 1994; 264: 413-15.

[3] Hur NH, Jin-Tae K, Yoo KH, *et al*. Effect of lanthanide ions on the magnetotransport properties in layered $Sr_{1.6}R_{1.4}Mn_2O_7$ (R=La, Pr, Nd, Gd). Phys Rev B 1998; 57: 10740-4.

[4] Zener C. Interaction between the d shells in the transition metals. Phys Rev 1952: 81: 440-4.

[5] Millis AJ, Littlewood PB, Shraiman BI. Double exchange alone does not explain the resistivity of $La_{1-x}Sr_xMnO_3$. Phys Rev Lett 1995; 74: 5144-7.

[6] Coey JMD, Viret M, Ranno L. Electron localization in mixed-valence manganites. Phys Rev Lett 1995; 75: 3910-13.

[7] Kimura T, Tomioka Y, Asamitsu A, Tokura Y. Anisotropic magnetoelastic phenomena in layered maganite crystals: impication of charge in orbital state. Phys Rev Lett 1998; 81: 5920-3.

[8] Hirota K, Ishihara S, Fujioka H, *et al*. Spin dynamical properties and orbital states of the layered perovskite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3< x< 0.5$). Phys Rev B 2002; 65: 064414.

[9] Wang AH, Cao GH, Liu Y, *et al*. Magnetic entropy change of the layered perovskites $La_{2-2x}Sr_{1+2x}Mn_2O_7$. J Appl Phys 2005; 97: 103906-3.

[10] Campbell BJ, Osborn R, Argyriou DN, *et al*. Structure of nanoscale polaron correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$. Phys Rev B 2001; 65: 014427-5.

[11] Dho J, Kim WS, Choi HS, Chi EO, Hur NH. Re-entrant charge-ordering behavior in the layered manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$. J Phys Condens Matter 2001; 13: 3655-63.

[12] Wikins SB, Spencer PD, Beale TAW, *et al.* Charge ordering and structural distortions at low temperature in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.475 and 0.5). Phys Rev B 2003; 67: 205110-9.

[13] Qiu X, Billinge SJL, Kmety CR, Mitchell JF. Evidence for nano-scale inhomogeneities in bilayer manganites in the Mn^{4+} rich region: $0.54 < x < 0.80$. J Phys Chem Solids 2004; 65: 1423-9.

[14] Daryl CE. Impact of the asymmetric pair distribution function in the analysis of XAFS. Physica B: Conden Matter 1995; 208-9: 330-3.

[15] Tyson TA, Mustre de Leon J, Conradson SD, *et al.* Evidence for a local lattice distortion in Ca-doped $LaMnO_3$. Phys Rev B 1996; 53: 13985-8.

[16] Lanzara A, Saini NL, Brunelli M, *et al*. Crossover from large to small polarons across the metal-insulator transition in manganites. Phys Rev Lett 1998; 81: 878-81.

[17] Moritomo Y, Asamitsu A, Kuwahara H. Giant magnetoresistance of manganese oxides with a layered perovskite structure. Nature 1996; 380: 141-4.

[18] Dong C. PowderX: Windows-95-based program for powder X-ray diffraction data processing. J Appl Cryst 1999; 32: 838.

[19] Matsukawa M, Ogasawara H, Sasaki T, *et al*. Anomalous Lattice Distortion in Pr-Substituted Double-Layered Perovskite Manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ Single Crystals: II. J Phys Soc Jpn 2002; 71: 1475-80.

[20] Ogasawara H, Matsukawa M, Hatakeyama S, *et al*. Anomalous lattice distortion in pr-substituted double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystals. J Phys Soc Jpn 2000; 69: 1274-7.

[21] Prellier W, Suryanarayanan R, Dhalenne G, *et al*. Colossal magnetoresistance in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ single crystal. Physica B 1999; 833-834: 259-61.

[22] Mahendiran R, Tiwary SK, Rao CNR. Structure, electron-transport properties, and giant magnetoresistance of hole-doped $LaMnO_3$ systems. Phys Rev B 1996; 53: 3348-58.

[23] Kimura T, Tomioka Y, Kuwahara H, Asamitsu A, Tamura M, Tokura Y. Interplane tunneling magnetoresistance in a layered manganite crystal. Science 1996; 274: 1698-1701.

[24] Arbuzova TI, Naumov SV, Arbuzov VL. Magnetic Properties of Electron-Irradiated Quasi-Layered Manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.3, 0.35, 0.4). Phys Solid State 2003; 45: 1513-8.

Received: March 8, 2008 Revised: April 8, 2009 Accepted: April 9, 2009