

Orbital Ordering in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$: Pr K-Edge XAFS Study

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Received June 26, 2003; accepted in revised form March 11, 2004

PACS number: 61.10.Ht

Abstract

Pr K-edge XAFS spectrum as a function of temperature in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ has been recorded on BL01B1 beam line at Spring-8, in order to study the effect of lattice distortions as the sample passes from a paramagnetic insulator phase at room temperature to ferromagnetic metal phase below 265 K and to an antiferromagnetic insulator phase at low temperatures. It is found that when the ferromagnetic to antiferromagnetic transition takes place, the MnO_6 octahedra rotate in the ab-plane and tilt away from the vertical along the c-axis. The tilting of the MnO_6 octahedra is responsible for the A-type antiferromagnetic phase.

1. Introduction

$\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ has been of great interest because of its peculiar magnetic and transport properties. This compound undergoes magnetic as well as structural transitions from a paramagnetic insulator (PMI) phase to ferromagnetic metal (FMM) phase at ~ 265 K and to an antiferromagnetic insulator (AFI) phase at ~ 140 K [1, 2]. The structure also changes from body centered tetragonal to face centered orthorhombic phase [3]. The antiferromagnetic ordering is A-type rather than CE-type and hence does not exhibit charge ordering. An important role in this context is played by the steric effects, macroscopic cooperative distortions, usually called tilting or buckling and the local deformations of the MnO_6 octahedra caused by size effects. Extended X-ray absorption fine structure (EXAFS) spectroscopy is an ideal tool to explore such distortions and local deformations and has been used quite successfully in lanthanum based manganites [4–7]. However, EXAFS at the Mn K-edge in other rare-earth based compounds is severely affected by the L edges of the rare-earth ions. One possible solution to observe the local structural changes in such perovskite oxides is by recording EXAFS at the K-edge of the rare-earth ion. Such a study requires EXAFS beamlines operating in the 40 keV range like the BL01B1 beamline at Spring-8. The present study was therefore undertaken with an aim to study the local structural changes around the Pr ion in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ as it traverses from PMI to FMM to AFI phase and to understand these changes in context of orbital ordering in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

2. Experimental

Polycrystalline $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ sample was synthesized using the conventional solid-state reaction method, which involved firing of stoichiometric amounts of starting materials at about 900 °C in a furnace three to four times with intermediate thorough grindings. Just before final sintering the sample was pressed into pellet and heated at 1000 °C for 16 hours. Powder X-ray diffraction pattern showed a single phase tetragonal perovskites structure without any

detectable impurities. Further characterization was done by a.c. susceptibility and resistivity measurements. The results obtained were similar to those reported earlier [1, 3, 8]. XAFS spectra at the Pr K-edge were recorded using the BL01B1 XAFS beamline at Spring-8. A Si (311) crystal plane served as the monochromator. The first mirror and the monochromator were fully tuned in order to get optimal resolution. The slit width of the monochromator exit was 0.3 mm vertical and 6 mm horizontal to ensure good signal to noise ratio. During the measurements the synchrotron was operated at an energy of 8 GeV and a current between 80 to 100 mA. The spectra were scanned in the range 41.6 to 43.3 keV for the Pr K-edge EXAFS. The photon energy was calibrated for each scan with the first inflection point of the Pr K-edge in Pr metal (42002 eV). Both the incident (I_0) and transmitted (I) synchrotron beam intensities were measured simultaneously using ionization chambers filled with a mixture of 15% Ar and 85% N_2 gases and 100% Ar gas respectively. The absorbers were made by pressing the samples into pellets of 10 mm diameter with boron nitride as binder. The thickness of the absorber was adjusted such that $\Delta\mu_0 x$ was restricted to a value ≥ 1 , where $\Delta\mu_0$ is edge step in the absorption coefficient and x is the sample thickness. Data analysis was done using the UWXAFS program [9].

3. Results and Discussion

EXAFS spectra at the Pr K-edge of the sample were recorded at room temperature, 180 K and 50 K so as to study the local structural changes in each of the three phases. The Fourier transforms (FT) of these spectra are presented in Fig. 1. The FT

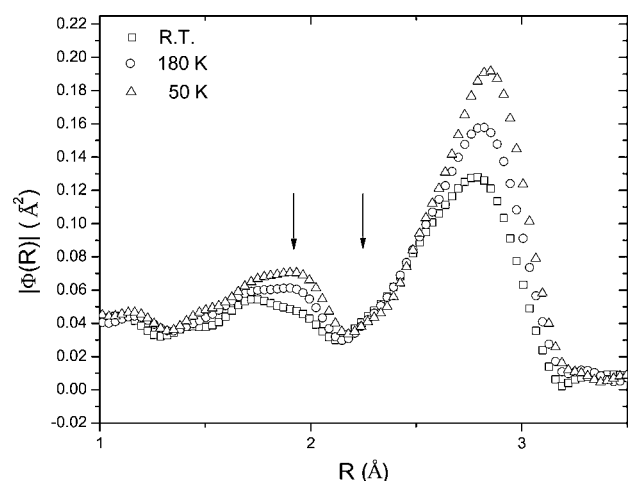


Fig. 1. FT spectra of Pr K-edge EXAFS in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at different temperatures.

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Table I. Structural parameters for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at different temperatures obtained from EXAFS analysis.

Bond Type	Coordination Number	Bond Length (Å)	σ^2 (Å ²)
R.T.			
Pr-O	4.0	2.527 (8)	0.007 (1)
Pr-O	4.0	2.701 (8)	0.006 (1)
Pr-O	4.0	2.880 (9)	0.006 (1)
Pr-Mn	8.0	3.339 (2)	0.005 (1)
180K			
Pr-O	4.0	2.520 (9)	0.005 (1)
Pr-O	4.0	2.668 (8)	0.005 (1)
Pr-O	4.0	2.810 (8)	0.004 (1)
Pr-Mn	8.0	3.327 (2)	0.004 (1)
50K			
Pr-O	4.0	2.690 (9)	0.002 (1)
Pr-O	4.0	2.810 (8)	0.002 (1)
Pr-O	4.0	2.533 (20)	0.003 (1)
Pr-O	2.0	2.869 (9)	0.001 (1)
Pr-Mn	8.0	3.315 (5)	0.002 (1)

Figures in brackets indicate uncertainties in the last digit.

spectra are not corrected for phase shift however; the values of bond lengths reported in the paper are the corrected values. The room temperature (R.T.) pattern shows two distinct correlations in the region 1.5 and 2 Å due to Pr-O bonds and a broad and most intense maximum at 2.8 Å comprising of a Pr-O and a Pr-Mn correlation. The FT spectrum at 180 K is similar to the one at R.T. One notable change however, is in the 1.5 to 2 Å range wherein there is a change in weight from first correlation to second. The 50 K spectrum has an additional subtle feature at about 2.3 Å, probably an indication of change of symmetry of the compound.

The EXAFS spectrum at R.T. was fitted using three Pr-O and a Pr-Mn correlations obtained from FEFF 6.01 [10] for I4/mcm symmetry. To reduce the number of fitting parameters the coordination numbers for all Pr-O correlations were constrained to be around 4.0 each and that of Pr-Mn correlation to be around 8.0. The final fitted parameters obtained are presented in Table I and the fitting in back transformed k -space is shown in Fig. 2. A good fit is obtained to the experimental data. For fitting low temperature data, the final parameters obtained for R.T. data served as starting guess parameters. In the first cycle only the debye-waller factors were varied followed by bond lengths to account for effect of lowering of temperature. A reasonably good fit was obtained for 180 K data. Although the metal – insulator transition in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ occurs only at about 140 K [11], neutron diffraction studies [3] have clearly shown that the structural transition starts around 180 K. This could be the reason for similarity between 180 K and 50 K F.T. spectra, especially in the 1.5 to 2.0 Å range. However, to fit the 50 K data the coordination number also had to be varied and resulted in physically unacceptable numbers. This data was therefore fitted with correlations obtained using FEFF for $Fmmm$ symmetry with four Pr-O correlations two of which are four coordinated and two are two coordinated. For this fitting cycle also, the coordination numbers were constrained to be around the theoretically obtained values. The resulting fit was quite good and is shown in Fig. 2 and the fitted parameters are tabulated in Table I.

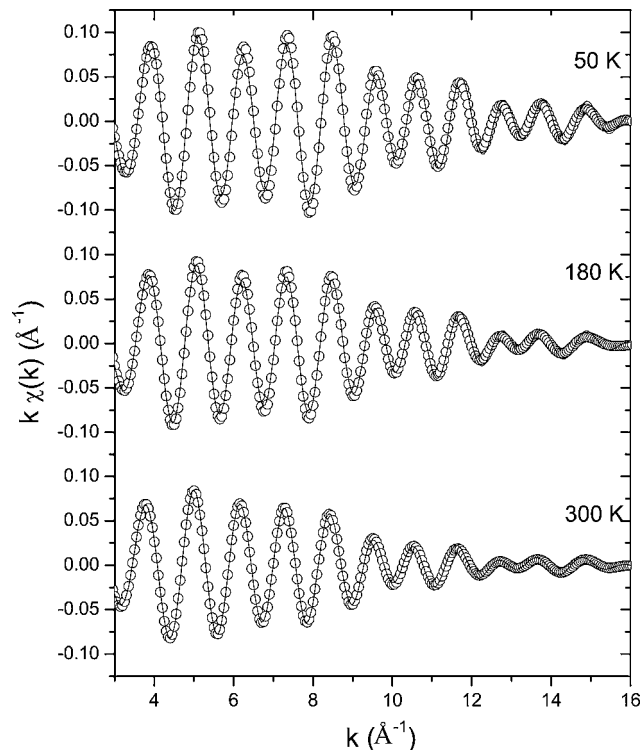


Fig. 2. k – weighted backtransformed EXAFS spectra (circles) along with fitted curves (lines) in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

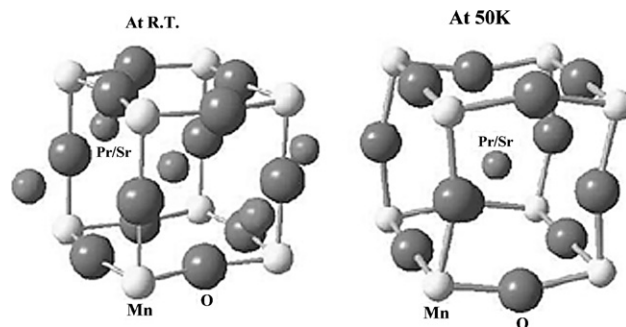


Fig. 3. Local structures around Pr ion at room temperature and 50 K in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

The local structure of Pr in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is depicted in Fig. 3. This structure has been drawn using the bond lengths obtained from above analysis and structural information. It can be seen that the MnO_6 octahedra rotate in the ab -plane and tilt away from the vertical along the c -axis when the sample undergoes ferromagnetic metal to antiferromagnetic transition. This leads to two Pr-O bond lengths at 2.534 Å and 2.810 Å instead of one at 2.701 Å at R.T. in the plane of Pr atom. Furthermore due to rotation of MnO_6 octahedra, the 2.880 Å and 2.527 Å Pr-O bond lengths at R.T. change to 2.691 Å, 2.869 Å and 2.534 Å. This rotation and tilting of the MnO_6 octahedra result in ordering of Mn $d_{x^2-y^2}$ orbitals along the x -axis that is responsible for A-type ordering in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

4. Conclusions

- (a) EXAFS at the Pr K-edge has been studied for the first time to explore structural changes in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ as the material undergoes a PMI to FMM to A-type AFI transition.

- (b) In the AFI phase the EXAFS spectra can only be fitted using Pr-O and Pr-Mn correlations obtained from *Fmmm* type orthorhombic structure.
- (c) This results in rotation in the a-b plane and tilting away from the vertical of MnO_6 octahedra that result in ordering of Mn $d_{x^2-y^2}$ orbitals along the *x*-axis that is responsible for A-type ordering in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

Acknowledgements

The authors (K.R.P. and P. R. S.) would like to gratefully acknowledge JASRI for beam time on BL01B1 under proposal No. 2002A0036-Nx-np, travel assistance from Department of Science and Technology, Government of India, New Delhi and local hospitality from Spring-8, JASRI, Japan.

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