LOCAL STRUCTURE OF THE CHARGE ORDERED La$_{0.5}$Ca$_{0.5}$MnO$_3$

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Local lattice of the charge ordered La$_{0.5}$Ca$_{0.5}$MnO$_3$ has been studied by temperature dependent Mn K-edge x-ray absorption measurements, using fluorescence detection method, to explore how the local lattice distortions are associated with the charge ordering in this system. The x-ray absorption near edge structure (XANES) reveals an abrupt change in the local MnO$_6$ octahedral geometry across the charge ordering temperature. The extended x-ray absorption fine structure (EXAFS) analysis shows largely distorted MnO$_6$ octahedra with coexisting Q$_2$-type and Q$_4$-type of Jahn-Teller (JT) modes at low temperature in the commensurate charge ordered phase. We find that small JT distortions persist also in the charge disordered phase at high temperature.

1 Introduction

Doped manganese oxides have been attracting considerable scientific and technological interest because of their remarkable electronic, magnetic and structural properties [1-10]. One of the significant physical properties of the manganese oxides is the charge striped ordering [1,2,4-6]. Moreover, it is now getting generally recognized that the presence of polarons in doped manganites [1-10] and in doped cuprates [6, 11-14] plays vital role in their peculiar electronic properties. Several experiments have revealed that polarons in these materials are associated with Jahn-Teller (JT) distortions. The JT distortions in the doped manganites and cuprates are found to be of Q$_2$-type and/or Q$_4$-type [11, 12].

Recently we have characterized [9] the local JT distortions of the MnO$_6$ octahedra by Mn K-edge EXAFS in the La$_{0.25}$Ca$_{0.75}$MnO$_3$ manganite showing colossal magneto-resistance (CMR). Quantitative determination of the local distortions of the MnO$_6$ has revealed that the JT distortions and their spatial distribution play important role to characterize the metal-insulator transition in the CMR phase. Here we have extended the work on the prototype charge ordered manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$ to quantify the JT polaronic distortions. Temperature dependent Mn K-edge x-ray absorption measurements, using fluorescence detection method, are exploited to identify the local distortions associated with the charge ordering. In this communication we report evolution of these MnO$_6$ distortions in a wide temperature range covering the commensurate to incommensurate charge order and the charge disorder phase. We find an abrupt change in the local MnO$_6$ geometry across the charge ordering temperature as seen by the XANES analysis. The EXAFS analysis reveals large JT polaronic distortions in the commensurate charge ordered phase which get reduced in the incommensurate charge ordered phase. There is a substantial decrease in the MnO$_6$ distortions, however, small JT distortions persist even in the charge disordered state at high temperature.
2 Experimental

The Mn K-edge x-ray absorption measurements were performed on high quality powder samples of \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \). The details on the sample synthesis and characterization could be found elsewhere \[8\]. The diffraction experiments \[5, 7\] have shown that the charge ordering occurs below the ~240 K. The charge ordering shows a large change in the commensurability above ~150 K \[5\].

The temperature dependent Mn K-edge x-ray absorption measurements were performed at the beamline BM29 of the European Synchrotron Radiation Facility (ESRF), Grenoble. High resolution x-ray absorption spectra were recorded using a Si(311) double crystal monochromator. The monochromator crystal was kept cooled to avoid any thermal drift in the energy position. The sample was mounted in a two stage closed-cycle He cryostat for the measurements. A reference sample (\( \text{MnO}_2 \)) powder was mounted beneath the sample to serve as a reference for the photon energy. The sample temperature was controlled and monitored within an accuracy of \( \pm 1 \) K. The absorption signal was detected by collecting the Mn K\( \alpha \) fluorescence signal using a 13 Ge element solid state detector. Several scans were measured at each temperature to attain high signal-to-noise ratio.

3 Results and discussion

3.1 XANES measurements

Figure 1 shows the high resolution Mn K-edge XANES spectra of \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) system measured in the charge ordered phase (at 60 K) and in the charge disordered phase (at 300 K). The spectra are normalized to the atomic absorption. The XANES spectra show the standard peaks; the pre-peak is due to the direct transition from the Mn 1s to the 3d \( e_g \) orbitals. Due to Jahn-Teller distortions of the \( \text{MnO}_6 \) octahedra the \( e_g \) orbitals show a small splitting. In fact the pre-peak appears with double peak structures (\( P_1 \) and \( P_2 \)).

\[ \text{Normalized absorption} \]

\[ \text{Energy (eV)} \]

\[ 6550 \quad 6555 \]

\[ 6545 \quad 6550 \]

\[ 6540 \quad 6545 \]

\[ 6535 \quad 6540 \]

\[ A \quad B \]

\[ \text{Dotted line} \]

\[ \text{Solid line} \]

\[ 60 \text{ K} \quad 300 \text{ K} \]

\[ \text{Figure 1. Mn K-edge XANES of } \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \text{ at 300 K (solid line) and 60 K (dotted line).} \]
We observe an energy shift of about 0.3 eV towards higher energy while going from charge ordered to the charge disordered phase. The energy shift of the main peak ($\Delta E_s$) is related to a variation of the average Mn-O bondlengths. In fact, the variation of the energy shift is consistent with an overall decrease of the Mn-O bondlengths across the charge ordered to charge disordered transition and consistent with the EXAFS analysis (see below).

Let us now turn to the intensity variation of the main peaks B and A. The main peaks are due to multiple scattering of the photoelectron emitted by the central Mn atom with the surrounding atoms. While peak B represents mainly the forward scattering with nearest neighbour O atoms, the shoulder-like peak A contains information about the contribution of the scattering due to the La/Ca atoms sitting at ~3.2 Å from the absorber Mn.

From the study of series of perovskite materials [14] we find that the ratio $r=(b-a)/(b+a)$ (where $a$ and $b$ are the intensities of the peaks A and B) is a good parameter to study stripe-charge ordering in these materials. We have plotted the temperature dependence of the $r$ in Figure 2. The $r$ shows a clear change across the charge ordered to the charge disordered transition reflecting an abrupt geometrical change across the charge ordering temperature.

![Figure 2. Temperature dependence of the ratio $r=(b-a)/(b+a)$.](image)

### 3.2 EXAFS measurements

The quantitative distortions of the MnO$_6$ octahedra were determined by the EXAFS analysis. Figure 3 shows the Fourier transform $|FT(k^2 \chi(k))|$ of the Mn-K edge EXAFS at several representative temperatures. The EXAFS signal was extracted from the absorption spectra using standard procedure and corrected for the fluorescence absorption. The Fourier transforms of the EXAFS (multiplied by $k^2$) have been performed between the k-range of 3-17 Å$^{-1}$.

We have used standard procedure [9, 13] to determine the pair distribution function (PDF) of the local Mn-O bondlengths from analysis of the EXAFS oscillations only due to the Mn-O distances expected in the range of 1.8-2.3 Å. In Figure 4 we show the PDF in the charge ordered phase ($T = 30$ K) and in the charge
disordered phase \((T = 300 \text{ K})\). Large JT distortions in the charge ordered phase could be evidently seen from a significant probability of a very long bond \(R_4\). The distortions get reduced substantially in the disordered phase, however, the MnO₆ octahedra are distorted even in the disordered phase showing an asymmetric PDF with contribution of the long bonds \(R_3\).

![Graph showing Fourier transforms of the Mn K-edge EXAFS at several temperatures.](image1)

**Figure 3.** Fourier transforms of the Mn K-edge EXAFS at several temperatures.

![Graph showing the Mn-O pair distribution function (PDF) of La₀.₅Ca₀.₅MnO₃ at 300 K (charge disordered) and 30 K (charge ordered).](image2)

**Figure 4.** The Mn-O pair distribution function (PDF) of La₀.₅Ca₀.₅MnO₃ at 300 K (charge disordered) and 30 K (charge ordered).

From the Fig. 4 we can identify that the charge ordered and disordered phases could be characterized by different octahedral distortions. While at high temperature the system shows distorted MnO₆ octahedra with two different distances \(R_1\) and \(R_3\), at low temperature the MnO₆ octahedra are largely distorted with four different distances. Indeed we have identified a clear evolution of the octahedral distortions as a function of temperature revealing different temperature regions. We find that; a) there are large MnO₆ octahedral distortions in the commensurate charge ordering phase at low temperature; b) these distortions persist (however with smaller
proportion) in the incommensurate charge ordering phase; c) there are greatly reduced distortions in the disordered phase at high temperature.

![Figure 6. Pictorial view of the MnO₆ distortions in the charge ordered and disordered phases.](image)

From the measured PDF we could characterize the different octahedral distortions in the charge ordered and disordered phases. At high temperature there are only two Mn-O distances, R₁ ~ 1.88 Å with probability N₁ ~ 4, and longer bonds, R₃ ~ 2.00 Å with a probability N₃ ~ 2. On the other hand, at low temperature there is very long Mn-O bonds (R₄ ~ 2.20 Å). Indeed the PDF at low temperature suggests that the MnO₆ octahedra has Q₂-type of JT distortions coexisting with Q₄-type of JT distortions (see Fig. 5). Instead the PDF at high temperature reveals presence of quasi Q₂-type of distortion.

4 Summary of conclusions

In summary we have studied local lattice of the prototype charge ordered La₀.₅Ca₀.₅MnO₃ system. High resolution Mn K-edge XANES suggests a particular change in the local geometry across the charge ordering temperature. We have quantitatively determined the MnO₆ octahedral distortions in the charge ordered phase at low temperature and charge disordered phase at high temperature. The results show that: a) the MnO₆ octahedron is strongly distorted in the commensurate charge ordering phase at low temperature; b) the distortions exist in the incommensurate charge ordering phase; c) the MnO₆ octahedral distortions get reduced in the disordered phase, above the charge ordering temperature. In conclusion, the Mn K-edge XANES and EXAFS results suggest that the charge ordered and disordered phases are characterized by different JT polaronic distortions revealing important role of electron-lattice interactions to drive the system to form
JT polaron stripes.

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