Temperature-Dependent X-Ray Absorption Spectroscopy of Colossal Magnetoresistive Perovskites

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The temperature dependence of the O K-edge pre-edge structure in the x-ray absorption spectra of the perovskites La1−xA2MnO3, (A = Ca, Sr; x = 0.3,0.4) reveals a correlation between the disappearance of the splitting in the pre-edge region and the presence of Jahn-Teller distortions. The different magnitudes of the distortions for different compounds is proposed to explain some dissimilarity in the line shape of the spectra taken above the Curie temperature.

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INTRODUCTION

The discovery of the colossal magnetoresistance (CMR) effect, i.e., the extremely large drop in resistivity accompanying the application of a magnetic field near the Curie temperature (Tc), has motivated intensive studies of manganese oxides based upon the perovskite structure \( \text{ABMO}_3 \) with the formula unit \( \text{ABMnO}_3 \), (A = rare earth atom, B = divalent atom). Despite intensive investigations, the CMR oxides are still not fully understood, thus posing continuing challenges for both experiment and theory. In fact, it has been recognized for a decade that the double-exchange (DE) model which provides a qualitatively correct description of the CMR effect, needs to be supplemented by more complex models, not necessarily mutually exclusive with each other, in order to explain the rich variety of properties exhibited by the CMR oxides. In particular, the presence of short-range-ordered Jahn-Teller distortions (JTDs) of the MnO6 octahedra and polaron formation has been intensively investigated both theoretically and experimentally due to its importance in the CMR effect.

X-ray absorption spectroscopy (XAS) at the O K-edge has proven to be a powerful tool for addressing important questions about the physics of manganites. The O K-edge absorption process is associated with the O 1s → Mn 2p dipole transitions. A typical XAS spectrum of \( \text{La}_1\text{−}_x\text{A}_x\text{MnO}_3 \) (A = Ca, Sr) consists of three main structures which have been identified as originating from strong hybridization of the O 2p orbitals with various unoccupied orbitals: Mn 3d at \( \approx 530 \) eV (often referred to as the "pre-edge" structure), La 5d/4f and Ca 3d/Sr 4d at \( \approx 535 \) eV, and Mn 4sp at \( \approx 545 \) eV. The pre-edge spectral region extending approximately 4 eV below the primary absorption threshold and extending over \( \approx 528\text{–}532 \) eV, has received a great deal of attention since it represents the Mn 3d-derived unoccupied states. The presence of strong absorption in the pre-edge region reveals strong hybridization between the O 2p and Mn 3d states, thus indicating that the holes introduced upon doping with a divalent metal have a mixed Mn 3d – O 2p character, as first recognized by Abbate and subsequently by other authors.

In light of these considerations, XAS spectra of the O K-edge should reveal signatures for the presence of JTDs, since the latter are expected to split the degeneracy of the Mn 3d-derived \( t_{2g} \) and \( e_g \) unoccupied levels. Indeed, the portion of the pre-edge structure extending from \( \approx 528.5 \) eV to \( \approx 530.3 \) eV can exhibit a double peak whose presence/disappearance has been discussed by some authors as a signature for JTDs. In particular, Dassau proposed that the presence of the splitting is a signature of the broken degeneracy of the \( e_g \) states due to JTDs of the MnO6 octahedra. On the other hand, in a temperature-dependent study of O K-edge pre-edge structure in \( \text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) and \( \text{Pt}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{MnO}_3 \) perovskites, Toulemonde and co-workers pointed out the existence of a correlation between the appearance of the splitting of the O K-edge pre-edge and the transition from an insulating to metallic state. On the contrary, no temperature dependence of the O pre-edge peak was detected in compounds which show the same insulating behavior over the whole temperature range, even when transitions from paramagnetic to ferromagnetic states are present. The authors thus inferred that the disappearance of the splitting is a signature for JTDs in the MnO6 octahedra.

Due to the significance of the JTDs in the CMR effect, it is thus important to get more insight into the modifications of the unoccupied states induced by the presence of JTDs as possibly revealed by signatures in XAS spectra. In light of this, we have studied the
temperature-dependence of the O K-edge pre-edge structure in La_{0.7}Ca_{0.3}MnO_3 (LCMO) and La_{0.6}Sr_{0.4}MnO_3 (LSMO, x = 0.3, 0.4) perovskites, both of which compounds which have been shown to be characterized by the presence of JTDs above T_C \[22\]. Our data show a correlation between the absence of the splitting in the pre-edge region and the presence of JTDs, even when no metal-insulator transition takes place and the electronic phase is metallic for all the temperatures accessed by the experiments. Minor differences exhibited in the high-temperature spectra of LCMO and LSMO are explained in terms of the relative magnitude of the JTDs.

**EXPERIMENTAL**

We used high-quality single crystals grown by the floating-zone method, with details on growth conditions and samples characterization being reported elsewhere \[22\]. The compounds studied exhibit a ferromagnetic-to-paramagnetic phase transition at T_C \(\approx 250\) K (LCMO, x = 0.3), T_C \(\approx 365\) K (LSMO, x = 0.3), and T_C \(\approx 370\) K (LSMO, x = 0.4) \[22\]. While LCMO undergoes a metal-insulator transition as the temperature is raised above T_C \[23\], LSMO is always in a metallic state for the compositions studied \[22\]. The crystals have been fractured at room temperature in situ at base pressures better than \(2 \times 10^{-10}\) torr. Quantitative x-ray photoelectron spectroscopy analyses of core-level peaks have routinely confirmed the expected stoichiometries and doping levels x to within experimental accuracy (\(\Delta x \approx \pm 0.03\)), and further shown that the degree of surface stoichiometry alteration or contamination was negligible, indicating a high surface cleanliness and stability.

The data have been taken with the Multi-Technique Spectrometer/Diffractometer endstation located on the elliptically-polarized undulator beamline 4.0.2 at the Berkeley Advanced Light Source, which permits photoemission, x-ray emission, and x-ray absorption to be carried out on a single sample. The x-ray absorption spectra reported here have been excited with linearly p-polarized light and detected with secondary electrons of \(\approx 0.7\)\(\times\)10\(^{-10}\) torr. Quantitative x-ray photoelectron spectroscopy analyses of core-level peaks have routinely confirmed the expected stoichiometries and doping levels x to within experimental accuracy (\(\Delta x \approx \pm 0.03\)), and further shown that the degree of surface stoichiometry alteration or contamination was negligible, indicating a high surface cleanliness and stability.

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**RESULTS AND DISCUSSION**

The O K pre-edge regions as measured with secondary electrons on La_{0.7}Ca_{0.3}MnO_3, La_{0.6}Sr_{0.4}MnO_3 and La_{0.7}Sr_{0.3}MnO_3 at several temperatures are shown in Figs. 2, 3a and 3b, respectively. Two main structures are observed in the pre-edge spectra, one extending from \(\approx 528.5\) to \(530.3\) eV and which can exhibit either one broad peak or two separated peaks, and a weaker one centered at \(\approx 531.5\) eV. The relevant Mn 3d states involved in the pre-edge region are majority spin e_g (e_G\(^\uparrow\)), minority spin t_2g (t_2G\(^\downarrow\)), and minority spin e_g (e_G\(^\downarrow\)). Many authors assign the first structure over \(\approx 528.5\) to \(530.3\) eV to O hybridization with e_G\(^\uparrow\) and t_2G\(^\downarrow\) states, while the second structure, located \(\approx 2\) eV higher in energy at \(531.5\) eV, has been assigned to e_G\(^\downarrow\) states \[12\].

The most remarkable characteristic of our data is the temperature dependence of the first structure located at 528.5 – 530.3 eV. In particular, this structure consists of two distinct peaks separated by \(\approx 0.65\) eV for temperatures lower than T_C (cf. Fig. 2 and Fig. 3), while the splitting disappears for temperatures above T_C (cf. Fig. 2, 3b and 3c). Also noticeable is the suppression of the structure at 531.5 eV for temperatures higher than \(\approx 531.5\) eV. The relevant Mn 3d states involved in the pre-edge region are majority spin e_g (e_G\(^\uparrow\)), minority spin t_2g (t_2G\(^\downarrow\)), and minority spin e_g (e_G\(^\downarrow\)). Many authors assign the first structure over \(\approx 528.5\) to \(530.3\) eV to O hybridization with e_G\(^\uparrow\) and t_2G\(^\downarrow\) states, while the second structure, located \(\approx 2\) eV higher in energy at \(531.5\) eV, has been assigned to e_G\(^\downarrow\) states \[12\].

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ior could be due to surface effects, since the spectra collected in the more bulk sensitive fluorescent yield mode in La_{0.7}Sr_{0.3}MnO_3 exhibit the same spectral features (Fig. 3c), with the only exception being that the structure at ≈ 531.5 eV is much more pronounced, possibly due to the different detection methods resulting in different matrix element and fluorescent-yield effects. This structure is equally well prominent in the fluorescent yield spectra reported in ref. [1].

The assignment of the splitting in the main pre-edge structure is still a matter of controversy in the literature. Pellegrin [16] and Park [17] assigned the first of the two peaks (529 eV) to e_g^1 states, the second one (529.65 eV) to t_{2g} states. Dessau assigned both peaks to e_g^1 states after observing that, although expected in the same energy range, the t_{2g}^1 states should have a low intensity because of the weak hybridization between the O 2p and Mn t_{2g} states, as predicted in a cluster model calculation by Saitoh [15, 18]. Consequently, Dessau interpreted the splitting as a signature of the broken degeneracy of the e_g states due to a JTD of the MnO_6 octahedra. On the contrary, Toulemonde and co-workers observed that the splitting appears when a transition from a paramagnetic-insulating to a ferromagnetic-metallic state occurs, thus arguing that the presence of strong JTDs is revealed by the disappearance of the splitting [19]. To interpret their data, Toulemonde et al. performed a crystal field analysis based on cluster calculations reported by Kurata and Colliex [28] and supplemented by introducing the splitting of the e_g and t_{2g} molecular orbitals due to distortions of the manganese octahedra [19]. Such strong distortions would be expected to split the degeneracy of both the e_g and t_{2g} levels, resulting in a set of energy states whose separation is smaller than the experimental resolution, and leading to a broad peak in the pre-edge structure of lowest energy. In this second interpretation, for compounds which exhibit an insulator-metal transition on lowering the temperature below T_C, the reduction of the JTD reduces considerably the unfolding of the e_g and t_{2g} states, resulting in a clear separation of the t_{2g}^3 from the e_g^1 states, visible in the dominant pre-edge structure as the presence of two distinct peaks [19].

Turning now to our experimental data for LCMO (Fig. 2), a compound generally agreed to be characterized by local JTDs [8, 9, 11], there is full agreement with what is reported by Toulemonde on Pr_{0.7}Sr_{0.3}MnO_3 and Pr_{0.7}Ca_{0.15}Sr_{0.15}MnO_3 perovskites. That is, at room temperature, which is above the temperature at which both a ferromagnetic-to-paramagnetic and a metal-insulator transition take place, the double peak structure observed below T_C disappears and JTDs are fully developed [8, 11], resulting in a broad peak centered at ≈ 529.4 eV. These results seem to rule out the hypothesis proposed by Dessau according to which the splitting is a signature for JTDs, since the splitting is clearly visible at 140K where the JTDs are weak and disappear at high temperatures (300K) where the JTDs are fully developed [8, 11, 12].

For La_{0.8}Sr_{0.2}MnO_3 (Fig. 3a), no substantial change in the splitting is observed when both spectra are measured below T_C, in the metallic state, in full agreement with what is reported by Toulemonde.

However, the existence of a correlation between the disappearance of the splitting and the transition from a metallic to an insulating state as proposed by Toulemonde is less obvious in the case of La_{0.7}Sr_{0.3}MnO_3 (Fig. 3b and 3c): in fact, while the double peak in the pre-edge structure is clearly visible below T_C, it disappears above T_C, even though La_{0.7}Sr_{0.3}MnO_3 is a metal over the whole temperature range accessed by our measurements. Our results are however in complete agreement with the La_{0.7}Sr_{0.3}MnO_3 data reported by Park, who interpreted the disappearance of the splitting as a spectral weight transfer associated with the reduction of the density of the e_g^1 states at the Fermi level at high temperatures [17].

Although the temperature dependence of the pre-edge peak splitting is qualitatively similar for LCMO and LSMO, the line shapes above T_C show some dissimilarity. Indeed, for both compounds the spectra show some broadening above T_C for photon energies > ≈ 528.75, but while in LCMO the disappearance of the splitting above T_C results in a broad peak centered at ≈ 529.4 eV, for LSMO it seems to take place primarily through a loss of intensity of the peak located at 529 eV, thus

![FIG. 2](image-url)
producing a broad peak less symmetric than in LCMO.

At first, it may thus seem like the results reported in Figs. 3b and 3c cannot be explained by the model proposed by Toulemonde. Nonetheless, we point out that in a recent multi-spectroscopic study of LSMO (x = 0.3, 0.4), we have observed an increase in the average spin moment of the Mn atom from ≈ 3 to ≈ 4 μB, corresponding to about 1 electron transferred to the Mn atom. This increase was concomitant with local JTDs at high temperature, providing strong evidence for direct detection of lattice polaron formation in the paramagnetic metallic phase [20].

In light of the results revealed by our previous work, we interpret the loss of intensity of the peak located at 529 eV and the consequent disappearance of the splitting as signatures for Jahn-Teller (JT) polaron formation. In fact, the loss of intensity of the peak located at 529 eV can be easily explained by a reduction of the density of the lowest unoccupied states due to the electron localization above T_C associated with JTDs, and resulting reduced O 2p-Mn 3d hybridization, an interpretation consistent with the one provided by Park [17].

Our results on LSMO and the interpretation framework proposed by Toulemonde are in addition not inconsistent once we acknowledge that polarons and metallic conductions are not mutually exclusive. We suggest that the differences in the line shapes above T_C for LCMO and LSMO are due to the difference in the magnitude of the JTDs for the two compounds. In fact, recent EXAFS results indicate that the size of the JTDs in LSMO is only about half that in the Ca-doped compound [20]. It is thus possible that in LSMO the reduced JTDs are not as effective as for LCMO in lifting the degeneracy of the \( t_{2g}^\uparrow \) and \( e_g^\uparrow \) states, which remain separated even when the JTDs are fully developed at high temperature, with the result that the splitting disappears by evolving into a structure less broadened than in LCMO [26].

Overall, our data thus seem to support the scheme previously proposed by Toulemonde and further indicate that the correlation between the absence of the splitting in the pre-edge region and the presence of JTDs may occur even when the electronic phase is metallic, without requiring a metal-insulator transition. According to Toulemonde, the lowest unoccupied state, as determined by the degree of distortion and by the relative magnitude between the exchange interaction and crystal field strength, is a \( t_{2g}^\uparrow \) state with filling depending on the substitution amount [19]. However, on the basis of the data reported, we can only assert that our results are qualitatively consistent with the scenario proposed by Toulemonde, but we cannot address the assignment of the peaks at 529 and ≈ 529.7 eV, an issue which requires further investigations.

FIG. 3: Temperature dependence of the pre-edge structure in O K-edge XAS spectra from La_{0.6}Sr_{0.4}MnO_3 (a) and La_{0.7}Sr_{0.3}MnO_3 (b and c). The spectra have been taken both in the electron yield (a-b) and fluorescent yield modes (c). The splitting is clearly visible in both compositions for temperatures below T_C. Above T_C (b-c), the splitting disappears, primarily due to the loss of intensity of the structure at 529 eV, resulting in a single peak less broadened than in LCMO.
CONCLUSIONS

In conclusion, we have measured the temperature dependence of the O K-edge pre-edge structure in La$_{1-x}$A$_x$MnO$_3$, (A = Ca, Sr, x = 0.3, 0.4) perovskites. Our data are in qualitative agreement with an interpretation scheme previously proposed according to which there exists a correlation between the disappearance of the splitting in the pre-edge region and the presence of JTDs. The difference in the magnitude of the JTDs for LSMO and LCMO likely explains the dissimilar line shape of the high temperature spectra.

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