Doping and temperature dependence of Mn 3d states in A-site ordered manganites

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We present a systematic study of the electronic structure in A-site ordered manganites as function of doping and temperature. The energy dependencies observed with soft x-ray resonant diffraction (SXR) at the Mn $L_{2,3}$ edges are compared with structural investigations using neutron powder diffraction as well as with cluster calculations. The crystal structures obtained with neutron powder diffraction reflect the various orbital and charge ordered phases, and show an increase in the Mn-O-Mn bond angle as function of doping and temperature. Cluster calculations show that the observed spectral changes in SXR as a function of doping are more pronounced than expected from an increase in bandwidth due to the increase in Mn-O-Mn bond angle and are best described by holes that are distributed at the neighboring oxygen ions. These holes are not directly added to the Mn 3d shell but centered at the Mn site. In contrast, the spectral changes in SXR as function of temperature are best described by an increase of magnetic correlations. This demonstrates the strong correlations between orbitals and magnetic moments of the 3d states.

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I. INTRODUCTION

Manganites have attracted a lot of attention in the past two decades because they show very rich phase diagrams with interesting electronic and magnetic properties that make them challenging to be described from first principles. For manganites crystallized in the perovskite structure ABO_3 , the A-site of the perovskite is coordinated by 12 oxygen sites with A as a trivalent ion R^{3+} ($R \equiv$ Lanthanide). This A-site can be doped with a divalent cation T^{2+} , normally Ca^{2+} , Ba^{2+} , or Sr^{2+} . This doping causes the Mn ions, that occupy the B site, to change its average electronic states from Mn^{3+} to Mn^{4+} . The B sites are sixfold coordinated and the surrounding O^{2-} ions form octahedral cages. Arising from the strong coupling between the electric, magnetic, and structural properties present in these systems, the physical and structural properties depend strongly on the doping content and on the nature of the A-site cation. The most important of these properties are the appearance of the colossal magnetoresistance (CMR) with the occurrence of phase separation and unusual spin, charge, lattice, and orbital order.

For the half-doped manganite, the generally assumed ground state consists of the checkerboard charge-order (CO) and orbital-order (OO) pattern, which is characterized by the alternation of Mn^{3+} and Mn^{4+} sites (Mn-centered charge ordering). In the last years other phases have been proposed to be present in manganites close to half doping.¹ Some of those phases present either bond-centered charge ordering, allowing the existence of magnetic Zener polaron-type phases; or an intermediate phase combining site centered CO and bond centered CO that allows the occurrence of ferro-

electricity. Experimentally, Zener polaron phases have also been proposed for A-site ordered systems of $RBaMn_2O_6$, in particular, for $R=Y$.² However, recent resonant x-ray diffraction experiments found no inversion symmetry breaking effects on the Mn sites confirming merely the checkerboard charge and orbital ordering pattern for different doping contents and materials studied.³ The A-site randomness (the R^{3+}/T^{2+} solid solution) has a significant influence on the properties of the system. It increases the magnetoresistance effect and decreases the charge and orbital order temperature $T_{CO/OO}$. It also makes the charge-spin-orbital correlation short ranged.⁴⁻⁶ It is therefore important to study the A-site ordered manganite system to quantify the effect of the quenched disorder on the CMR physics.

The crystal structure of the cation-ordered material $RBaMn_2O_6$ is of $a_p \times a_p \times 2a_p$ type with $a_p \approx 3.9$ Å being the cubic perovskite unit cell parameter (see Fig. 1). It was shown that the A-site ordered half-doped system $SmBaMn_2O_6$ exhibits a CO/OO transition at $T_{CO/OO} \approx 360$ K and an antiferromagnetic transition at $T_N = 250$ K followed by a reorientation of the OO at $T_{CO2} = 200$ K.^{5,7} Resonant soft x-ray diffraction has found an OO of e_g electrons with $\begin{bmatrix} x^2-z^2 \\ y^2-z^2 \end{bmatrix}$ type.⁷ When the system is hole doped, a linear dependence of the ordering wave vector of the orbital reflection $\vec{k} = (\delta_x, \delta_x, 0)$ with doping x was found with $\delta = \frac{(1-x)}{4}$ in $Tb_{1-x}Ca_xBaMn_2O_6$, while, $\vec{k}$ was found to be constant $\vec{k} = (\delta_y, \delta_y, 0) = (\frac{1}{4}, \frac{1}{4}, 0)$ for doping contents equal and below half doping $TbBa_{1-y}La_yMn_2O_6$.^{3,5} One possible OO layout for the $\frac{2}{3}$ doped system is shown in Fig. 2.

Our previous resonant x-ray diffraction study showed that the spectral shape of the orbital reflection exhibits distinct

FIG. 1. (Color online) Perovskite structure of the A-site ordered half-doped manganite $\text{TbBaMn}_2\text{O}_6$. The A-site of the perovskite is occupied by Tb and Ba ordered in different planes. The Mn ions are placed at the B site within the oxygen octahedra.

changes as function of doping at the Mn $L_{2,3}$ edges.³ The characteristic features of the spectra are similar as for other manganites^{8–13} but the relative intensities are altered and indicate a progressive alteration of the electronic Mn states as a function of hole doping. It was deduced that the anomalous OO melting and change in $(\delta_x, \delta_x, 0)$ with hole doping are not related to the structure nor to the magnetic interactions but rather due to increased two-dimensional character of the orbital interactions.

In this paper we continue our investigations of the hole doped A-site ordered manganites with neutron powder diffraction, SXR and cluster calculations in order to understand the alteration of the electronic Mn states as function of doping and as function of temperature. The crystal structures obtained with neutron powder diffraction reflect the various orbital and charge ordered phases and show an increase of the Mn-O-Mn bond angle as function of doping and temperature.

Theoretical simulations of the OO reflections $(\delta, \delta, 0)$ recorded at the Mn $L_{2,3}$ edges^{3,7} for the various hole doping concentrations and as function of temperature are presented. The cluster calculations consider the effect of the bandwidth,

FIG. 2. (Color online) Possible OO ground state in the ab plane for $\frac{2}{3}$ doping in $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$. The unit cell is indicated in the center of the double layer of Mn octahedra and includes the oxygen ions. The Mn^{3+} ions exhibit alternating x^2-y^2 and y^2-z^2 orbitals.

hole doping and magnetic correlations, and give insight into the electronic ordering of the Mn-O hybridized states.

II. EXPERIMENTS

We have investigated polycrystalline samples of $\text{Tb}_{1-x}\text{Ca}_x\text{BaMn}_2\text{O}_6$ with doping contents $x=0.05, 0.1, 0.2, 0.33$, and 0.4 , $\text{TbBa}_{1-y}\text{La}_y\text{Mn}_2\text{O}_6$ with $y=0.1$, and the half-doped materials $\text{SmBaMn}_2\text{O}_6$ and $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$. The compounds were synthesized following the same procedure as in Ref. 7. A detailed structural investigation was performed on compositions $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ and $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$ using neutron powder diffraction. The measurements were carried out at the high-resolution diffractometer for thermal neutrons, HRPT (Ref. 14), at the SINQ neutron spallation source of the PSI, Switzerland. The normal intensity mode of HRPT was used with the neutron wavelength $\lambda=1.49$ Å. All the temperature scans were carried out on heating. The refinements of the crystal structure parameters were performed using FULLPROF.¹⁵

Resonant soft x-ray diffraction experiments were performed at the RESOXS (Ref. 16) endstation at the SIM beamline of the Swiss Light Source of the Paul Scherrer Institut (PSI), Switzerland. Polycrystalline pellets of the manganite with 10 mm diameter were glued onto a copper sample holder mounted on a He flow cryostat which achieves temperatures between 10 and 400 K. Experiments were performed using linear horizontal or vertical polarized x-rays leading to π or σ incident photon polarization in the horizontal scattering geometry, respectively. Two-dimensional data sets were collected with a commercial Roper Scientific charge-coupled-device (CCD) camera mounted in vacuum. The sections of the resonant orbital powder-diffraction rings measured with the CCD camera are integrated along the vertical direction and fitted with a pseudo-Voigt function. This results in the integrated intensity, the position in 2θ and the background, which is mainly due to the fluorescence.

III. RESULTS

The aim of this study is to compare the energy dependencies of the resonant soft x-ray diffraction data from present A-site ordered manganites (Figs. 3 and 4) with theoretical simulations and structural investigations. Since the neutron diffraction investigation of $\text{SmBaMn}_2\text{O}_6$ is hampered by the large neutron absorption coefficient of Sm, we replace this cation by a mixture of Nd and Tb of the same average radius. The crystal structure of resulting compound $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$ is determined by neutron powder diffraction without large absorption. Although the tolerance factor in $\text{SmBaMn}_2\text{O}_6$ remains to be slightly different than in $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$, this produces only a small difference in the temperature at which the MI transition takes place. This temperature corresponds to $T_{\text{CO/OO}} \approx 360$ K for $\text{SmBaMn}_2\text{O}_6$ and $T_{\text{CO/OO}} \approx 400$ K for $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$. Figure 3 shows the energy dependence of the OO reflection $(\frac{1}{4}, \frac{1}{4}, 0)$ measured in the vicinity of the Mn $L_{2,3}$ edges for both half-doped compounds. The data is normalized at $E=643$ eV to unity and shifted vertically for comparison. The

FIG. 3. (Color online) Energy dependence of the integrated intensity of the orbital reflection $(\frac{1}{4}, \frac{1}{4}, 0)$, measured at the Mn L edges for polycrystalline $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$ (solid line) at 26 K and $\text{SmBaMn}_2\text{O}_6$ (Ref. 7) (striped line) at 120 K. Both sets of data were collected with π incident radiation and normalized and shifted for clarity.

spectral shape of the orbital reflection $(\frac{1}{4}, \frac{1}{4}, 0)$ is identical within the experimental uncertainty. This shows that the electronic ground state in both compounds can be assumed to be the same, which makes a direct comparison between structural data obtained by neutrons and the spectroscopic x-ray data feasible.

The crystal structure of half doped $R_{1-x}T_x\text{MnO}_3$ manganites for which R and T ions are randomly distributed (solid solution), such as $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, can be described in orthorhombic symmetry at high temperatures ($T \geq T_{\text{CO/OO}}$). The space group of this crystal structure is $Pnma$, which contains only one symmetry equivalent Mn site and therefore does not describe long-range CO at Mn sites.¹⁷ Below $T_{\text{CO/OO}}$, the crystal structure is refined in a monoclinic $P2_1/m$ symmetry $2\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$ superstructure, with two inequivalent

Mn sites in the unit cell, consistent with a charge and orbital ordering.¹⁸ The structures of several other half-doped manganites have subsequently been fitted using the same model.^{19–21}

As concerns the A-site ordered manganites such as $\text{TbBaMn}_2\text{O}_6$, their high-temperature crystal structure is described by the orthorhombic space group $Cmmm$. Similarly to solid solutions $R_{1-x}T_x\text{MnO}_3$, all Mn sites are equivalent.²² At $T_{\text{CO/OO}}=473$ K, the system undergoes a crystal structure transition from orthorhombic to monoclinic $P2_1/m$, associated with a diversification of Mn valences or formation of Zener polarons.^{2,22} However, the major monoclinic $P2_1/m$ superstructure reflections were observed to be very weak in our measured powder patterns. Therefore the neutron-diffraction data were refined with orthorhombic ($Cmmm$) crystal symmetry and $2a_p \times 2a_p \times 2a_p$ crystal structure¹⁵ for all temperatures and doping contents. It was observed that when the stoichiometry of the system changes, the diffraction pattern changes too. However, this changes do not result in a detectable new crystal symmetry but can simply be described by the atomic motions and changes of the unit cell parameters. The diffraction pattern at 300 K and the refinement plot for the $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ sample are shown in Fig. 5. The structure parameters obtained from this refinement are shown in Table I.

The MI transition is a first-order transition leading to the coexistence of two phases in the vicinity of the transition temperature. The temperature dependence of the unit cell parameters and volume are shown in Fig. 6 for the half-doped compound $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$ and $\frac{2}{3}$ -doped compound $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$. The lattice constants undergo dramatic changes. Two transitions can be distinguished in the temperature evolution of the unit cell parameters and the volume, one in the vicinity of $T_{\text{CO/OO}} \sim 410$ K, (Fig. 6) and the other in the vicinity of $T_{\text{CO2}} \sim 210$ K.

When increasing the temperature above $T_{\text{CO/OO}}=410$ K [see Fig. 6(a)] in the half-doped material, the unit cell pa-

FIG. 4. (Color online) (a) Energy dependence of the integrated intensity of the orbital reflection $(\delta_x, \delta_x, 0)$, measured at the Mn L edges for systems above half doping $\text{Tb}_{1-x}\text{Ca}_x\text{BaMn}_2\text{O}_6$ and below half-doping $\text{TbLa}_y\text{Ba}_{1-y}\text{Mn}_2\text{O}_6$ in polycrystalline samples (Ref. 3). The experimental data have been normalized to the intensity at the L_3 edge (643 eV) for comparison. (b) Energy dependence of the integrated intensity of the $(\frac{1}{4}, \frac{1}{4}, 0)$ reflection at half doping of polycrystalline $\text{SmBaMn}_2\text{O}_6$ with π incident radiation, measured at 120 K, 180 K, 235 K and 300 K, renormalized to the intensity at the L_3 edge (643 eV) (Ref. 7).

FIG. 5. (Color online) The Rietveld refinement pattern and difference plot of the neutron-diffraction data for the sample $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ at $T=300$ K measured at HRPT with the wavelength $\lambda=1.49$ Å. The rows of ticks show the Bragg peak positions. The structural parameters are shown in Table I.

parameters a and c show sharp positive jumps at $T_{\text{CO/OO}}$ of 0.13% and 0.81%, respectively, while b drops by -1.05% . Those anisotropic changes in the crystal unit cell result in an abrupt drop of the unit cell volume at $T_{\text{CO/OO}}$ by -0.11% . A similar volume collapse was also observed at the MI transition in A -site ordered $\text{HoBaCo}_2\text{O}_{5.5}$.²³ In this cobaltite, the volume collapse of the unit cell has been associated to the occurrence of orbital order of the Co^{3+} ions. In the vicinity of $T_{\text{CO}_2}=210$ K, where a restacking of the OO has been observed,^{5,7} a small drop in the unit-cell volume is observed.

Similar behavior is observed close to the MI transition in $\frac{2}{3}$ -doped $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ [see Fig. 6(b)]. The unit cell parameters a and c show a sharp increase at $T_{\text{CO/OO}}$ of 0.97% and 0.30%, respectively, while b decreases by -1.41% . The anisotropic changes in the crystal unit cell result in an abrupt drop of the unit-cell volume at $T_{\text{CO/OO}}$ of -0.16% . Surprisingly, the changes in the lattice constants a and b are larger than in the half-doped system. In contrast, in the vicinity of $T_{\text{CO}_2}=210$ K, a decrease in unit-cell volume as in the case of $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$ is absent, yet a change in slope is noted.

This agrees with the fact that OO restacking does not occur for the hole doped compounds. We note that additional reflections are observed for $T < 200$ K, indicative for antiferromagnetic ordering with $T_N < T_{\text{CO}_2}$. In summary, a similar contraction of the crystal structure is seen for all hole doped systems near the MI transition at $T_{\text{CO/OO}}$ whereas the changes in crystal structure near T_{CO_2} are different.

IV. DISCUSSION

Previously the energy dependence of the orbital reflection $(\delta_x, \delta_x, 0)$, where $[\delta_x = \delta(x)]$, for $x > 0$ and $(\frac{1}{4}, \frac{1}{4}, 0)$ for $y = 0.1$, in the vicinity of the Mn $L_{2,3}$ edges was recorded for different doping contents close to half doping [Ref. 3 reproduced in Fig. 4(a)]. The spectra are normalized to their maxima at the Mn L_3 edge. It shows that there is a distinct trend in the shape of the spectra with doping, i.e., some features of the energy become broader or more intense compared with others. These differences indicate a variation of the electronic Mn states. In a simple view such a change is not expected. When the doping is increased beyond half doping, the holes are disposed as far as possible from each other, giving rise to the linear behavior of q versus doping.³ In this case, the local structure around the Mn^{3+} ions (considering the nearest neighbors only) is not directly affected by doping.

In Fig. 4(b) the energy dependence of the OO reflection $(\frac{1}{4}, \frac{1}{4}, 0)$ measured in the vicinity of the Mn $L_{2,3}$ edges for the half doped material $\text{SmBaMn}_2\text{O}_6$ is shown for temperatures between 120 and 300 K normalized at $E=643$ eV to unity. In a previous study of this half-doped compound it was shown that the energy dependences do not change dramatically with temperature⁷ in contrast to what was observed in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$.²⁴ In the latter, the different features of the energy scan were shown to follow different trends as function of temperature, which was interpreted in terms of different order parameters of orbital order and Jahn-Teller distortion. Features labeled C and F correspond to Jahn Teller distortion, features A and B mostly to the OO. Although this clear different behavior is absent for $\text{SmBaMn}_2\text{O}_6$, small but distinct dissimilarities of different type can also be seen be-

TABLE I. Structure parameters in $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ [space group $Cmmm$ (No.65)]. The data are refined from the powder neutron-diffraction pattern measured at HRPT/SINQ with wavelength $\lambda=1.49$ Å (Fig. 5). The Bragg reliability factor is $R_{\text{Bragg}}=11.3\%$ and the conventional reliability factors are $R_{\text{wp}}=8.95$, $R_{\text{exp}}=4.70$, and $\chi^2=3.62$.

Atom	Position	x	y	z	B
Tb	$4h$	0.243(1)	0	0.5	0.92(7)
Ca	$4h$	0.243(1)	0	0.5	0.92(7)
Ba	$4g$	0.246(1)	0	0	0.51(7)
Mn	$8n$	0	0.247(1)	0.2563(6)	0.49(5)
O1	$4j$	0	0.2069(7)	0.5	1.5(2)
O2	$4i$	0	0.263(1)	0	1.10(9)
O3	$4l$	0	0.5	0.2856(9)	1.3(1)
O4	$4k$	0	0	0.2446(7)	1.5(1)
O5	$8m$	0.25	0.25	0.2807(7)	1.73(8)

FIG. 6. (Color online) (a) (Above) Unit-cell parameters as a function of temperature for $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$. (Below) Variation in volume with temperature for $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$. (b) (Above) Unit-cell parameters as a function of temperature for $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$. (Below) Variation in volume with temperature for $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ (Ref. 3). L.T. stands for low-temperature phase and H.T. for high-temperature phase.

tween energy dependences measured at different temperatures. Features D, E, and F become more intense upon heating while feature C broadens in comparison to features A and B. The evolution of the spectra as a function of temperature follows a similar trend as the ones observed as a function of doping.

The $L_{2,3}$ edges are sensitive to the local environment of the scattering atom. Doping and temperature modify the local environment structurally and/or electronically.

Concerning structural changes, in the $Cmmm$ space group and with the $2a_p \times 2a_p \times 2a_p$ cell we have five different oxygen sites leading to several Mn-O-Mn angles, and different oxygen positions (see Table I). To simplify the comparison we merge those angles obtained from the structural refinements to obtain an average Mn-O-Mn bond angle [Fig. 7(a)]. As can be seen in Fig. 7(a), the average Mn-O-Mn angle increases for increasing doping. The work of García-Muñoz

*et al.*²⁵ indicates that this corresponds to an increase in bandwidth. We plot in Fig. 7(b) the analogous result obtained as a function of increasing temperature, showing a similar trend.

The change of the average angle as a function of doping is about twice as large compared to the one upon temperature. The error bars versus temperature obtained from statistical error propagation of the individual errors are very large compared to the scattering of the data points. This indicates that the obtained individual bond angles are significantly correlated. Therefore the accuracy of the average angle is much better than the plotted error bars obtained from statistical error propagation.

Another interesting point is the relation between the orbital restacking transition at half doping and the anomalous orbital melting for the $\frac{2}{3}$ doping. Both transitions, which have been previously observed in soft x-ray resonant scattering measurements, can also be detected in the temperature de-

FIG. 7. (Color online) (a) Evolution of the average angle Mn-O-Mn as a function of doping content in $\text{Tb}_{1-x}\text{Ca}_x\text{BaMn}_2\text{O}_6$. The inset shows the unit cell of the high-temperature structure of $\text{Tb}_{1-x}\text{Ca}_x\text{BaMn}_2\text{O}_6$ in which the Mn-O-Mn angle is visualized as a tilt between the two neighboring oxygen octahedra. (b) Evolution of the average angle between Mn-O-Mn as a function of temperature in $\text{Nd}_{0.4}\text{Tb}_{0.6}\text{BaMn}_2\text{O}_6$.

pendence of the unit-cell volume of both compounds (Fig. 6). For the half-doping case, at low temperatures the orbital planes (Mn^{3+}) are aligned along the c axis, whereas above T_{CO_2} , the stacking of the orbital planes is pair wise shifted in the plane. This orbital stacking transition is sketched in the inset of Fig. 6(a). For the $\frac{2}{3}$ doping, at low temperatures we could assume again a ferro-type staking along the c axis, but above T_{CO_2} , differently to the previous case, there's much more freedom to stack the individual planes along the c axis. Shifting a plane perpendicularly to c by one perovskite unit cell, in one direction or its opposite, does not lead to the same result [see inset Fig. 6(b)]. The extended possibilities of having different stacking along the c axis, lead to many states which differ very little in energy. This allows having a thermally excited switching between the different stacking representing a dynamical sliding of the planes and that is equivalent to a correlated motion of electrons. This decoupling of ordered planes leads then to the slight volume increase above the onset of the dynamics that is visible in Fig. 6(b). Moreover, such dynamical sliding will also be expected to affect the correlation in the ab plane. The change in ordering period in this dynamical regime might then reflect a slightly smaller doping than the one expected from the exact Ca content. The OO unit cell is free to relax in the plane due the diminishing coupling along the c axis for increasing temperatures. Such sliding planes might possibly be related to the recently proposed sliding character of the charge density.²⁶

Calculations to describe the spectral shape of the orbital reflection have been done using the model of Ref. 27. This model describes, in second quantization, a small cluster consisting of a central Mn^{3+} site and the first neighboring shells of O and Mn^{4+} sites. The interaction term T_1 of Eq. 2 of Ref. 27 has been modified in order to obtain an orbital ordering of the e_g electron of x^2-y^2 kind in the ground state which corresponds to the presumed ordering for our physical system.⁷ Here we like to note that the calculation of the structure factor does not depend directly on the ordering wave-vector change for increased doping, as the scattering factors are calculated in the cluster code. It merely is reflected by the phase difference of π of the two orbital oriented sites ($\frac{x^2-z^2}{y^2-z^2}$) in the resonant x-ray structure factor. The T_1 term hybridizes the Mn 3d orbitals with the 2p orbitals of the neighboring oxygen ions and T_1 is given by

$$T_1 = \sqrt{2}t \sum_{\sigma} (g o_{x,\sigma}^\dagger d_{x2,\sigma} + o_{z,\sigma}^\dagger d_{z2,\sigma} + g o_{y,\sigma}^\dagger d_{y2,\sigma}) + \text{c.c.}, \quad (1)$$

where the symbols o and d are second quantization operators for the oxygen and central Mn orbitals, respectively. The y axis is in the crystal c direction. The value $g=0.7$ from Ref. 27 is used. In the original model the g factor multiplies only the $o_{x,\sigma}^\dagger d_{x2,\sigma}$ term, thus favoring a $3x^2-r^2$ orbital ordering. Here, the g factor multiplies also the $o_{y,\sigma}^\dagger d_{y2,\sigma}$ hopping operator, favoring x^2-y^2 -type OO.

The effect of change in the bandwidth on the OO spectra can be simulated by changing the t prefactor in the T_1 term and/or in the T_2 one [Eq. 3 of Ref. 27] which hybridizes the 2p oxygen orbitals with the Mn^{4+} ones. By varying t propor-

FIG. 8. (Color online) Change in spectral shape of the $(\delta_x, \delta_x, 0)$ reflection as a function of ε_p which results in a variation in the hole density at the oxygen sites.

tionally to the cosine of the Mn-O-Mn angle from Fig. 7 we did not observe noticeable effects. An angle variations on the order of 1% has a too small effect on the bandwidth. This indicates that the change in bandwidth does not directly reflect the changes in the spectral shape of the orbital reflection. Correspondingly, it might be a secondary effect caused by the doping and not relevant in the understanding of the electronic changes versus doping.

The direct effect of doping on the electronic structure has been simulated in the hypothesis of hole density concentrated on oxygen sites. To do so we have varied the ε_p parameter in Eq. 4 of Ref. 27 to take into account the electrostatic interaction of holes on the oxygen orbitals. ε_p represents the bare energy of the oxygen p orbitals, and is deduced from the charge transfer energy Δ , which is defined as the energy to transfer an electron from the oxygen onto a bare Mn atom (in the absence of hybridization). Lowering ε_p reflects therefore a transfer (or condensation) of holes at the oxygen. The oxygen U_{pp} Hubbard term being estimated to 5 eV (Ref. 27), an increase in x of 0.4 corresponds to a decrease in ε_p of 1 eV in the case of holes going to in-plane oxygen sites.

Figure 8 shows the change in spectral shape of the $(\delta_x, \delta_x, 0)$ reflection as a function of ε_p . A decrease in the energy of the oxygen 2p orbitals leads to an increase of the L_2 edge and of feature C. The agreement between these calculations in Fig. 8 and the experimental result obtained as function of hole doping [Fig. 4(a)] is prominent.

We have also tested the hypothesis of hole density increase at the Mn ion site by changing the bare energy of the Mn d orbitals ε_d . These simulations of increased holes at the Mn sites show an opposite trend in the energy dependencies compared to those calculated for increased holes at the oxygen sites. We conclude therefore that the holes are introduced in the oxygen 2p shell rather than in the Mn 3d shell. The fact that the hole doping leads to a linear dispersion of the orbital reflection with a $\frac{2}{3}$ doping being represented by a tripling of the unit cell, indicates that the holes are neither centered at the oxygen nor at the bond but are centered

around the Mn ions. In other words, it suggests that each neighboring oxygen gets the same fraction of the hole so that the center of mass stays at the Mn site but is not directly affecting the 3d electron count.

This view is consistent with very recent investigation of the Mn K_β fluorescence spectroscopy²⁸ and theoretical calculations based on LDA+ U of the electronic structure of manganites.²⁹ They find that the holes are introduced at the oxygen sites, forming an e_g symmetry orbital, leaking charge to the former Mn⁴⁺ sites. This results in a reduced charge transfer between the former Mn³⁺ and Mn⁴⁺ sites, representing a strong covalent character of the Mn-O sublattice.

The temperature dependence of the energy dependence of the OO reflection at half doping cannot be explained by an increase in hole density at the oxygen site. Such increase of holes is expected to increase the intensity at the oxygen K edge, as there are more empty states accessible as intermediate states in the resonant process. In addition the intensity at the Mn L_3 main edge (643 eV) is expected to decrease, as the total charge is temperature independent. This is in contrast with the observed temperature dependence of the OO intensity at the oxygen K edge and Mn L_3 edge, respectively, which are equal.³ Moreover, the observed increase in Mn-O-Mn angle, which remains small, does not support the observed increase in relative intensity at the L_2 edge. This suggests that the temperature effect on the spectral shape of the orbital reflection is probably more complex. It has been shown previously that the magnetic moment direction as well as spin correlations changes the spectral shape of the orbital reflection.^{27,30}

To investigate the influence of spin correlations on the spectral shape at half doping we consider the lowest calculated energy eigenstates, in particular, the first five eigenstates. They are contained within an energy range of the order of 10 meVs and correspond to different orientations of the central Mn spin S . They originate from the polarizing term H_2 (Ref. 27) which acts on the e_g orbitals of the cluster Mn⁴⁺ external ions. This polarizing term accounts, for the on-site mean-field exchange with the t_{2g} orbitals. These outer Mn t_{2g} orbitals, are absent from the model, and are represented by this mean field term. The inclusion of the external t_{2g} states in the model would be computationally very expensive.

Therefore we have performed two calculations. The first calculation, named LT (low temperature), has been performed as described above inducing magnetic correlations H_2 as in Ref. 27 at low temperature. The scattering factors from the first five eigenstates are averaged with weights decreasing versus eigenenergy.

For the second calculation, named HT (high temperature), we reduce the slope of the weights dependence versus eigenenergy and at the same time we reduce the polarizing term by dividing h by two in H_2 .²⁷ The parameter h is a direct measure of the spin correlations and reducing it, mimics the effect of temperature-induced spin disorder and the consequent reduction of the Mn-Mn magnetic correlation. The factors that we use describe qualitatively a temperature increase from 120 K at LT to 300 K at HT. The result of these calculations is shown in Fig. 9. The spectral shape changes mainly by an increase in intensity at the L_2 edge

FIG. 9. (Color online) Theoretical simulation of the effect of changing the magnetic correlations on the energy dependence of the orbital reflection ($\delta_x, \delta_x, 0$) in the vicinity of Mn $L_{2,3}$ edge.

compared to the L_3 edge. Our simulation reproduces the main trend in spectral shape giving further support of the importance of magnetic correlations in the description of the electronic properties of these manganites systems.

V. CONCLUSIONS

The hole doping and temperature dependence of A-site ordered manganites has been studied with neutron powder diffraction. In addition, we compare the resonant soft x-ray powder diffraction spectra to cluster calculations. The orbital order of the Mn³⁺3d states exhibits electronic changes as function of hole doping and as function of temperature. We have explored the origin of these electronic changes. The spectral changes observed in the orbital reflection with resonant diffraction at the Mn $L_{2,3}$ edges resemble similarity as function of hole doping and temperature. Our theoretical modeling demonstrates that the relative intensity at the L_2 edge increases, both for increased hole density at the oxygen and for induced spin disorder as function of temperature. In case of hole doping, the resonant spectra are well described with additional holes residing in the oxygen 2p shell yet centered around the Mn³⁺ ions. In contrast, the electronic changes observed as function of temperature are more likely caused by spin correlations.

The structural study found a volume increase at the anomalous orbital melting transition temperature for the $\frac{2}{3}$ -doping system, interpreted in terms of a decoupling and an onset of a dynamical sliding of two-dimensional OO planes. However, including these changes in the bandwidth in the model calculations do not lead to observable changes in the calculated spectra, and therefore indicate that the bandwidth change as a function of doping and temperature is a secondary effect.

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