I. INTRODUCTION

The correlated electron systems realized in transition-metal oxide (TMO) materials attracted an enormous deal of attention due to their outstanding electronic properties. Most prominent examples are the high-temperature superconducting cuprates or the colossal magnetoresistive manganites. Conventional theoretical concepts often fail to explain the electronic properties of TMO materials. For instance, many of these compounds have a partially filled d shell but, at the same time, exhibit insulating ground states: a clear fingerprint of strong electronic correlations. Since a general theoretical treatment of electron correlations is currently beyond the available computing power, an essential step toward a better understanding of TMOs is the development of effective models, which retain only the most relevant electronic degrees of freedom, while still providing a realistic description.

In the case of the doped cuprates, it is now well established that such a model has to contain the Cu 3d as well as the O 2p bands. This is demonstrated by the fact that holes doped to the CuO2 planes are largely localized on the oxygen ligands, forming the famous Zhang-Rice singlet (ZRS) with the central Cu 3d spin.1 These ZRSs are an important concept to describe the complex charge dynamics in the doped cuprates.

For the doped manganites, the situation regarding the relevant electronic states is less clear: until recently, many studies did not consider the oxygen 2p orbitals explicitly2–4 while latterly others have highlighted the importance of the oxygen states.5–7 In this paper, we address the issue of identifying the relevant electronic degrees of freedom for a prototypical manganite material, namely, La1−xSr1+xMnO4. These compounds, which are isostructural to high-temperature superconducting La1−xSr1+xCuO4, do not show magnetoresistive behavior8 but exhibit a wide range of electronic phases as a function of temperature and hole doping.9,10

The undoped parent compound LaSrMnO4 (x=0) displays an antiferromagnetic and ferro-orbital ordered ground state.11 It formally only contains high-spin Mn3+ sites (d5) coordinated by a distorted oxygen octahedron. According to an ionic picture, the distortion lifts the eg5 degeneracy and stabilizes the 3z2−r2 orbital, which is singly occupied while the x2−y2 level remains empty. However, since a half-filled d5 configuration is particularly stable, the ground state of such an octahedron is not a pure d5 but has a large admixture of d3Lz, which already shows that the covalency between the transition metal and the oxygen ligands plays an important role.

Upon substitution of La by Sr in La1−xSr1+xMnO4, holes are doped into the system. This has a strong impact on the lattice structure, the electrical resistivity, and the magnetic properties.6 In particular, a complex spin, charge, and orbital ordered ground state develops around x=0.5 below 230 K. The charge order in this state was mostly discussed in terms of a checkerboard ordering of Mn3+ and Mn4+ sites.12 However, such an integer charge segregation has been both experimentally13,14 and theoretically15–17 questioned. According to these studies, the spatial modulation of the manganese valence within the insulating and electronically ordered phase of half-doped La0.5Sr1.5MnO4 are very small, which would again point toward an active contribution of oxygen in the Mn-O bonding.

Experimentally, the doping-induced electronic changes can be examined in an element specific way by means of x-ray absorption spectroscopy (XAS), which probes the unoccupied states.18 In the case of TMOs, the relevant valence
states can be accessed directly by measuring the transition metal $L_{2,3}(2p \rightarrow 3d)$ and oxygen $K(1s \rightarrow 2p)$ absorption edges in the soft x-ray range. Indeed, recent XAS and resonant soft x-ray scattering (RSXS) studies at the oxygen K edge do indicate that the O 2p states play a prominent role in these materials.\textsuperscript{5–7} In the hard x-ray region, the transition-metal K edges, where the main edge corresponds to $1s \rightarrow 4p$ transitions, can be used to obtain information about the 3d states. In this case, the 3d states are probed indirectly via the 4p states, which are also sensitive to structural distortions.

Complementary to probing the unoccupied states by XAS and related techniques such as RSXS, K-shell x-ray emission spectroscopy (XES) provides access to the occupied density of electronic states.\textsuperscript{19} The $K\beta$ main lines arise from intraatomic $3p^2$ to 1s transitions. The hole in the $3p$ shell in the final state of the transition strongly interacts with the valence electrons.\textsuperscript{20} The $(3p, 3d)$ exchange interaction splits the $K\beta$ main lines into a sharp $K\beta_{1,3}$ and a broad $K\beta'$ feature.\textsuperscript{21,22} The intra-atomic origin of the strongest interactions in the $K\beta$ main lines is well established by comparison between spectra obtained on free metal atoms and solid-state systems.\textsuperscript{23} Several studies of the $K\beta$ lines in manganites have been reported previously.\textsuperscript{24–26} The chemical sensitivity of the $K\beta$ main lines arises from a modification of the $(3p, 3d)$ interaction as a result of changes in the valence shell. The exchange interaction dominates and, for instance, a high-spin/low-spin transition has a very pronounced effect.\textsuperscript{25} In the present case, where Mn is always in a high-spin configuration, a change in the Mn spin directly translates into a variation in the charge on the Mn.\textsuperscript{26} Structural changes will only affect the $K\beta$ line if they are accompanied by a change in the electronic structure that changes the $(3p, 3d)$ interactions. A change in crystal-field splitting, for example, may barely modify the $K\beta$ spectral shape as shown by Peng et al.\textsuperscript{28}

In this paper, we report the $K\beta$ main line spectra in polycrystalline and single-crystalline samples of La$_{1-x}$Sr$_x$MnO$_4$ with $x=0, 0.3,$ and 0.5 at room temperature. Many-body cluster calculations including the in-plane neighboring Mn sites are presented that successful reproduce some of the experimental observations. The limitations of this approach are discussed.

II. EXPERIMENTAL

Preparation of polycrystalline samples was done by solid-state reaction from the stoichiometric amounts of La$_2$O$_3$, SrCO$_3$, and MnCO$_3$. The resulting powders were pressed into rods and sintered at 1500 °C for 24 h in an oxygen atmosphere. Single crystals were grown from the rods by using a homemade floating-zone furnace as described in Ref. 13. They were cut with a surface normal to the [001] direction. Some pieces were ground and characterized by x-ray powder diffraction. All compounds exhibited patterns typical of a single phase. Magnetic characterization was also performed on these samples using a commercial Quantum Design superconducting quantum interference device magnetometer. The temperature scans of the dc magnetization for all samples were in agreement with the data reported in the literature.

X-ray emission spectra were recorded at beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The incident x rays were selected by means of a pair of cryogenically cooled Si (311) crystals. The total flux on the samples was $5 \times 10^{12}$ photons/s. Nonresonant XES was performed at 6600 eV incident energy. The emission spectrometer employed one spherically bent ($R=1$ m) Si crystal in (440) reflection that was arranged with sample and detector (avalanche photodiode) in a horizontal Rowland geometry at 90° scattering angle. All experiments were performed at room temperature. The beam size was 0.3 $\times$ 1 mm$^2$ (horizontal $\times$ vertical). A slit with 1.5 mm horizontal opening was placed in front of the detector. The energy bandwidth of the spectrometer was 0.6 (0.9 eV) eV at 6490 eV for the 15° (75°) geometry (vide infra). The influence of the change in spectral resolution on the measurements was tested by artificially broadening the spectra and forming difference spectra. It was found that the change in spectral broadening does not influence the results presented here. The step size for all recorded spectra was 0.2 eV. Three independent sets of data were recorded in order to determine the systematic experimental error to $\sim 0.1$ eV. LaMnO$_3$ and CaMnO$_3$ were used as reference systems. The count rate in the maximum of the $K\beta_{1,3}$ line is $10^4$ counts/s.

The integral of the spectral area between 6465 and 6545 eV was normalized to one in all recorded emission spectra. The $K\beta$ lines can be quantified either by a moment analysis of the $K\beta_{1,3}$ line\textsuperscript{19} or of the integral of the absolute value of the difference (IAD).\textsuperscript{27} The latter procedure proved to be more robust, i.e., less dependent on the spectral range, and was therefore chosen in the present study. The area below the emission curve of LaMnO$_3$ was taken as a reference for the IAD analysis.

The geometry for the polarization-dependent study of the single-crystalline samples is shown in Fig. 1. We consider nonresonant x-ray emission where absorption and emission are not coherently coupled. The incident light is linearly polarized with the polarization in the plane that is spanned by (k, k'). The core hole s (spherical) symmetry, the polarization of the incident x-ray beam is not relevant. The emit-
HARD X-RAY PROBE TO STUDY DOPING-DEPENDENT...

We will refer to the two experimental geometries by $k' \sim n$ ($k' \sim \perp n$) throughout the paper. The crystal $c$ axis coincides with the normal $n$ on the crystal surface.

We treat the emitted x rays within the dipole approximation. As a consequence, only $3p_{x,y,z}$ orbitals that are normal to $k'$ are observed in $3p$ to $1s$ transitions in single crystals. It follows that the $k' \sim \perp n$ geometry probes the crystal $ab$-plane components while $k' \sim n$ contains a 50% contribution from the crystals $c$ axis.

III. THEORY

We have simulated the effect of doping along the series using a many-body cluster model from a previous work devoted to a RSXS study at the Mn $L_{2,3}$ edge in La$_{0.5}$Sr$_{1.5}$MnO$_4$. In this model, the 3$d$ electrons of a central Mn site are coupled to the neighboring $p$-oxygen orbitals by a hopping term modulated by Slater-Koster parameters. Beyond the MnO$_6$ octahedra, in-plane oxygen orbitals are in turn coupled to the orbitals of the neighboring Mn sites. To keep the Hilbert space dimension below an affordable limit, only one external $e_g$ orbital per external Mn atom is considered: the one directed toward the central Mn. Different electronic configurations were considered while keeping constant the total number of electrons in the cluster, and limiting the oxidation state of the central Mn atom between +1 and +5. Using a larger number of configurations does not change the computed results. We have used our model to simulate the Mn 3$d$ occupancy as a function of doping and to simulate the Mn $K\beta$ emission as well as its polarization dependence.

For the Mn 3$d$ occupancy study, we have kept the same set of parameters used for the fit of RSXS spectra in Ref. 16, except for $e_g$ in Eq. 5. This term determines the energy level of the external, i.e., nonphotoexcited, Mn 3$d$ orbitals and thus models in-plane oxygen mediated Mn-Mn interactions. By lowering (increasing) this level, we can increase (diminish) the electron occupancy on external orbitals. The external orbitals can hence be considered as a charge reservoir that allows to mimic the effect of doping on the MnO$_6$ octahedra. Indeed, when $e_d$ increases (decreases), the ground-state energy is minimized by decreasing (increasing) the expectation value of electron occupancy on the external orbitals. As the total charge in the cluster is fixed, such doping affects the electron occupancies on the central Mn atom and on the six neighboring oxygen atoms.

To simulate the Mn $K\beta$ emission and its polarization dependence, we have reset $e_d$ to its RSXS fit value, and added 1$s$ and 3$p$ shells to the model. Atomic values for the spin-orbit coupling $\xi_{3p}$ and the Slater integrals between 3$p$ and 3$d$ were calculated using Cowan’s Hartree-Fock code. These Slater integral values were then scaled down by a factor of 0.7. The renormalized Slater integrals $F_{3p3d}^0$ and $F_{1d3d}^0$ are both taken equal to 1.1$F_{dd}^0$. The effect of the variation in the Mn-O apical distance as a function of doping was taken into account by rescaling the Mn-O hopping for the apical bond. For the emission process, only the lowest energy configurations of the system with one 1$s$ core hole were taken as initial states. Due to a weak 1$s$–3$d$ coupling, these low-energy configurations correspond to differently coupled 1$s$-shell and 3$d$-shell spins. Higher energy configurations were not taken into account.

In the calculation of the spectra, the final states in the region of the strong $K\beta_{1,3}$ line (which corresponds to $S = 5/2$ in an ionic picture) were broadened with a Lorentzian function with width of 1.1 eV. For those corresponding to the $K\beta'$ shoulder ($S = 3/2$), we used 4.4 eV. These values were adjusted in order to fit the data. The reason for the larger width observed for the $S = 3/2$ states resides in the fact that the 3$d$ to 3$p$ radiative decay channel is favored by the spin alignment of the 3$p$ hole with the 3$d$ spin.

IV. RESULTS AND ANALYSIS

A. Single crystals

The experimental $K\beta$ main emission lines from single crystals of La$_{1-x}$Sr$_{1+x}$MnO$_4$ ($x = 0$, $x = 0.3$, and $x = 0.5$) with...
The relative energy calibration between MnIII and MnIV systems in Ref. 19. The absolute energy calibration using crystalline samples of the model systems LaMnIIIO3 and MnIVO2 is less correct because they were taken in the same experimental conditions. Thus the shape and not the position of the difference spectra can be compared. In all cases, the shift of the Kβ1,3 line with increasing oxidation state is accompanied by a decrease in the Kβ’ intensity giving rise to a typical difference signal. Difference spectra between high-spin and low-spin Fe and Co systems have been reported by Vankó et al.27 and Glatzel et al.33 where a similar difference signal is observed. The strong similarity between the perovskites (CaMnIVO3-LaMnIII03), binary oxides, and fluoroiodides difference curves compared to the linear dichroism for x=0 suggests that the latter arises from a change in electronic structure, namely, a change in the valence-shell orbital population. Indeed, a decrease in 3d orbital population results in a weaker Kβ’ feature and a shift to lower energies of the Kβ1,3 peak.

We thus find based on the linear dichroism that for the system with the strongest tetragonal distortion (x=0) more electron density is present along the c direction than in the ab plane. This is readily understood since the 3z²−r² orbital (z coincides with c axis) is the first axial 3d orbital that is populated in tetragonal symmetry with elongation along z while the x²−y² orbital remains empty. The dichroic signal for x=0.5 is small and the spectral shape markedly different. The signal is inverted as compared to the compounds with Sr doping. The angle-resolved emission spectra thus coincide with the next section.

The changes in the Kβ main line along the doping series for the different polarizations [Fig. 2(b)] indicate an increase in electron density in the ab plane and a decrease along c with Sr doping. The angle-resolved emission spectra thus indicate that hole doping facilitates the charge transfer from the 3z²−r² to the x²−y² orbitals as already proposed in Ref. 6 based on XAS and XRD measurements. It now needs to be determined by how much the integrated electron density in the Mn valence shell changes upon doping. To this end, the measurements on polycrystalline samples are discussed in the next section.

B. Polycrystalline samples

The Kβ main emission spectra from polycrystalline samples of LaSrMnO4, La0.5Sr1.5MnO4, and La0.5Sr1.5MnO4...
are shown in Fig. 4 together with the reference systems LaMnO3 and CaMnO3. The expected spectral change (vide supra) is observed between formal MnIII in LaMnO3 and MnIV in CaMnO3. We followed the procedure as suggested in Ref. 27 to quantify the spectral changes by means of the integrals of the absolute values of the difference spectra (IAD). The results are shown in Fig. 5.

Within a simple ionic picture, one would assign the spectral change from LaMnO3 to CaMnO3 to an integer decrease in charge on Mn. Formally, the spectral changes in the La1−xSr1+xMnO4 series should span half of the change in the reference systems. This is based on the assumption that only Mn takes part in balancing of the charge upon hole doping. The charge on the oxygen ions is fixed at 2− in an ionic picture.

However, the Mn Kβ main line spectral shapes as well as the IAD values are nearly identical for the three samples of the La1−xSr1+xMnO4 series. The change in IAD value between x=0 and x=0.5 is approximately 15% of the change between LaMnO3 and CaMnO3 as opposed to the expected 50%. The electronic structure at the Mn sites therefore changes much less than it would be anticipated based on an ionic model.

We also show in Fig. 5 the energy position of the Mn K main absorption edge (taken as the first maximum in the derivative of the absorption spectra) from the XANES measurements reported in Ref. 13 on polycrystalline samples of this series of compounds. The shifts of the main edge within the La1−xSr1+xMnO4 series relative to the reference systems LaMnO3 and CaMnO3 are considerably larger than for the Kβ emission lines. While the K-edge position follows approximately what would be anticipated based on the formal valence, the spectral changes in the Kβ lines are substantially less than expected.

This apparent contradiction can be reconciled by noting that the K absorption edge is sensitive to both, the electronic structure and the local coordination while the Kβ lines are mainly sensitive to the electronic structure. We thus conclude that the edge shift in the La1−xSr1+xMnO4 series mainly arises from changes in the interatomic distances and that the charge on the Mn ion changes only very little as evidenced by Kβ spectroscopy.

As a consequence, we find that the injected holes are mainly localized on the oxygen lattice as it was suggested by Ferrari et al.34 We also point to the fact that the Kβ main line for LaSrMnO4 is already markedly different from LaMnO3 even though both compounds formally contain MnIII ions. Layered and cubic structures thus give a different charge at the Mn site. In fact, Mn in LaSrMnO4 appears more oxidized than in LaMnO3. We note that Tyson et al. invoked for the LaMnO3 and CaMnO3 reference systems a strong covalent character based on Kβ spectroscopy,35 i.e., the difference in charge density on the Mn ions between the two systems is less than one electron.

X-ray emission lines that arise from transitions between core levels have been successfully modeled using ligand-field multiplet theory.18,19,28 The reason for the good agreement between experiment and theory is that these deexcita-

FIG. 5. Integrals of the absolute values of the difference spectra (IAD) for the Mn Kβ main emission lines from polycrystalline samples with x=0, 0.3, and 0.5, and CaMnO3 (circles) with LaMnO3 as reference. The energy position of the Mn K absorption spectra is shown along the right ordinate axis (crosses). The scale of the ordinate axes is chosen such that the IAD values and edge positions coincide for LaMnO3 and CaMnO3.

FIG. 6. (Color online) (a) Calculation of the occupancy variation for the 3d shell of the central photoionized Mn and the 2p states of the nearest six O as a function of the $\delta' - \varepsilon_d$ energy difference; (b) Kβ main emission lines calculated for $\mathbf{k'} = \mathbf{ln}$ (dotted gray) and $\mathbf{k'} = \pm \mathbf{n}$ (solid black) as a function of the tetragonal distortion parameter $\delta$ of the MnO6 octahedra.
tron processes are not directly sensitive to the fine structure of the energy levels in the valence shell. Correct treatment of the electron-electron interactions within an atomic multiplet model already provides good overall explanation of the spectral features. The influence of the valence electrons on the spectral shape is indirect via electron-electron interactions between the core hole and valence shell. Crystal-field splittings and orbital hybridizations may change the valence-shell electron configuration and thus influence the $K\beta$ spectral shape. This can be considered in a ligand-field multiplet model as described in the following.

In Fig. 6(a), we show the occupancy variations for the central photoionized Mn 3d, O 2p, and external Mn 3d orbitals as a function of the difference $\epsilon_d^0-\epsilon_d$ of the external Mn $e_g$ energy with respect to the $e_g$ value established in Ref. 16. When the external orbital energy increases, electronic charge of these orbitals moves to the central MnO$_6$ cluster. The cluster calculation shows that the central Mn 3d occupancy variation is less than 0.1 electrons while the total charge on oxygen 2p orbitals, in the O$_6$ octahedra, varies by about 0.5 electrons. Our theoretical model therefore predicts that the effect of doping mainly affects the occupancy of oxygen orbitals while the variation in the charge on the Mn ions remains small. The model shows that holes are injected in Mn-O or orbitals with a higher probability to find holes on oxygen atoms.

This behavior is due to the energy position of the oxygen bands relative to the Mn bands. We have done a numerical test, where we have “switched off” the Mn-O hopping term and kept the oxygen band filled and Mn in a 3$d^5$ configuration. Under these conditions, the energy of the filled oxygen band is $\sim$0.7 eV higher than the first unoccupied level on the Mn ion. This energy difference gets even larger in the intermediate state of the fluorescence process due to electron-hole interaction.

As an effect of hopping, ($t=1.8$ eV) electrons are back-donated to Mn through the Mn-O bonds. The average back-donated charge is $\sim$0.7 electrons collectively given through all six bonds of the MnO$_6$ octahedra. We have verified that the quantum numbers of the Mn ion remain almost constant under the effect of this backdonation. In particular, $S^z$ is about 5.2, not far from 6, which is the Hund-rule predicted value for a 3$d^5$ electronic filling.

Figure 6(b) shows the calculated XES spectra for different values of the tetragonal distortions as described by $\delta$, where $(1+\delta)$ is the ratio between c axis and in-plane Mn-O bond lengths. We have set equal distances for the a and b axes. In the model, we have rescaled the hopping parameters according to the length of the corresponding bonds, the scaling factor being $(1+\delta)^{-3}$. It can be observed that the anisotropy, in particular, the separation between the main peaks for in-plane and perpendicular polarizations, has the correct order of magnitude. We performed the same calculation for an isolated atom (setting the Mn-O hybridization to zero) and using a crystal field to remove the degeneracy in the 3$d$ orbitals (spectra not shown). This calculation strongly overestimates the linear dichroism and the agreement with experiment in this case is very poor.

The reason is that in the nonhybridized case, the 3$d_{3z^2-r^2}$ orbital has an occupation equal to one in the presence of a crystal field while in the hybridized model, the occupation is less than one. This is due to the hopping between O and external orbitals, and between Mn and O. For the same reason, the 3$d_{x^2-y^2}$ occupation is nonzero in the presence of hybridization. Thus, orbital hybridization reduces the charge anisotropy around the Mn ion as compared to the ionic model. We define $\delta$ as the difference between apical and basal Mn-O distances normalized by the average Mn-O bond length in each compound of the series. We observe that the linear dichroism has the correct sign for $\delta=0.2$ (corresponding to LaSrMnO$_4$) with the peak separation decreasing when $\delta$ is reduced. This trend in the calculations is the result of the competition between two effects: first, the c-axis distortion which tends to increase the charge density along the c axis, and second, a kinetic effect which favors in-plane occupancy to lower the energy due to the oxygen-mediated hopping to external Mn orbitals. This conclusion is verified by a calculation for an isolated MnO$_6$ octahedron where the external orbitals have been removed. In this case, the anisotropy is obtained immediately as soon as the octahedral symmetry is broken and remains practically independent of $\delta$. The model therefore implies that increase in the in-plane occupancy is related to intersite hopping processes within the ab plane.

Our calculations give, for $\delta$ going to zero, a lower energy of the $K\beta_{1,3}$ peak for $k' \parallel n$ than for $k' \perp n$ configuration. The experiment shows instead almost identical positions for the two peaks. We think that the reason for this discrepancy lies in the limited size of our model. In reality, the ground state in manganites is realized by a symmetry-broken phase which consists of different nonequivalent Mn sites, long-range ordered at low temperatures. We think that in the real system some of these sites conserve a charge anisotropy with more charge along the c axis which counterbalance the effect of those sites whose charge is reoriented into the ab plane by Mn-Mn interaction.

A more realistic calculation that takes a larger cluster into account may yield a better agreement. However, such calculations including all relevant interactions are beyond cur-
mentally available computing power. A feasible approximation consists of performing separate calculations for the two Mn sites and average their contributions. We assume that inequivalent Mn sites can be characterized by different 3d-shell configurations: one shows an occupied in-plane $e_g$ orbital while in the other site, the out-of-plane orbital is occupied. In the absence of distortion ($\delta=0$), the first case is favored while a tetragonal distortion with $\delta=0.1$ suffices to realize the latter configuration.

Another experimental technique that has been used to study the reorientation of the occupied $e_g$ orbitals is XAS linear dichroism at the $L$ edge. Huang et al.\textsuperscript{36} observed that the occupied $e_g$ orbitals, in La$_{1-x}$Sr$_x$MnO$_4$ have a prevalent component along the $c$ axis. In Fig. 7, we show our calculation for the XAS linear dichroism at the $L_{2,3}$ edges for tetragonally distorted MnO$_6$ clusters. The difference between the absorption for light polarization perpendicular and parallel to the $c$ axis has been calculated for $\delta=0$ and $\delta=0.1$. The average of these two calculations is also shown in the figure which corresponds to La$_{0.5}$Sr$_{1.5}$MnO$_4$ ($\delta=0.05$) where there are two nonequivalent Mn sites present. Here the calculated XAS linear dichroism has on average a positive component and it agrees reasonably well with the experimental data.\textsuperscript{36}

V. CONCLUSIONS

We have presented a $K\beta$ study on polycrystalline and single-crystalline samples of the La$_{1-x}$Sr$_x$Ca$_y$MnO$_4$ series. The $K\beta$ main emission lines from powders show that the electron density that is localized on the Mn atoms changes very little for $0 \leq \kappa \leq 0.5$. This is not consistent with a change in the electron density by 0.5 electrons per Mn atom. A similar behavior had been reported in La$_{1-x}$Ca$_x$MnO$_4$ for $0 < \gamma < 0.3$ where it was related to the transition from the insulator to the metallic character of the samples that occurs in this doping range.\textsuperscript{35} We explain our results with an active role of the neighboring O atoms in the charge-transfer process and an almost unchanged total Mn 3d occupancy.

In addition, the polarization-dependent measurements done on single crystals reveal that the main change related to Mn 3d orbitals is a redistribution of the $e_g$ charge from states oriented out-of-plane to states parallel to the $ab$ plane.

These two main results, namely, (i) the small change in the charge on Mn upon increasing $x$ and (ii) the redistribution of the $e_g$ electrons have been reproduced by many-body cluster calculations. They yield a pronounced O 2$p$ character of the doped charge carriers, which explains (i). Further, the extended cluster calculation evidences that the charge redistribution related to the $e_g$ orbitals is mainly caused by non-local effects (kinetic energy, exchange interactions) within the $ab$ planes.

These conclusions are in good agreement with a previous O K edge study,\textsuperscript{8} where complementary results regarding the unoccupied O 2$p$ states were reported.

Taken together the above discussion shows that the doping-induced changes to the electronic structure involve both the oxygen 2$p$ and the Mn 3d bands, which both play an active role, and contrast with the classical ionic model perspective as previously stated.\textsuperscript{5,7,37,38}

We believe that this result is an important input for the development of effective models which is an essential step toward a better understanding of these complex materials. Other theoretical approaches to the physics of manganites include recent local-density approximation plus dynamical mean field theory (DMFT) calculations that have led to promising results.\textsuperscript{39} It would be interesting to apply this formalism to the series of compounds studied here and compare the results to our analysis of the experimental data.

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30 We have only considered the fully relaxed eigenvectors and verified the validity of our approach by taking the lowest energy eigenvector of the nonionized system. The resulting vector projects to 90% over the two almost-degenerated lowest levels of the 1s core-hole system.