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Hole distribution between the Ni 3d and O 2p orbitals in Nd$_{2-x}$Sr$_x$NiO$_4$$_\delta$

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We present a joint experimental and theoretical study of x-ray absorption at the O-K and Ni-L$_{2,3}$ thresholds of Nd$_{2-x}$Sr$_x$NiO$_4$$_\delta$ providing an analysis of the distribution of the doped holes induced by Sr substitution between Ni 3d and O 2p orbitals. The preedge peak in the O-K x-ray absorption (XAS) spectra, reflecting holes located in the O 2p orbitals, increases monotonically with the degree of Sr doping up to the maximum doping level studied ($x=1.4$). The saturation in the relative intensity of the O-K preedge peak in the analogous lanthanum nickelate reported in the literature is shown to be most likely due to surface oxygen deficiency. Furthermore, the experimental Ni-L$_{2,3}$ XAS spectrum of the Ni(III) nickelate Nd$_{1.1}$Sr$_{0.9}$NiO$_{3.95}$ was simulated by a cluster approach, including charge-transfer and complete multiplet interactions, and compared with the corresponding spectrum of the Ni(III) system Nd$_2$La$_{0.5}$Ni$_{0.5}$O$_4$. The 3d$^1$ weight in the ground state of Nd$_{1.1}$Sr$_{0.9}$NiO$_{3.95}$ was found to be 42%, somewhat smaller than the value of 51% found for Nd$_2$La$_{0.5}$Ni$_{0.5}$O$_4$. This indicates the influence of nonlocal effects in x-ray-absorption spectroscopy, which, in this case is due to the increased covalency in the Sr-doped system as a result of inter-NiO$_6$-cluster interaction. Such interactions are absent in Nd$_2$La$_{0.5}$Ni$_{0.5}$O$_4$, which is characterized by having isolated NiO$_6$ clusters.

I. INTRODUCTION

The electronic and magnetic properties of the nickelate La$_{2-x}$Sr$_x$NiO$_4$$_\delta$ have been extensively studied in the past$^{1-4}$ as it possesses many features similar to those of the high-$T_c$ superconductor La$_{2-x}$Sr$_x$CuO$_4$. Both systems have the same basic tetragonal K$_2$NiF$_4$ structure, which consists of an alternate stacking of KF rock-salt-type layers and KNiF$_3$ perovskite-type layers.$^5$ Their parent compounds La$_2$NiO$_4$ and La$_2$CuO$_4$ possess antiferromagnetic order that disappears at low doping levels.$^6$ There are, however, some striking differences between the two systems. La$_{2-x}$Sr$_x$CuO$_4$ turns metallic for $x>0.05$ and exhibits superconductivity for 0.05 $< x < 0.3$. In contrast, La$_{2-x}$Sr$_x$NiO$_4$$_\delta$ becomes metallic only at much higher Sr doping levels ($x>1.0$) and does not turn superconducting. In the nickelate, for high doping levels, the NiO$_6$ octahedra are nearly equiaxial. Therefore the $e_g$ orbitals are almost degenerate and the charge carriers are found in hybrid states that arise from interactions between the Ni3$d_{3z^2-r^2}$/Ni3$d_{1z}$,3$d_{3z^2-r^2}$ states and the O 2p states. It has been suggested that strong electron-phonon coupling may well be the main reason for the insulating behavior of the doped ($x<1$) nickelates,$^7,8$ and the doped states have been discussed in terms of polarons which behave quantum mechanically on the length scale of the lattice constant.$^7$ For particular doping levels (e.g., La$_{1.5}$Sr$_{0.5}$NiO$_4$) polaron lattices or stripe phases have been observed in the doped nickelates.$^9$

Regarding the nature of the doped charge carriers, it has generally been stated that the doped holes have mainly O 2p character in La$_{2-x}$Sr$_x$NiO$_4$$_\delta$,$^{7-11}$ in analogy to the situation in La$_{2-x}$Sr$_x$CuO$_4$$_\delta$.$^{12}$ For the nickelates this conclusion was based upon the observation of a pre-edge peak in the O-K x-ray-absorption (XAS) spectra whose intensity increases with increasing Sr doping. Up to now, however, studies by high-energy spectroscopies have been reluctant in discussing the issue of the number of holes located in Ni 3d states. This is a consequence of the overlap between the La-M$_1$ and the Ni-L$_3$ absorption thresholds, which prevents a thorough experimental and theoretical analysis of the Ni-L$_{2,3}$ XAS spectra.

In the present work we present the results of a joint experimental and theoretical study of the O-K and Ni-L$_{2,3}$ XAS spectra of the Nd$_{2-x}$Sr$_x$NiO$_4$$_\delta$ system, with particular emphasis put on high Sr doping levels. With the reasonable assumption that the identity of the trivalent lanthanide element in the block layers is not crucial for the electronic states in the NiO$_2$ plane, the choice of Nd instead of La brings the advantage of full accessibility of the Ni-L$_{2,3}$ absorption thresholds, thus enabling a study of the distribution of holes between O 2p and Ni 3d states.

In general, the L$_{2,3}$-XAS spectra of 3d-TM compounds have been reproduced successfully in the framework of charge-transfer multiplet calculations truncating the basis to retain only terms involving $d^n$ and $d^{n+1}$L in the ground state as well as $d^{n+1}$ and $d^{n+2}$L in the final state.$^{13}$ However, many-body interactions induced by covalency are important...
for both Cu(III) and Ni(III) oxides. In such situations, it has been shown recently that an approximation involving a truncated basis could result in erroneous parameters for strongly covalent compounds. Thus in the calculations presented here we include the complete basis along with all the interaction terms (i.e., full multiplet, charge-transfer, and hopping interactions).

II. EXPERIMENTAL DETAILS

Solid samples of Nd$_2$-$x$Sr$_x$NiO$_4$-$\delta$ were prepared as described in Ref. 16 for the analogous La mixed crystals. The phase purity (>98%) was controlled by x-ray diffraction and the oxygen content was determined by iodometric titration. We will report about the phase characterization and further spectroscopic properties in detail elsewhere. The XAS measurements were performed at the SX700/II plane-grating-monochromator beamline operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). For the O-K spectra, the fluorescence-yield (FY) mode with an escape depth of typically 2000 Å was used, while the Ni-L$_{2,3}$ data were taken in the total-electron-yield (TY) mode with a typical escape depth of 50 Å. The O-K spectra were corrected for the energy-dependent incident flux and for self-absorption effects according to a procedure described elsewhere, and they were normalized at 60 eV above threshold. The experimental energy resolution was set to 0.3 and 0.6 eV at the O-K and Ni-L$_3$ thresholds, respectively. The surfaces of the samples were cleaned in UHV by scraping with a diamond file. Unfortunately, the surfaces of these highly oxidized TM compounds are not very stable in vacuum, particularly when exposed to x rays, leading to an oxygen deficiency in the surface layer. However, this is not a serious problem for the O-K XAS spectra recorded in the volume-sensitive FY mode. In order to limit the influence of such surface effects on the Ni-L$_{2,3}$ XAS spectra, the data acquisition time was restricted to ten minutes after each cleaning procedure. Under these conditions, the O-K and Ni-L$_{2,3}$ spectra of different samples with the same doping level measured during different beam times were found to be identical.

III. RESULTS AND DISCUSSION

A. O-K XAS spectra

To start with, and also to enable a detailed comparison with previous investigations, we discuss first the O-K XAS spectra of Nd$_2$-$x$Sr$_x$NiO$_4$-$\delta$ which are shown in Fig. 1 together with the spectrum of NiO as a reference. The observed spectral profiles of the Nd nickelates studied here are very similar to the previously published spectra of polycrystalline La$_2$-$x$Sr$_x$NiO$_3$ samples recorded in the TY mode, with $x$ values up to 1.1, as well as to data from single-crystalline samples recorded in the FY mode for $x$ up to 0.6. The main change in the spectral features with increasing doping level is an increase in the intensity and a shift to lower energy of the pre-edge peak below 530 eV, which is assigned to ligand hole states induced by doping. Polarization dependent XAS studies of single crystals indicate that this peak is comprised of three features, related to final states with $^3B_1$, $^1A_1$, and $^1B_1$ symmetry (listed in order of increasing energy). These final states contain either single holes in: the Ni 3$d_{x^2-y^2}$ and 3$d_{3z^2-r^2}$ orbitals in a high spin arrangement ($^3B_1$), the Ni 3$d_{x^2-y^2}$ and 3$d_{3z^2-r^2}$ orbitals in a low spin arrangement ($^1A_1$), or two holes in the Ni 3$d_{x^2-y^2}$ orbital.

The feature at 531.8 eV in NiO, which is assigned to O-$\delta$ as reference. The data were recorded using the bulk-sensitive FY method (filled circles). For comparison, the spectrum obtained for the $x=1.4$ sample in the TY mode (dashed curve) is also given by the solid line. The solid curves through the data points serve as a guide to the eyes.

3$d_{x^2-y^2}$ and 3$d_{3z^2-r^2}$ orbitals in a low spin arrangement ($^1A_1$), or two holes in the Ni 3$d_{x^2-y^2}$ orbital ($^1A_1$).

As regards the O-K edge data, the main difference with the previous observations for La$_2$-$x$Sr$_x$NiO$_4$-$\delta$ is that here the intensity of the pre-edge peak steadily increases with the Sr content, right up to the highest doping level of 1.4. In the data from the La system, the pre-edge peak decreased in intensity from $x=0.8$ to $x=1.1$. This difference might be due to oxygen deficiency in the surface layer of the sample, which is a serious problem for higher Sr doping levels. In this context, we note that the TY mode used in Ref. 8 is significantly more sensitive to surface oxygen deficiency than the FY mode employed here. To illustrate this, we also show the TY spectrum of the $x=1.4$ sample in Fig. 1 (dashed line), in addition to the data recorded in the FY mode. Our TY curve is similar to previously published data for the La system with $x=1.4$. The lower spectral weight of the pre-edge peak in the TY spectrum in comparison with the FY spectrum reflects a lower concentration of oxygen hole states in the sample surface. The XAS data measured in the FY mode from single crystals, with surfaces prepared ex situ, revealed a slowing down in the growth of the ligand-hole peak approaching the maximum doping level studied.
For the data presented here, the evolution of the spectral weight (integrated areas) of the pre-edge peak with doping is summarized in Fig. 2. It is clear from this figure that the intensity grows with \( x \) up to \( x = 1.4 \).

**B. Ni-\( L_{2,3} \) XAS spectra**

In this section, we first present the Ni-\( L_{2,3} \) XAS spectra of the \( \text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4 \) system, followed by a comparison of the two formal Ni-III systems, \( \text{Nd}_{0.9}\text{Sr}_{1.1}\text{NiO}_{3.95} \) and \( \text{Nd}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4 \). We will then discuss the physical picture used for an interpretation of such TM-\( L_{2,3} \) XAS spectra, before proceeding on to the final section that deals with the results of the charge-transfer atomic-multiplet calculations.

**1. The Ni-\( L_{2,3} \) XAS spectra of \( \text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4-\delta \)**

Figure 3 shows the XAS spectra at the Ni-\( L_{2,3} \) thresholds together with a spectrum of NiO for reference. We would like to point out that these are the first Ni-\( L_3 \) XAS data of the \( \text{Sr} \)-doped \( L_2 \text{NiO}_4 \) system, which are free of overlap with spectral structures from other elements, i.e., these spectra show directly the experimental data and are not obtained by subtraction or other data manipulation procedures.

A striking change in the Ni-\( L_3 \) spectral structure is observed upon increasing the level of \( \text{Sr} \) doping. In particular, the spectral weight of the high-energy component at 853 eV (about 1.7 eV above the main peak in the Ni-\( L_3 \) XAS spectrum of NiO) increases dramatically with \( x \), becoming the dominant feature for \( x > 1.0 \). At the Ni-\( L_2 \) threshold, the lower energy component of the double-peaked structure loses intensity relative to the higher energy structure. This higher energy structure also shifts up in energy by about 0.5 eV for \( x = 1.4 \). It is furthermore evident that the \( L_{2,3} \) spectra as a whole turn progressively broader with increasing doping level. This broadening appears to be intrinsic to \( \text{Ln}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta} \) systems, in which the NiO\(_6\) octahedra form an extended network. The spectrum of the \( x = 1.1 \) material shown here [\( \delta = 0.05 \), corresponding formally to Ni(III)] is qualitatively similar to that observed in a XAS study of \( \text{NdNiO}_3 \), performed with a somewhat better energy resolution.\(^{21}\)

**2. Comparison of the two Ni(III) systems \( \text{Nd}_{0.9}\text{Sr}_{1.1}\text{NiO}_{3.95} \) and \( \text{Nd}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4 \)**

We now compare the two formally trivalent \( \text{Ni} \) systems, \( \text{Nd}_{0.9}\text{Sr}_{1.1}\text{NiO}_{3.95} \) and \( \text{Nd}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4 \). Both of these materials crystallize in the \( K_2\text{NiF}_4 \) structure and contain low-spin Ni(III). The difference between these two compounds is the nature of the connection between the NiO\(_6\) octahedra. In the former compound, the octahedra are linked via corner-sharing to form two-dimensional planes. In the latter, the Li ions occupy every second Ni site in the plane, thus resulting in isolated NiO\(_6\) octahedra.\(^{16,22}\) A comparison of these two materials will therefore allow us to assess the impact of additional delocalization effects that arise from the interaction between neighboring NiO\(_6\) clusters.

Figure 4 shows a comparison of the O-K and Ni-\( L_{2,3} \) XAS spectra of the two compounds. The pre-edge peak in the O-K spectrum of \( \text{Nd}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4 \), presented in the left panel of Fig. 4, is shifted by 0.5 eV to higher energy relative to that of \( \text{Nd}_{0.9}\text{Sr}_{1.1}\text{NiO}_{3.95} \) and is also narrower by 0.6 eV. A similar shift has been observed between the O-K absorption spectra of \( \text{Li}_{1-x}\text{Ni}_x\text{O} \) and \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) and was attributed...
to the different impurity potentials of the Li and Sr ions.\textsuperscript{23} This point alone, however, is not enough to explain the similarity of the O-K XAS spectra of La\textsubscript{2−x}Sr\textsubscript{x}NiO\textsubscript{4+δ} doped either by Sr (δ=0, x>0) or by oxygen excess (x=0, δ>0).\textsuperscript{7,25} The crucial additional factor is the site within the structure at which the induction of doping takes place. A substitution at the Ni sites (Li in Li\textsubscript{1−x}Ni\textsubscript{x}O or Nd\textsubscript{2}Li\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{4}d) does not necessarily have the same effect as a substitution at sites in the block layers (Sr or excess O in La\textsubscript{2−x}Sr\textsubscript{x}NiO\textsubscript{4+δ}). Indeed, the isolation of the Ni sites caused by Li doping in Nd\textsubscript{2}Li\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{4} leads to a narrow O-K pre-edge peak in this system;\textsuperscript{14} it is therefore a manifestation of the localized nature of these doping-induced states. A similar conclusion concerning the nature of doped hole states was reached for the closely related system La\textsubscript{2}Li\textsubscript{0.5}Cu\textsubscript{0.5}O\textsubscript{4} by recent local-density approximation (LDA) + $U_{dd}$ calculations.\textsuperscript{25}

The Ni-L\textsubscript{2,3} XAS spectrum of Nd\textsubscript{0.9}Sr\textsubscript{1.1}NiO\textsubscript{3.95} shown in the right panel of Fig. 4, contains also significantly broader spectral features than that of Nd\textsubscript{2}Li\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{4}, and the weak satellite observed at about 6 eV above the higher energy component of the main peak in the latter spectrum is absent in the Sr-doped material. A similar satellite had been observed in TM-L\textsubscript{2,3} XAS spectra of NaCuO\textsubscript{2} (Refs. 26 and 27) and La\textsubscript{2}Li\textsubscript{0.5}Cu\textsubscript{0.5}O\textsubscript{4}.\textsuperscript{14} In this case of these cuprates, the satellite can be assigned to final states dominated by the 2p3d\textsuperscript{0} configuration (2p denotes a hole in the 2p states).

### 3. Physical basis for the interpretation of the Ni-L\textsubscript{2,3} XAS spectra

In order to assess the charge distribution between the O and the TM sites in such hybridized systems, it is vital to consider not only the O-K XAS spectra but also to carry out a quantitative analysis of the TM-L\textsubscript{2,3} XAS data.\textsuperscript{14} It is instructive at this stage to consider a simplified model for illustrating the essential ideas involved in the more complete treatment of the XAS spectra, which will be presented further below.

The Hamiltonian matrix and the ground state of a 3d\textsuperscript{n} system are given by (for simplicity we neglect any admixture of d\textsuperscript{n+m}L\textsuperscript{m} configurations with m≥2):

$$H = \begin{pmatrix} 0 & T \\ T & -\Delta \end{pmatrix}$$

(1)

$$\Phi_\gamma = \alpha_0 |3d^n\rangle + \beta_0 |3d^{n+1}L\rangle, \quad (\alpha_0^2 + \beta_0^2) = 1,$$

(2)

where $\Delta$ is the charge-transfer energy for the many-electron system; $L$ denotes a hole in an O 2p orbital and $T$ is the transfer integral between the TM 3d states and the ligand orbitals; $\Phi_\gamma$ denotes the ground-state wave function of the system. The configuration mixing coefficients in the ground state, $\alpha_0$ and $\beta_0$, are related to each other by the following equation:

$$\beta_0 / \alpha_0 = [(\Delta^2 + 4T^2)^{1/2} - \Delta] / 2T.$$  

(3)

When $\Delta>0$, as for example in NiO and CuO, $\beta_0 / \alpha_0 < 1$ is obtained from Eq. (3). This implies that the $3d^n$ configuration ($n=8, 9$ for Ni(II) and Cu(II), respectively) dominates the ground state; in other words, the $3d^{n+1}L$ contributions are small. It has been pointed out that $\Delta$ decreases by as much as 3 eV when going from Cu(II) to Cu(III), and can even become negative in materials like NaCuO\textsubscript{2} (Refs. 26 and 27) and La\textsubscript{2}Li\textsubscript{0.5}Cu\textsubscript{0.5}O\textsubscript{4}.\textsuperscript{14} In this case, $\beta_0 / \alpha_0 > 1$, which implies that the $3d^{n+1}L$ configuration is the dominant one. The intensity of the pre-edge peak in the O-K XAS spectrum reflects then the fraction of holes residing in O 2p states, which is proportional to $\beta_0^2$.\textsuperscript{14,23}

Problems can arise, however, in TM systems with higher oxidation states, where $\Delta$ remains positive. In such cases, the $3d^{n+1}L$ configuration does not always dominate, and the result is a significant contribution from the $3d^n$ configuration to the ground state. An example for this behavior is the class of compounds Ln\textsubscript{2}Li\textsubscript{0.5}TM\textsubscript{0.5}O\textsubscript{4}, which formally contains TM(III) ions. In a previous study, a theoretical analysis of the TM-L\textsubscript{2,3} XAS spectra of these materials, with TM=Cu, Ni, and Co, has shown that the contribution of the $3d^n$ configuration to the ground state is as high as 30, 57, and 72%, respectively.\textsuperscript{14} This highlights the problem discussed in the following. The observation of a doping-related increase in intensity of the pre-edge peak in the O-K XAS spectra for systems such as these can lead to oversimplified statements, such as “the holes always go into the O 2p states.” The validity of this statement depends critically on the details of the system involved, as can be seen from the Ln\textsubscript{2}Li\textsubscript{0.5}TM\textsubscript{0.5}O\textsubscript{4} example discussed above.\textsuperscript{14} Indeed, such considerations have led to the conclusion\textsuperscript{26} that the ground state of La\textsubscript{2}Li\textsubscript{0.5}Cu\textsubscript{0.5}O\textsubscript{4−δ} contains no admixture of the 3d\textsuperscript{8} configuration at all, but can be written as $\alpha_0 |3d^n\rangle + \beta_0 |3d^{n+1}L\rangle$. As mentioned above, a full analysis of the Cu-L\textsubscript{2,3} XAS data for this system gives a different picture, with a significant contribution (30%) of the 3d\textsuperscript{8} configuration to the ground state.\textsuperscript{14}

The final state of a TM-L\textsubscript{2,3} XAS experiment can be described by a similar theoretical framework, where $\Delta$ in Eq. (1) is replaced by $U_{jj} = U_{cd} + U_{dd}$ ($U_{cd}$ and $U_{dd}$ represent the Coulomb interaction energies 2p/3d and 3d/3d, respectively), and the other parameters have modified, “final-state” values.
It has been pointed out recently that the effects of covalency in XAS spectra can be enhanced by nonlocal effects. As was briefly mentioned above, such nonlocal effects occur in systems where the TMO$_6$ octahedra form interconnected networks, leading, e.g., to a broadening of the spectral features, a shift to lower energies, and an increase in intensity of the pre-edge peak in case of the O-K XAS spectra. This is seen in Fig. 4 when going from the isolated cluster system Nd$_2$Li$_{0.5}$Ni$_{0.5}$O$_4$ to the Sr-doped system, which contains a continuous Ni-O network.

In order to arrive at a more quantitative understanding of the charge distribution in the two Ni(III) systems compared in Fig. 4, we present in the next section results of a calculation based on local NiO$_6$ clusters including charge-transfer hopping, as well as a full multiplet interaction within a complete basis approach for these compounds. We note that a complete-basis calculation expresses the ground-state wave function as

\[ \Phi_n = \sum \alpha \langle \text{basis function} | d^{n+1} \rangle, \]

where the summation over \( i \) is from 0 to (10 - \( n \)). This is in contrast to Eq. (2) where the summation over \( i \) corresponds to 0 and 1 only, with \( \alpha_0 \) and \( \alpha_1 \) being equal to \( \alpha_0 \) and \( \beta_0 \).

C. Charge-transfer atomic-multiplet calculations

In these calculations, we have considered a single cluster with one Ni atom surrounded by six O atoms. In order to reduce the size of the Hamiltonian matrix without introducing any further approximation, only linear combinations of the O 2p orbitals with the same symmetry as the Ni 3d orbitals were considered. Apart from the O 2p and Ni 3d orbitals, the Ni 2p orbitals were also included in the calculations. The Hamiltonian used to describe the system includes the Coulomb interaction between the Ni 2p and 3d electrons, defined in terms of the Slater integrals \( F_{pd}, G_{pd}^1 \), and \( G_{pd}^3 \), as well as that between the 3d electrons given by the Slater integrals \( F_{dd}, F_{dd}^0 \), and \( F_{dd}^1 \). The spin-orbit interaction has also been considered within the 2p and the 3d manifold at the transition-metal site, the strengths of which are determined by \( \xi_p \) and \( \xi_d \), respectively. An ionic-crystal-field term was also included in the Hamiltonian to simulate the observed splitting of the fivefold degenerate d orbitals. While for the case of octahedral symmetry in Nd$_{0.9}$Sr$_{1.1}$NiO$_3$, the crystal-field splitting is expressed in terms of 10Dq, for the D$_{4h}$ symmetry in Nd$_{0.95}$Li$_{0.5}$Ni$_{0.5}$O$_4$ the splitting is defined by 10Dq and Ds. Hybridization has been included between the symmetry-adapted combinations of oxygen orbitals and Ni 3d orbitals. The charge transfer between the ligand and the transition-metal atom is determined by the ionic configuration at the transition-metal site and is defined as the difference between the multiplet-averaged energies of the \( d^n \) and \( d^{n+1} \) configuration at the transition-metal atom:

\[ \Delta = E_{vd} - E_{vp} + n \frac{U}{2}. \]

Hence the charge-transfer energy can be expressed in terms of the bare energies of the 3d transition metal and the 2p ligand orbitals (\( e_d \) and \( e_p \), respectively), the configuration \( n \), and \( U \), which is the multiplet-averaged Coulomb interaction strength between the 3d electrons. The multipole terms of the Coulomb interactions were set to 80% of the Hartree-Fock values, while the monopole terms, \( F_{dd}^0 \) and \( F_{dd}^i \), were estimated by fitting the experimental spectrum. The other parameters, \( pd\sigma \), \( \Delta \), 10Dq, and \( Ds \), were estimated by fitting the experimental spectra. Although atomic values for the spin-orbit strength were usually seen to be sufficient, in some cases \( \xi_p \) was varied slightly to get a better fit of the experimental spectrum. For comparison with experiment, the spectral functions, evaluated by using the Lanczos method, were broadened by a Gaussian and an energy-dependent Lorentzian to simulate experimental resolution and lifetime effects, respectively.

As a test case, we first treat the standard Ni(II) system NiO. The parameters obtained from a fit to the experimental spectra are given in Table I. For NiO, 94% 3d$^8$ was obtained in the ground state, indicating a basically ionic Ni$^{2+}$ state in agreement with the results of previous studies.

As has been mentioned above, considering its slight oxygen deficiency, Nd$_{0.9}$Sr$_{1.1}$NiO$_3$ represents formally a pure Ni(III) state. The transition-metal site in both NiO and Nd$_{0.9}$Sr$_{1.1}$NiO$_3$ has the same octahedral symmetry. However, the structure in the Ni-L$_3$ XAS spectra at 854 eV is much weaker in NiO, whereas it is the most intense feature in the spectra of the two Ni(III) compounds. The results of a simulation of the spectra of all three Ni compounds are shown in the right panel of Fig. 4. With reference to Table I, it can be seen that, when moving from the Ni(II) to the Ni(III) compounds, the extracted parameters indicate an increase in covalency: the Ni(III) systems have larger hybridization strengths as well as reduced charge-transfer energies.

Comparing the two Ni(III) compounds, we can directly see the influence of nonlocal effects on the electronic configuration: Nd$_{0.9}$Sr$_{1.1}$NiO$_3$, is more covalent than Nd$_{0.95}$Li$_{0.5}$Ni$_{0.5}$O$_4$, which is a consequence of the continuous Ni-O network in the former material. To get a reasonable simulation of the experimental spectra, we have to increase \( \Delta \) and decrease \( pd\sigma \) from Nd$_{0.9}$Sr$_{1.1}$NiO$_3$ to Nd$_{0.95}$Li$_{0.5}$Ni$_{0.5}$O$_4$. This means that the 3d$^7$ contribution in the ground state in the former material is 42% as compared to 51% in the isolated cluster system. Nevertheless, these data and their theoretical analysis clearly show that the general trend derived from the lithium-doped system is preserved: the doping-induced holes have a substantial Ni 3d weight in systems with a formal Ni(III) oxidation state.

IV. CONCLUSIONS

We have presented the results of an experimental study of both the O-K and Ni-L$_{2,3}$ XAS spectra of the nickelate NiO.
Nd$_{0.9}$Sr$_{1.1}$NiO$_{3.95}$, together with a detailed theoretical analysis of the Ni-L$_{2,3}$ XAS spectra within a charge-transfer atomic-multiplet approach. The experimental spectra represent a reliable data recorded at the Ni-L$_{2,3}$ thresholds for this system, as the choice of Nd avoids overlap of the La-M\textsubscript{4} with the Ni-L$_{2}$ XAS spectra, which has marred experiments on the La analog up till now. The main points arising from the experimental spectra and their theoretical interpretation are as follows:

- The number of hole states in the O 2p orbitals increases linearly with the doping level $x$ up to the maximum value studied of $x = 1.4$. Previous reports of a saturation of the O-K pre-edge spectral weight for high $x$ values are not confirmed and are probably due to surface oxygen deficiency.
- The holes induced by Sr doping reside, about equally, in the Ni 3d and O 2p orbitals. This is expressed in terms of a ground-state population of 42% for the 3d$^7$ configuration in the formal Ni(III) system Nd$_{0.9}$Sr$_{1.1}$NiO$_{3.95}$.

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