Orbital and Spin Character of Doped Carriers in Infinite-Layer Nickelates

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The recent discovery of superconductivity in Nd1−xSrxNiO2 has drawn significant attention in the field. A key open question regards the evolution of the electronic structure with respect to hole doping. Here, we exploit x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) to probe the doping dependent electronic structure of the NiO2 planes. Upon doping, a higher energy feature in Ni L3 edge XAS develops in addition to the main absorption peak. By comparing our data to atomic multiplet calculations including Dkh crystal field, the doping induced feature is consistent with a d8 spin singlet state, in which doped holes reside in the d2−y2 orbitals, similar to doped single band Hubbard models. This is further supported by orbital excitations observed in RIXS spectra, which soften upon doping, corroborating with Fermi level shift associated with increasing holes in the d2−y2 orbital.

Infinite-layer nickelates have been proposed more than two decades ago as promising materials that may host unconventional superconductivity [1]. Inspired by the crystal and electronic structure of high-temperature superconducting cuprates, Anisimov et al. [1] investigated LaNiO2 that shares some of their essential characteristics: two-dimensional NiO2 planes, nominal 3d6 valence configuration, and a 3d2−y2-derived band crossing the Fermi level. However, superconductivity in nickelates remained elusive until very recently, when Li et al. reported the first experimental evidence of a zero-resistance state in thin films of Nd0.8Sr0.2NiO2 [2] with a transition temperature around 10 K at optimal doping [3, 4].

Although the early theoretical investigation was motivated by the search for cuprate analogs [1], some differences between the parent compounds of cuprates and nickelates emerge [5]. NdNiO2 is a poor conductor [2] and lacks evidence of long-range magnetic order [6]. Recent x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) experiments [7] have indicated that the charge-transfer energy to the O ligands is large, resulting in a much reduced hybridization between Ni and O states with respect to cuprates and other charge-transfer compounds. The half-filled two-dimensional Ni 3d2−y2 orbital behaves as a Hubbard-like band coupled to a three-dimensional Nd 5d2−y2 band that crosses the Fermi level. The coupling between Ni 3d and Nd 5d bands may resemble an Anderson or Kondo lattice typical of heavy fermion systems, where the role of magnetic “impurities” is played by strongly-correlated Ni 3d2−y2 electrons [7].

Since superconductivity emerges in NdNiO2 when trivalent Nd is substituted by divalent Sr [2–4], it is important to establish the evolution of the electronic structure upon doping. To date, theories have proposed distinct scenarios that depend on the interplay between electronic correlation, charge-transfer energy, crystal field splitting and Hund’s coupling [8–13]. For example, doped holes may give rise to Ni 3d8 sites, where the two holes may arrange in a singlet (double occupation of 3d2−y2 orbital) [1, 14–17] or triplet (occupation of different orbitals) [18–21] configuration; or they may form d8L states (where L denotes a hole in the O 2p orbitals) that resemble Zhang-Rice singlets [22] typical of doped cuprates [23]; also, carriers may be introduced into the Nd 5d states [12, 24]. Experimental determination of the orbital and spin character of doped holes is therefore highly desirable to clarify this issue.

Notably, using electron energy loss spectroscopy (EELS), Goodge et al. [25] recently reported changes in the absorption spectra of Nd1−xSr2NiO2 at the O, Ni and Nd edges, suggesting that doped carriers appear to reside primarily on Ni sites forming d8 states with little change in oxygen content – much less than that observed in cuprates [26]. Yet, further spectroscopic studies are needed to confirm these results and establish whether the two holes in the Ni 3d states form a singlet or triplet.

In this Letter, we use a combination of high-resolution XAS and RIXS and multiplet calculations to investigate the orbital and spin states of doped holes in
Nd$_{1-x}$Sr$_x$NiO$_2$. We consider three doping levels: $x = 0$ (undoped), 0.125 (non-superconducting), and 0.225 (superconducting, $T_c \approx 10$ K). XAS and RIXS are suitable techniques for our purpose since the resonant excitation grants element selectivity while enhancing the scattering cross-section, which is crucial for thin film samples. We find that doped holes are primarily introduced in the Ni 3$d_{x^2−y^2}$ Hubbard band in a low-spin configuration associated with a shift of Fermi level that is reflected in the softening of orbital excitations by approximately 0.2 eV between compounds with Sr content of $x = 0$ and 0.225.

Thin films of the precursor perovskite Nd$_{1−x}$Sr$_x$NiO$_3$ with a thickness of 10 nm were grown on a substrate of SrTiO$_3$(001). The c-axis oriented infinite-layer Nd$_{1-x}$Sr$_x$NiO$_2$ was obtained by means of a topotactic reduction process [27]. To protect and support the crystalline order, a capping layer made of five unit cells of SrTiO$_3$(001) was grown on top of the nickelate film. XAS and RIXS measurements were performed at beamline I21 of the Diamond Light Source (United Kingdom). The combined energy resolution of the beamline and the spectrometer was approximately 40 meV at the Ni $L_3$ edge. Measurements were taken at 20 K. RIXS spectra are normalized to the incident photon flux.

We first study the doping evolution of the electronic states of Nd$_{1-x}$Sr$_x$NiO$_2$ by examining XAS spectra at relevant Ni, O, and Nd absorption edges. Figure 1 shows Ni $L_3$ edge XAS spectra taken with two different light polarizations $\epsilon$ set by the incidence angle $\theta$ (see inset for a sketch of the experimental geometry). The XAS spectrum of NdNiO$_2$ measured with $\theta = 90^\circ$ ($\epsilon \parallel a$) shows one dominant peak attributed to the $2p^63d^9−2p^53d^{10}$ transition [7, 25]. Upon doping, XAS spectra measured with $\epsilon \parallel a$ develop an additional shoulder at higher energy than the main peak. This spectral feature is consistent with the broadening of the main absorption peak reported in EELS measurements [25], but is unambiguously resolved in our high-resolution data. For the XAS taken at $\theta = 10^\circ$ ($\epsilon$ mostly along the c axis), we observe a strong linear dichroism, suggesting a pronounced in-plane orientation of the unoccupied 3$d$ orbitals.

XAS spectra of Nd$_{1-x}$Sr$_x$NiO$_2$ measured at the O $K$ edge (see Supplemental Material [28]) do not reveal the emergence of a pre-peak usually associated with hole doping into the charge-transfer band [26]. While the signal from the SrTiO$_3$ capping layer could obscure the absorption from the underlying nickelate film, our results nonetheless suggest that the doping induced signature in O $K$ edge XAS is minor, as confirmed by the spatially-resolved EELS measurements [25]. The Nd $M_5$ edge XAS spectra are also unaffected by doping (see Supplemental Material [28]), implying well-localized Nd 4$f$ states. Since calculations indicate that Nd 5$d$ bands give rise to a metallic state [5], they should exhibit changes upon doping; however, spectroscopic validation of this point is beyond the scope of this work and will be addressed in future studies. Overall, our findings support the scenario in which the large charge-transfer energy favors the formation of Ni 4$d^8$ states rather than 4$d^9 3d$ states. This corroborates the classification of infinite-layer nickelates into the Mott-Hubbard region of the Zaanen-Sawatzky-Allen scheme [7, 25, 29, 30].

After establishing that doped holes are introduced primarily into Ni 3$d$ orbitals, we further analyze the energetics of 3$d$ states and their doping dependence using RIXS. Figure 2 displays the RIXS intensity maps of NdNiO$_2$ (a) and Nd$_{0.775}$Sr$_{0.225}$NiO$_2$ (b) as a function of incident photon energy across the Ni $L_3$ edge. RIXS spectra were collected at an incidence angle of 35$^\circ$ and scattering angle of 154$^\circ$. The dashed line marks the incident energy selected for the measurement of the angular dependence of RIXS spectra.
visible in both compounds. This feature is specific to infinite-layer nickelates and has been attributed to the hybridization between Ni and Nd orbitals [7]. For incident photon energies above 853 eV, a fluorescence-like excitation is observed. Low energy-loss excitations below 0.3 eV will be discussed in separate works.

We focus on the $dd$ transitions that carry direct information about the Ni 3$d$ orbitals. The energy and orbital character of the $dd$ excitations are analyzed using an ionic model including crystal field. Although simple, the model has proven successful to characterize the orbital excitations of cuprate [33]. We consider a single Ni$^{+}$ cation surrounded by four negative point charges in square planar geometry. The $D_{4h}$ tetragonal symmetry of the crystal field lifts the degeneracy of the Ni 3$d$ orbitals such that the $d_{3z^2}$ becomes the lowest energy state, followed by $d_{xz}$, $d_{yz}$, and $d_{x^2−y^2}$. In the $L_3$ edge RIXS process, illustrated in Fig. 3(a), a $2p_{3/2}$ core electron is first promoted into the empty $3d_{x^2−y^2}$ orbital, then a 3$d$ electron radiatively decays producing an electronic redistribution within the 3$d$ shell that gives rise to $dd$ transitions in the RIXS spectra. Since the 3$d$ orbitals have distinct spatial symmetry, their orientation relative to the polarization vectors of the incident and scattered photons produces a modulation of the RIXS matrix elements and therefore of the $dd$ intensity. Indeed, as shown in Figs. 3(c,d), while the energy and width of the $dd$ excitations of a particular sample do not exhibit notable variation, the relative intensity varies as a function of the incidence angle $\theta$, which effectively alters the polarization direction relative to the orbital orientation (see the sketch of the experimental geometry in Fig. 3(b)). This variation can be used to determine the orbital character of the $dd$ excitations and verify whether the 3$d$ energy levels follow the expected $D_{4h}$ crystal field splitting.

We calculate the RIXS cross section of $dd$ transitions using the single ion model, following Ref. 33, which is also described in the Supplemental Material [28]. We considered the incidence and scattering angles reported in Fig. 3(c), but the calculations equally apply to panel (d) since the minor differences in the two experimental geometries do not appreciably affect the $dd$ intensity modulation. The cross sections, reported in panel (e), not only qualitatively reproduce the angular dependence of the experimental intensity for a given incident polarization, but also capture the relative modulation between $\pi$ and $\sigma$ polarizations at a given angle. This agreement allows us to attribute the peaks in the RIXS spectra of NdNiO$_2$ at 1.39 and 2.0 eV and the broad tail centered at 2.7 eV to transitions into the $d_{xy}$, $d_{yz}$, and $d_{x^2−y^2}$ orbitals, respectively, as shown in panel (e). A similar assignment can be made for Nd$_{0.875}$Sr$_{0.125}$NiO$_2$. We note that the weaker cross section of the $d_{3z^2−r^2}$ excitation and its larger width compared to other $dd$ transitions prevent us from precisely constrain its energy position. Nevertheless, our assignment is consistent with experimental and theoretical findings on CaCuO$_2$ [33, 36, 37] and Nd$_2$CuO$_4$ [38] that possess the same square planar environment around the $\text{Cu}^{2+}$ ion. Though, the $dd$ excitation peaks are broader than those of undoped cuprates and appear to deviate from a simple Gaussian or Lorentzian lineshape. These discrepancies may be due to the coupling to the particle-hole excitation continuum of the metallic state of Nd$_{1−x}$Sr$_x$NiO$_2$, and to the disorder associated with possible incomplete chemical reduction [25, 27].

We now explore the evolution of orbital excitations upon doping. Figure 4(a) shows the RIXS spectra of three samples with doping of $x = 0$ (black), 0.125 (blue),

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FIG. 3. (a) Schematics of the RIXS process at the Ni $L_3$ edge. (b) Ni cation (orange sphere) surrounded by O anions (black spheres) and sketch of the experimental geometry. The incoming photon wave vector $k_{\text{in}}$ forms an angle $\theta$ with the sample $ab$ plane. The scattered photon wave vector $k_{\text{out}}$ forms an angle $\Theta$ with $k_{\text{in}}$. The incident photon polarization is either parallel ($\pi$) or perpendicular ($\sigma$) to the scattering plane, which coincides with the $ac$ plane. (c, d) Stack plot of RIXS spectra of NdNiO$_2$ (c) and Nd$_{0.875}$Sr$_{0.125}$NiO$_2$ (d) collected at various incidence angles $\theta$ and fixed scattering angle $\Theta$. The incident energy was fixed to 852.5 eV for NdNiO$_2$ (dashed line in Fig. 2(a)) and 852.44 eV for Nd$_{0.875}$Sr$_{0.125}$NiO$_2$. (e) Angular dependence of the intensity of $dd$ transitions calculated for the angles of panel (c).
and 0.225 (red) collected at three representative incidence angles. With increasing doping, the dd excitations are broadened and, most importantly, softened by approximately 0.2 eV at x = 0.225. We note that the doping evolution of the dd transitions is distinct from the case of hole-doped cuprates, where dd excitations are broadened upon doping but their center of mass is little influenced [39]. This is because holes are doped into the O-derived charge-transfer band, which induces little effects in the energetics of the Cu 3d manifold. Conversely, in electron-doped cuprates the dd excitations harden upon doping. This has been considered as a signature of electron doping into the Cu-derived upper Hubbard band, which effectively increases the energy difference between the Fermi level and other filled 3d orbitals [40]. Similarly, the softening of the dd excitations in hole-doped infinite-layer nickelates indicates that doped carriers are introduced into the Ni 3d band corroborating with the shift of Fermi level toward the occupied 3d orbitals due to injection of holes.

What is the electronic state of the doped hole on Ni sites? Depending on the competition between crystal field splitting of the lowest energy 3d orbitals and Hund’s rule coupling, doped holes on Ni sites (i.e., a d⁸ state) can arrange either in a spin singlet or triplet configuration, as exemplified in the two-level diagrams of Fig. 4(b). A large Hund’s exchange J_H promotes the population of different orbitals in a high-spin state to minimize Coulomb repulsion (right diagram); instead, a strong crystal field D favors a large orbital polarization where holes fill the first available state in a low-spin configuration (left diagram). To shed light on which scenario resembles the doped nickelates, we first extract the doping-induced change in the unoccupied states probed by Ni L₃ edge XAS. Figure 4(c) displays XAS spectra of NdNiO₂ (black) and Nd₀.₇₇₅Sr₀.₂₂₅NiO₂ (red) measured with ε // a (θ = 90°) and ε mostly along the c axis (θ = 10°). Assuming that the main peak in both compounds originates from the 2p^63d⁸-2p^53d⁸1⁰ transition, the spectra of NdNiO₂ are scaled and shifted by -0.05 eV and 0.05 eV for θ = 90° and θ = 10°, respectively, to match the position and height of the first peak of Nd₀.₇₇₅Sr₀.₂₂₅NiO₂. The difference of the two spectra (blue lines) represents the additional contribution generated by doping; it mainly consists of a single peak that is strongly reduced when the polarization is mostly out of plane. Next, we calculate the multiplet spectrum of the d⁸ ion in tetragonal crystal field in the two regimes, corresponding to spin triplet and spin singlet states. The parameters used, reported in the Supplemental Material [28], are set to demonstrate the XAS gross features for the two respective scenarios which are robust against fine tuning. The multiplet spectra of the high- and low-spin states (Fig. 4(d)) have distinct characteristics: the former is made of multiple peaks with similar weight over a wide energy range (light grey). When ε // c, the first peak is enhanced, while the intensity of the high-energy features is reduced. Conversely, the multiplet spectrum of the spin-singlet configuration (dark grey) is dominated by a single peak that is strongly suppressed with out-of-plane polarization. Thus, the spin-singlet scenario where the doped hole occupies the dₓ²−ᵧ² orbital agrees with our data.

In conclusion, our results indicate that the doping evolution of the Ni 3d orbitals in infinite-layer nickelates is reminiscent of doping a single Hubbard band, namely, doped holes tend to reside in the dₓ²−ᵧ² orbital forming a d⁸ spin singlet state. A low-spin configuration is highly uncommon for d⁸ nickel compounds; however, it may become energetically favorable when the Ni ion is embedded in a low-symmetry environment, such as in planar complex K₂Ni-dithio-oxalate [41], trilayer (La,Pr)₁Ni₃O₈ [42] and one-dimensional Sr₂Cu₀.₉Ni₀.₁O₃ [43]. Given the little change in O absorption spectra [25] and small electron pocket arisen from rare-earth 5d bands [5], it is likely that the low-energy electronic properties of Nd₁−ₓSrₓNiO₂...
are dominated by the Ni $3d_{x^2−y^2}$ orbitals. Note that the sign change of the Hall coefficient with temperature and doping [3, 4] has been interpreted as the contribution from multiple bands. However, a similar behavior is also observed in cuprates [44, 45] where a single band description is well established. The complex dependence of the Hall coefficient may be related to electron correlations that influence the topology of the Fermi surface [46]. Yet, the minor influence of other orbitals in the low-energy physics of infinite-layer nickelates remains an important open question. Nevertheless, our work provides a solid reference for future experimental and theoretical studies on the electronic structure of this new class of oxide superconductors.

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Supplemental Material

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Supplemental Material

Orbital and Spin Character of Doped Carriers in Infinite-Layer Nickelates

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 FIG. 1. Stack plot of total fluorescence yield O K edge XAS spectra of NdNiO2 (black), Nd0.75Sr0.25NiO2 (orange) and Nd0.75Sr0.25NiO2 (red). The XAS signal is dominated by peaks from SrTiO3 (thick black line), which has been used as substrate and capping layer. In particular, we do not detect the development of a pre-peak feature that is attributed to the doping-induced hole-population of the O-derived charge-transfer band [2, 3]. To show the sensitivity of our XAS measurements to the signal from buried nickelate thin film, we plot in Fig. 1 the spectrum of a thin film of NdNiO3 (grey dots) measured under the same conditions and with the same capping layer of five unit cells of SrTiO3 (we note that Nd0.75Sr0.25NiO2 was grown with a thicker capping layer of 20 nm). A pre-edge feature at 527.8 eV is clearly visible in the XAS spectrum of NdNiO3, due to charge transfer between the transition metal and ligand states [4].

Our O K edge XAS measurements suggest that O-derived bands play a subdominant role in the low-energy physics of infinite-layer nickelates, consistent with spatially-resolved EELS measurements [5].

Neodymium M5 edge XAS

Figure 2 shows the Nd M5 edge XAS spectra of NdNiO2 (black solid line) and Nd0.75Sr0.25NiO2 (red dashed line). XAS spectra were collected at beamline I21 of the Diamond Light Source (United Kingdom). Measurements were taken at 20 K. The photon polarization vector was parallel to the sample a axis. The XAS spectrum of NdNiO3 is taken from Ref. 1. The incident photon polarization was parallel to the sample a axis.

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Intensity (arb. units)
990 985 980 975 970
Photon energy (eV)
Nd M5 edge XAS
ε // a
NdNiO2
Nd0.775Sr0.225NiO2

FIG. 2. Background-subtracted Nd M5 edge XAS spectra of NdNiO2 (black solid line) and Nd0.775Sr0.225NiO2 (red dashed line) measured with photon polarization parallel to the a axis. Spectra are collected in total electron yield mode and are normalized to the peak height.

Intensity (arb. units)
3
2
1
0
Intensity (arb. units)
3
2
1
0
Photon energy (eV)
Nd M5 edge XAS
ε // a
NdNiO2
Nd0.775Sr0.225NiO2

FIG. 3. Angular dependence of the L3 edge RIXS cross section for transitions from the doxy ground state to the final doxy (top panel), dyz/xz (middle) and dyz/xz (bottom) orbitals. Blue and red lines correspond to RIXS intensities calculated for π and σ incident photon polarizations, respectively.

Single ion RIXS cross sections

We consider the RIXS transition from the ground state g with energy Eg to the final state f with energy Ef. The scattering amplitude Afg is given by the Kramers-Heisenberg expression [7]:

\[ A_{fg} = \sum_n \frac{\langle f | D' | n \rangle \langle n | D | g \rangle}{E_g + \omega_{in} - E_n + i\Gamma_n}, \]

(1)

where n denotes the intermediate state with energy En and lifetime broadening \( \Gamma_n \); \( \omega_{in} \) is the incident photon energy; D and D' are the dipole transition operators for photon absorption and emission, respectively. For a given edge, we consider that all intermediate states have approximately the same energy and lifetime, so that Eq. 1 simplifies to:

\[ A_{fg} \approx \sum_n \langle f | D' | n \rangle \langle n | D | g \rangle. \]

We assume that the ground state is the atomic orbital \( \{ x^2 - y^2, 1/2 \} \), where \( 1/2 \) refers to the spin angular momentum. The final state can be one of the \( d \) orbitals and includes both spin-conserving and spin-flip channels: \( f = \{ xy, \pm 1/2 \}, \{ yz/xz, \pm 1/2 \}, \{ 3z^2 - r^2, \pm 1/2 \} \). The direction of the spin quantization axis is irrelevant as long as the final state involves both spin channels. The dipole operator \( D = \epsilon \cdot r \) contains information on the electric field polarization vector \( \epsilon \) and thus on the scattering geometry. The polarization of the incoming photon is known, while the one of the scattered photon is not measured. Hence, the RIXS intensity is averaged over all outgoing polarizations that lie on a plane normal to the scattered photon wave vector.

Figure 3 displays the L3 edge RIXS cross sections for transitions into the final doxy (top panel), dyz/xz (middle) and dyz/xz (bottom) orbitals as a function of incidence angle \( \theta \) and for fixed scattering angle \( \Theta = 154^\circ \). Blue and red lines correspond to incident photon polarization parallel (π) and perpendicular (σ) to the scattering plane, respectively.

Multiplet calculations

In the calculations, the atomic multiplet splitting is determined by the 3d-3d Slater-Condon parameters \( F_{dd}^0 \), \( F_{dd}^2 \) and \( F_{dd}^4 \), while the final state effects are included considering the 2p spin-orbit coupling (11.5 eV) and the interaction between the valence shell and the core hole, given by the 2p-3d Slater-Condon parameters \( F_{pd}^0 \), \( F_{pd}^2 \), \( G_{pd}^1 \) and \( G_{pd}^3 \) [8]. We neglect hybridization between Ni and O orbitals in view of the large charge-transfer energy and weak weight of O bands in the ground state. The \( D_{4h} \) crystal field splitting is obtained from the analysis of the RIXS dd transitions of NdNiO2. The energies of the d orbitals relative to doxy are: 1.39 eV for doxy, 2.0 eV for dyz/xz and 2.7 eV for d3z2-r2.

For the \( d^8 \) high-spin configuration, we used the Slater-Condon integrals for \( Ni^{2+} \) from Ref. 8, which correspond to \( J_H = 1.0 \) eV and Coulomb repulsion \( U = 7.3 \) eV. We then reduced these parameters in order to obtain a low-spin ground state, where both holes occupy the doxy orbital. The set of parameters employed for the low-spin configuration were \( J_H = 0.69 \) eV and \( U = 6 \) eV, while the 2p-3d Slater-Condon parameters were \( F_{pd}^0 = 3.0 \) eV, \( F_{pd}^2 = 3.09 \) eV, \( G_{pd}^1 = 2.315 \) eV, and \( G_{pd}^3 = 1.315 \) eV.

The calculated spectra have been convoluted with a Lorentzian with full width at half maximum of 0.5 eV to take into account the 2p3/2 core hole lifetime [9].
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