PHYSICAL REVIEW B **111**, 165101 (2025)

Valence, charge transfer, and orbital-dependent correlation in bilayer nickelates $Nd_3Ni_2O_7$

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(Received 24 November 2024; revised 13 March 2025; accepted 17 March 2025; published 1 April 2025)

We examine the bulk electronic structure of $Nd_3Ni_2O_7$ using Ni $2p$ core-level hard x-ray photoemission spectroscopy combined with density functional theory + dynamical mean-field theory. Our results reveal a large deviation of the Ni $3d$ occupation from the formal $Ni^{2.5+}$ valency, highlighting the importance of the charge transfer from oxygen ligands. We find that the dominant d^8 configuration is accompanied by nearly equal contributions from d^7 and d^9 states, exhibiting an unusual valence state among Ni-based oxides. Finally, we discuss the Ni $d_{x^2-y^2}$ and d_{z^2} orbital-dependent hybridization, correlation and local spin dynamics.

DOI: 10.1103/PhysRevB.111.165101

I. INTRODUCTION

Nickel-based complex oxides—nickelates—have drawn considerable attention due to their rich phase diagrams of strongly correlated behavior including metal-to-insulator transitions [1–5], density waves [6–8], magnetism [9–11], and superconductivity [12–16]. The Ruddlesden-Popper nickelates $R_{n+1}Ni_nO_{3n+1}$ in particular also provide a platform for exploring the interplay between structural distortions, electronic correlations, and charge-transfer physics [17,18]. The recent discoveries of superconductivity in the bi- and trilayer compounds ($n = 2, 3$) [14–16,19] have reinvigorated efforts to understand their electronic structure while introducing a new fundamental challenge: the valency of Ni.

In square-planar nickelates, such as prototypical $NdNiO_2$, the low formal valency of Ni^{1+} accommodates self-doping of holes from the rare-earth $5d$ states to the Ni ions, introducing additional complexities in low-energy excitations that are absent in high-T_c cuprates superconductors [20–23]. The bilayer Ruddlesden-Popper $R_3Ni_2O_7$, by comparison, has a formal valency of $Ni^{2.5+}$. The higher Ni valency, i.e., lower Ni $3d$ levels, avoids self-doping from the rare-earth while a stronger charge transfer from the O $2p$ bands may be present [24,25], as is often observed in $RNiO_3$ with a formal Ni^{3+} valency [4,26,27]. Furthermore, the noninteger $Ni^{2.5+}$ valency poses a fundamental question in modeling the electronic structure, particularly regarding the appropriate starting point for the Ni valency and whether it aligns more closely with Ni^{2+} (d^8) or Ni^{3+} (d^7). It is worth stressing that these two electronic configurations exhibit different atomic multiplet structures and effective hybridization with ligands when forming covalent bonds. Thus, this detail represents a fundamental issue that underpins various open questions, including, for example, the importance of multiorbital physics, the origin of the strong orbital dependence in the mass renormalization, and the absence of a static charge order or disproportionation in the quest to understand superconductivity in the bilayer compounds.

One of the most well-established tools for investigating the electronic states of such complex transition metal systems is core-level photoemission spectroscopy (PES) [28,29]. The Ni $2p$ core-level PES measures the dynamical charge response of low-lying valence electrons to the sudden creation of a highly localized core hole at the excited Ni ion, leading to distinct peaks in the spectrum caused by the charge-transfer (CT) from O $2p$ and Ni metallic electrons. These are traditionally referred to as local and nonlocal screening, respectively. By analyzing these peaks, we determine the CT energy parameter

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that governs valency and effective hybridization with oxygens in CT-type Ni oxides [30,31]. Core-level PES is particularly suited for such studies due to its high sensitivity to CT effects, unlike charge-neutral methods such as x-ray absorption spectroscopy [29]. This approach, complementary to the low-energy studies about the details at the Fermi level, moves beyond limitations of formal electron counting to extract critical information on Ni $3d$ configuration, correlation effects, and orbital hybridization.

Here, we address this key question by performing core-level hard x-ray photoemission spectroscopy (HAXPES) experiments combined with local density approximation (LDA) + dynamical mean-field theory (DMFT) simulations. By making use of the higher probing depth provided by HAXPES, we are able to study the bulk electronic structure of the bilayer nickelates. Measuring the intrinsic Ni $2p$ core-level spectrum in $La_3Ni_2O_7$, however, is impossible due to severe overlap between the Ni $2p_{3/2}$ and La $3d$ core levels [32–34], as shown in Fig. S3 and discussed more in detail in the Supplemental Material (SM) [35] (see also Refs. [36–40] therein). This overlap has led to conflicting interpretations of the Ni charge state in previous experimental studies [34,41], preventing the extraction of a reliable spectrum for theoretical modeling of the $R_3Ni_2O_7$ system. To overcome this issue, we synthesized $Nd_3Ni_2O_7$ thin films [42,43] which enable direct access to the intrinsic Ni $2p$ spectrum as input for theoretical modeling using the LDA+DMFT method. We show that the system presents a dominant d^8 configuration, with nearly equal contributions from d^7 and d^9, differing from typical Ni^{3+} and Ni^{2+} oxides and requiring all configurations to be considered in theoretical models. We furthermore explore the distinct hybridization and correlation behaviors in the Ni $d_{x^2-y^2}$ and d_{z^2} orbitals, highlighting the orbital-dependent nature of the electronic structure.

II. METHODS

A ∼30 nm thin film of $Nd_3Ni_2O_7$ was grown by ozone-assisted molecular-beam epitaxy (MBE) on a stabilizing $LaAlO_3$ substrate, similarly to previous descriptions [42,43] [44]. Comparison of the nominal in-plane bulk and substrate lattice constants indicates a resulting compressive strain of $\varepsilon = (a_{\text{bulk}} - a_{\text{substrate}})/a_{\text{substrate}} \approx -0.9\%$ [42,43], smaller than that reported in thin films of $La_3Ni_2O_7$ which exhibit superconductivity [16,19]. Annular dark-field scanning transmission electron microscopy (ADF-STEM) investigation of the film structure shows good adherence to the bilayer Ruddlesden-Popper structure [35]. HAXPES measurements were performed at the Max-Planck-NSRRC HAXPES end station with the MB Scientific A-1 HE analyzer, Taiwan undulator beamline BL12XU of SPring-8 [45]. Photon energies of $h\nu = 6.5$ keV and 10 keV with resolutions of around 270 meV and 320 meV, respectively, were used. Soft x-ray photoelectron spectroscopy experiments were performed at the NSRRC-MPI TPS 45A submicron soft x-ray spectroscopy beamline at the Taiwan Photon Source in Taiwan [46]. The photon energy was set to 1.2 keV, with a resolution of around 150 meV. All measurements were performed at 80 K.

LDA+DMFT calculations were performed with the implementation in Refs. [30,31,47] for a lattice model spanning Ni $3d$ and O $2p$ bands derived from the LDA calculations [48–50]. Based on previous DMFT studies for $La_3Ni_2O_7$ [51–53], we used Hubbard U and Hund's J values of (6.0 eV, 0.95 eV) within the Ni $3d$ shell. These values give the configuration-averaged Coulomb interaction of $U_{dd} = U - 4/9J = 5.57\,\text{eV}$ [31]. After obtaining a converged DMFT solution with the continuous-time quantum Monte Carlo solver for the Anderson impurity model (AIM), we calculated valence-band spectra and hybridization densities $\Delta(\varepsilon)$ on the real frequency axis, followed by analytical continuation of the self-energy using the maximum entropy method [54]. Finally, we computed the Ni $2p$ core-level PES spectrum from the AIM, incorporating $\Delta(\varepsilon)$ and $2p$ core orbitals [30,31]. Computational details and the robustness of our results with the model parameters are provided in the SM [35] (see also Refs. [55–57] therein).

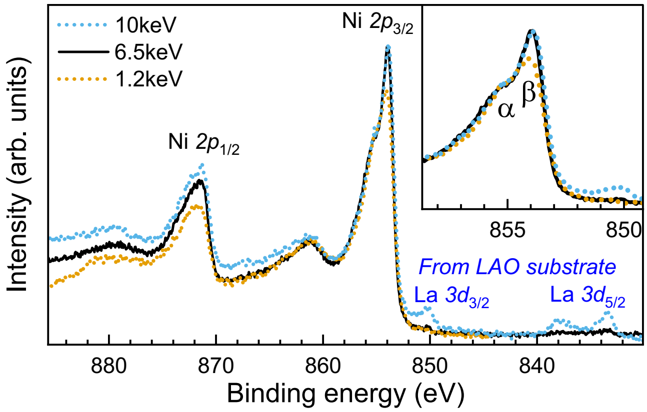

FIG. 1. Ni $2p$ core level spectra measured with photon energies of 10 keV (blue dotted line), 6.5 keV (black line), and 1.2 keV (orange dotted line).

In LDA+X methods, a double-counting correction μ_{dc} needs to be introduced to account for dd interaction effects present in the LDA results. Though a universally accepted form for μ_{dc} is unavailable [58–60], it controls Ni $3d$ levels relative to O $2p$ bands, thus the CT energy. Following Ref. [30], we use the linear function $\Delta_{dp} = (\varepsilon_d - \mu_{\text{dc}}) + 7.5 \times U_{\text{dd}} - \varepsilon_p$, mimicking the CT energy in a cluster model analysis. Here, ε_d and ε_p refer to the LDA orbital energies of Ni $3d$ and O $2p$, and U_{dd} is the averaged d–d interaction. Realistic Δ_{dp} values are obtained by comparing simulated Ni $2p$ core-level results to the experimental HAXPES spectrum.

III. RESULTS

Figure 1 shows the Ni $2p$ core-level photoemission spectra obtained using 10, 6.5, and 1.2 keV photons. Overall, the Ni $2p$ core level displays a set of structures commonly seen in other nickelates [34,61,62]. The main Ni $2p_{3/2}$ peak shows two distinct features corresponding to the local (α) and nonlocal metallic (β) screening processes, and a CT satellite at around 861.5 eV. Around 17 eV above the Ni $2p_{3/2}$, we observe a similar structure for the Ni $2p_{1/2}$, albeit broader due to the shorter core-hole lifetime. Depending on the photon energy, we observe some differences in the spectra. In the 10 keV data, there is a weak double peak at 833 and

838 eV, as well as one peak at 850 eV next to the Ni $2p_{3/2}$, matching the double peak structures of La $3d$ commonly seen in La-containing perovskite oxides [38], with the La $3d_{3/2}$ partially overlapping with the Ni $2p_{3/2}$ [34]. These peaks are contributions from the $LaAlO_3$ substrate below the $Nd_3Ni_2O_7$, which appear when using high photon energies with larger probing depth [63]. Indeed, at 6.5 keV, the La $3d$ features are reduced almost completely despite the relative increase of the La $3d$ cross sections compared to those of Ni $2p$ [64], indicating that the probing depth using 6.5 keV is barely enough to reach the substrate. This thus confirms the bulk sensitivity of the measurements and that the collected Ni $2p$ spectra are well representative of the whole $Nd_3Ni_2O_7$ film depth, as evidenced by good agreement in the Ni $2p$ derived features for 10 keV and 6.5 keV despite their different probing depths.

The surface-sensitive 1.2 keV spectrum, on the other hand, shows noticeable differences compared to the higher probing energy data. The electronic structure at the vicinity of the surface is thus clearly distinct from that of the bulk, with the significant reduction of the peak β indicating a suppression of the nonlocal metallic screening at the surface layers. Differences between the bulk and surface electronic structure are often known to occur in strongly correlated transition metal oxides [65–71], with phenomena like polar surfaces, relaxation, or reconstructions in the surface, etc., leading to significantly different properties and band structure near the surface, thus making bulk sensitivity crucial to ensure that the experimental results are intrinsic and representative of the bulk of the material. It is important to note the observation of these differences at 1.2 keV, i.e., Ni $2p$ core level photoelectrons with 300–350 eV kinetic energy, which are expected to have higher probing depths than common vacuum ultraviolet (VUV) valence band ARPES experiments.

Having established that the 6.5 keV HAXPES measurements best represent the bulk $Nd_3Ni_2O_7$ thin film, we use these measurements to determine the Δ_{dp} parameter by comparison to LDA+DMFT calculations. In Figs. 2(a) and 2(b), the Ni $2p_{3/2}$ spectra are computed for selected Δ_{dp} values. With increasing Δ_{dp}, the ligand levels shift deeper relative to the Fermi level, leading to a larger energy splitting between the local screening α (mainly from nearest-neighboring oxygens) and the nonlocal metallic screening β features. In the close-up shown in Fig. 2(b), we observe that the experimental splitting and $\alpha - \beta$ ratio is best reproduced by $\Delta_{dp} = 3.5$ eV, with 4.5 eV also yielding a reasonable agreement. Next, we observe in Fig. 2(a) that the weight ratio between the main peak and the satellite is also highly sensitive to the Δ_{dp} value, with the satellite spectral weight decreasing with increasing Δ_{dp}. Here, the best agreement is obtained between $\Delta_{dp} = 3.5$ eV and 2.5 eV. These two observations allow us to constrain its realistic value of around $\Delta_{dp} = 3.5$ eV. In the SM [35], we computed the Ni $2p$ spectrum for not only different values of Δ_{dp} but also for different values of U. We found that the experimental spectrum is best reproduced by the chosen U, although the sensitivity to the precise value of U is not very large.

The Δ_{dp}, which measures energy splitting of the Ni $3d$ and O $2p$ levels, is a key parameter for the d-electron charge states in CT-type systems according to the Zaanen-Sawatzky-Allen (ZSA) diagram [73]. In Fig. 2(c), the Ni $3d$ charge state is quantified by computing an atomic histogram at the Ni site in DMFT solutions for various Δ_{dp} values. Regardless of Δ_{dp}, the d^8 configuration exhibits a dominant peak in the histogram, with a large distribution toward the d^7 and d^9 configurations which depend on the Δ_{dp} value: a smaller Δ_{dp} increases the d^9 weight, and vice versa. At the optimal value determined above, the d^7 and d^9 weights are nearly identical. As shown in Fig. S6 of the SM [35], the d-configuration distribution in the atomic histogram is predominantly determined by Δ_{dp}, with negligible influence from the Coulomb interaction U, as expected for a system in the CT-type regime of the ZSA diagram.

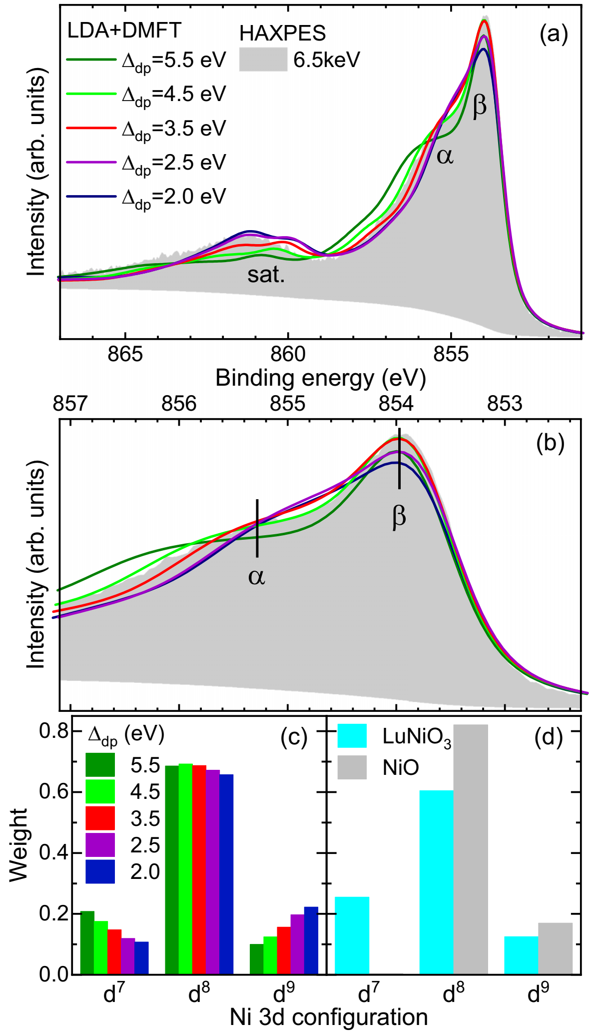

FIG. 2. (a) LDA+DMFT fit together with the experimental Ni $2p_{3/2}$ HAXPES spectrum. (b) Close-up of the Ni $2p_{3/2}$ α and β features. (c) Atomic configuration histogram of the Ni $3d$ states in $Nd_3Ni_2O_7$, computed with the selected Δ_{dp} values. (d) Atomic configuration histograms for reference Ni oxides: metallic $LuNiO_3$ (cyan) [72] and NiO (gray) [35].

The charge state contrasts with that of divalent or trivalent Ni oxides. In Fig. 2(d), the histograms for NiO and metallic $LuNiO_3$, which are prototype systems of formally Ni^{2+} and Ni^{3+} oxides, respectively, are shown. The reference data are taken from Ref. [72,74] and an additional DMFT simulation based on Ref. [47]. NiO exhibits a predominant d^8 peak with a distribution toward the d^9 state. In the high-valency LuNiO$_3$, with deeper Ni 3d levels, the CT energy is, as in other formally Ni^{3+} oxides [4,75,76], small or even negative, facilitating CT from O 2p states and resulting in a dominant d^8 state. The larger weight of the d^7 state compared to that of d^9 reflects its high formal valency. For an optimal Δ_{dp} of 3.5 eV, the charge state of Nd$_3$Ni$_2$O$_7$, with formally Ni$^{+2.5}$, is qualitatively different from these reference Ni oxides, and all the d^7–d^9 electronic configurations need to be considered when modeling its electronic structure. The mean Ni occupation of nearly d^8, deviating from the expected $d^{\sim 7.5}$ for a formal Ni$^{+2.5}$ valency, suggests that charge-transfer from O 2p states is significant in Nd$_3$Ni$_2$O$_7$. Note as Δ_{dp} is reduced (increased), the d configuration shifts to more closely resemble either divalent (trivalent) case. The d occupation in LuNiO$_3$ [72] is 7.84, exhibiting a larger deviation from its formal valency than that in Nd$_3$Ni$_2$O$_7$, which is consistent with Δ_{dp} of 3.5 eV in Nd$_3$Ni$_2$O$_7$ being moderate.

IV. DISCUSSION

Our results are consistent with the recent study [34] which indicated the absence of charge disproportionation (CD) signatures in La$_3$Ni$_2$O$_7$. Our LDA+DMFT calculations do not indicate any instability toward a CD [77]. Its absence would be unsurprising, given that the Ni d charge states [Figs. 2(b) and 2(c)] as well as the crystal structure of R_3Ni$_2$O$_7$ differ from those of RNiO$_3$, where CD is widely observed. The standard picture of CD in RNiO$_3$ depends on a delicate balance between the three-dimensional tilting pattern of NiO$_6$ octahedra and the correlated Ni 3d charge states [1,78–82], while the bilayer Ruddlesden-Popper compounds should host distinct octahedral distortions due to their reduced structural dimensionality. Theoretical models suggest these distortions are likely tied to the emergence of superconductivity under suitable pressure conditions [83], particularly in relation to orbital anisotropy, which we return to below.

The clarification of the Ni d state has implications for understanding low-energy excitations. Although the Ni d^8 valence configuration weight remains almost unchanged over a wide range of Δ_{dp}, as shown in Fig. 2(c), this does not necessarily imply that low-energy excitations are unaffected. In Fig. 3(a), the quasiparticle mass enhancement m^*/m of the Ni $d_{x^2-y^2}$ and d_{z^2} states was calculated from the converged DMFT self-energies $\Sigma(i\omega_n)$, as $m^*/m = Z^{-1} = [1 - \partial \mathrm{Im}\,\Sigma(i\omega)/\partial\omega]_{\omega\to 0^+}$, where the m is noninteracting band mass and Z is the renormalization factor. In addition to strong orbital dependence, the m^*/m of the two orbitals exhibits a pronounced dependence on the Δ_{dp} value, as the O 2p states are present near the Fermi energy E_F in this CT-type oxide and thus directly influence the degree of the localization of the Ni 3d electrons, see the SM [35] for the Δ_{dp} dependence of the DMFT valence-band spectra. A recent ARPES study on La$_3$Ni$_2$O$_7$ estimated m^*/m to be in the range of 1–3 for the $d_{x^2-y^2}$ state and 5–8 for the d_{z^2} state by rescaling DFT and DFT+U bands to match ARPES results in part of the Brillouin zone [84]. The calculated m^*/m values for the Δ_{dp} range that reproduces the Ni 2p data in Fig. 2, highlighted in gray in Fig. 3(a), are comparable to the reported values.

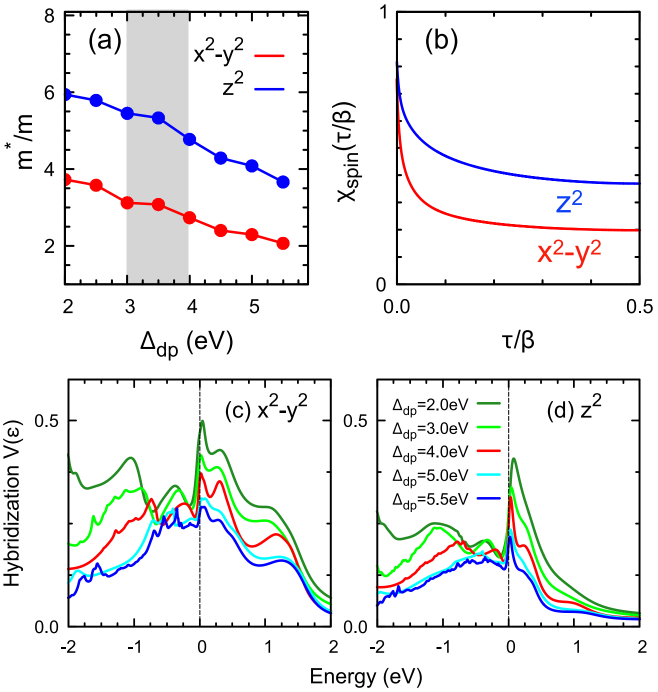

FIG. 3. (a) The mass enhancement m^*/m of the Ni $d_{x^2-y^2}$ and d_{z^2} states as a function of the Δ_{dp} parameters. The region in gray shadow indicates the realistic values estimated by the Ni 2p XPS analysis in Fig. 2. (b) The orbital-diagonal component of the local spin correlation function $\chi_{\mathrm{spin}}(\tau)$ with $\Delta_{dp} = 3.5$ eV, where τ represents the imaginary time. The Ni hybridization densities $V_\gamma(\omega)$ for (c) the $d_{x^2-y^2}$ state and (d) the d_{z^2} state, calculated with the different Δ_{dp} values. All results in the panels are calculated using the LDA+DMFT method at $T = 300$ K.

Orbital dependence has been at the center of discussions in the bilayer nickelates [51,84–88]. To gain an insight into it, in Figs. 3(c) and 3(d), we compare the Ni hybridization densities $V_\gamma(\omega)$ ($\gamma = x^2 - y^2, z^2$), which represent the exchange amplitude of an electron between the local d_γ state and lattice. The sharp evolution near E_F in $V_\gamma(\omega)$ as a function of Δ_{dp} accounts for the sensitivity of the metallic screening feature β in Ni 2p core-level PES to the Δ_{dp} values in Fig. 2(a). Overall, the Ni $d_{x^2-y^2}$ state exhibits stronger hybridization with the low-energy states compared to the Ni d_{z^2} state, which is likely responsible for the weaker m^*/m for the former orbital than the latter one. This observation is consistent with the orbital-dependent spin screening encoded in the time-dependent local spin correlation function $\chi_{\mathrm{spin}}(\tau)$, calculated for the LDA+DMFT result with the optimal Δ_{dp} in Fig. 3(b). $\chi_{\mathrm{spin}}(\tau)$ characterizes the dynamics of the local spin, influenced by hybridization with the crystal and many-body correlations [39,89,90]. We find a finite and nearly identical response at $\tau = 0^+$ for both orbitals, indicating that an instantaneous spin of approximately $S = 1/2$ is present in each. However, the Ni $d_{x^2-y^2}$ electron undergoes faster spin screening than the d_{z^2} orbital over time, reflecting the orbital-dependent hybridization. In the Appendix, we demonstrate through additional LDA+DMFT AIM calculations that the orbital-dependent hybridization near E_F is also important for the formation of the β feature observed in the experimental Ni $2p$ core-level spectrum in Fig. 2(a).

The m^*/m values obtained for the ambient pressure phase in this study differ from those calculated for the high-pressure phase in several theoretical studies of $La_3Ni_2O_7$ [51,87], e.g., $m^*/m \sim 3$ and 2.3 for the $d_{x^2-y^2}$ and d_{z^2} states, respectively, in Ref. [51]. As expected, m^*/m is reduced in the high-pressure phase due to the increased bandwidth of the Ni $3d$ states compared to the ambient pressure, while the orbital-dependent localization behavior persists in the high pressure phase. In the future, extending the approach described here to epitaxially strained thin films could provide further insight to the evolution of such parameters with structural tuning.

V. CONCLUSIONS

In summary, we have characterized the bulk electronic structure of a bilayer nickelate $Nd_3Ni_2O_7$ thin film using Ni $2p$ core-level hard x-ray photoemission spectroscopy (HAXPES) combined with LDA+DMFT simulations. Comparison of the surface-sensitive PES and bulk-sensitive HAXPES measurements show significant differences between the surface and bulk electronic structures in this compound. We experimentally observed both local and nonlocal screening features in the Ni $2p_{3/2}$ core-level spectrum, which was not feasible in La-based samples studied so far due to overlapping La $3d$ and Ni $2p$ core levels. Guided by the observed core-level features, we performed parameter optimization in the LDA+DMFT calculations and determined the charge-transfer energy, a key parameter for the Ni valency and the hybridization with the oxygen ligands in this charge-transfer-type system. Our results show a dominant d^8 (Ni^{2+}) configuration ($\sim$70%), with nearly equal contributions from d^7 (Ni^{3+}) and d^9 (Ni^{1+}) ones. This charge distribution differs from typical Ni^{3+} oxides like $RNiO_3$ and Ni^{2+} oxides like NiO, requiring all configurations to be considered in theoretical models. Moreover, the Ni $d_{x^2-y^2}$ orbital exhibited stronger hybridization compared to the d_{z^2} orbital, leading to distinct correlation (mass renormalization) and spin dynamic behaviors in the two orbitals. This highlights the orbital-dependent nature of the electronic structure and correlations in this system.

ACKNOWLEDGMENTS

We thank M. Kitatani for valuable discussions. D.T. acknowledges the support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under the Walter Benjamin Programme, Projektnummer 521584902. A.H. was supported by JSPS KAKENHI Grants No. 21K13884, No. 23K03324, and No. 23H03817. B.H.G. was supported by Schmidt Science Fellows in partnership with the Rhodes Trust. We acknowledge the support for the measurements from the Max Planck-POSTECH-Hsinchu Center for Complex Phase Materials. G.A.P. and D.F.S. are primarily supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DE SC0021925; and by NSF Graduate Research Fellowship Grant No. DGE-1745303. G.A.P. acknowledges additional support from the Paul and Daisy Soros Fellowship for New Americans. Q.S. was supported by the Science and Technology Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319. J.A.M. acknowledges support from the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DE SC0021925. Materials growth was supported by PARADIM under National Science Foundation (NSF) Cooperative Agreement No. DMR-2039380. The computation in this work has been done using the facilities of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo.

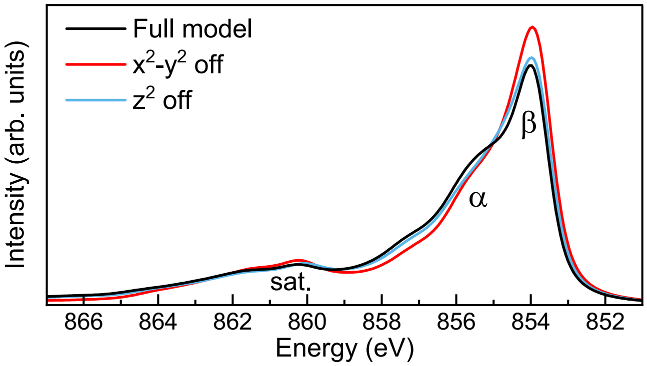

FIG. 4. Ni $2p$ core-level PES spectra calculated using the LDA+DMFT AIM method for the full (black) and modified models with no hybridization of the $d_{x^2-y^2}$ orbital (red) and the d_{z^2} orbital (blue) with metallic states near E_F. See text for detailed explanations of models.

APPENDIX: ORBITAL DEPENDENT HYBRIDIZATION EFFECT IN Ni 2p SPECTRUM

In Fig. 4, we calculate the PES spectra using the LDA+DMFT AIM with modified $V_\gamma(\omega)$, where the hybridization densities within the [−1.0 eV, 1.0 eV] window in Figs. 3(c) and 3(d) are manually set to zero when simulating the PES final states, meaning that CT screening from the metallic states near E_F does not appear in the simulated spectra. The spectra exhibit intensity modulations of the metallic screening feature β, with the large suppression of β being more closely related to the hybridization of the Ni $d_{x^2-y^2}$ state rather than the d_{z^2} state. This additional piece of evidence derived from the Ni $2p$ core-level PES spectra further confirms that there is an orbital-dependent hybridization, with the Ni $d_{x^2-y^2}$ state exhibiting a stronger hybridization with the low-energy states compared to the Ni d_{z^2}.

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