

Supplemental Material: Role of oxygen states in low valence nickelate $\text{La}_4\text{Ni}_3\text{O}_8$

(Dated: January 13, 2022)

This document provides details on the definitions of U and Δ , electron versus hole notation, the choice of model parameters, the parameter dependence of the spectra, and the angular dependence of the spectra.

I. DEFINITIONS OF U AND Δ

Here we provide further details on the definition of the Coulomb and charge transfer energies. Since we need to accurately account for the many body effects, U and Δ are defined in terms of specific electronic configurations in the atomic limit. U is the energy required for a $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$ transition and Δ is defined in terms of a $d_i^n \rightarrow d_i^{n+1} \underline{L}$ transition, where i and j label transition-metal (TM) sites and $\underline{L}$ denotes an oxygen ligand hole. In the present case, the reference occupation is $n = 9$ electrons (or one hole). These definitions are the same as that of the widely used Zaanen-Sawatzky-Allen (ZSA) scheme [1]. We start by writing the Hamiltonian in hole language, which is the notation used throughout the main text:

$$H = \sum_{\sigma} \epsilon_d d_{\sigma}^{\dagger} d_{\sigma} + \sum_{\delta, \sigma} \epsilon_p p_{\delta, \sigma}^{\dagger} p_{\delta, \sigma} + U n_{\uparrow}^d n_{\downarrow}^d + \sum_{\delta} U_{pp} n_{\delta, \uparrow}^p n_{\delta, \downarrow}^p. \quad (1)$$

For simplicity, this and the following equations involve only the $d_{x^2-y^2}$ and O $2p$ orbitals. The same analysis applies when the whole d shell is included. In hole language, the relevant energies are

$$E(d^0 p^0) = 0 \quad (2)$$

$$E(d^1 p^0) = \epsilon_d \quad (3)$$

$$E(d^2 p^0) = 2\epsilon_d + U \quad (4)$$

$$E(d^0 p^1) = \epsilon_p. \quad (5)$$

Coulomb repulsion follows the expected definition

$$U = E(d^0 p^0) + E(d^2 p^0) - 2E(d^1 p^0) = 2\epsilon_d + U - 2\epsilon_d = U. \quad (6)$$

The charge transfer energy is

$$\Delta = E(d^0 p^1) - E(d^1 p^0) = \epsilon_p - \epsilon_d \quad (7)$$

consistent with the main text. Most literature on cuprates and the low valence nickelates use this hole notation.

II. ELECTRON VERSUS HOLE NOTATION

How does Eq. 1 change when we convert to electron language? In this case, we will use tilde notation to label terms in electron language. Applying the expected transformations to the operators, $H \rightarrow \tilde{H}$, $d_{\sigma} \rightarrow \tilde{d}_{\sigma}^{\dagger}$, $n_{\sigma}^d \rightarrow (1 - \tilde{n}_{\sigma}^d)$, etc. we obtain the Hamiltonian in electron language

$$\tilde{H} = \sum_{\sigma} \epsilon_d \tilde{d}_{\sigma}^{\dagger} \tilde{d}_{\sigma} + \sum_{\delta, \sigma} \epsilon_p \tilde{p}_{\delta, \sigma}^{\dagger} \tilde{p}_{\delta, \sigma} + U(1 - \tilde{n}_{\uparrow}^d)(1 - \tilde{n}_{\downarrow}^d) + \sum_{\delta} U_{pp}(1 - \tilde{n}_{\delta, \uparrow}^p)(1 - \tilde{n}_{\delta, \downarrow}^p). \quad (8)$$

We transform the first two terms via commutation rules to give

$$\tilde{H} = - \sum_{\sigma} \epsilon_d \tilde{d}_{\sigma}^{\dagger} \tilde{d}_{\sigma} - \sum_{\delta, \sigma} \epsilon_p \tilde{p}_{\delta, \sigma}^{\dagger} \tilde{p}_{\delta, \sigma} + U(1 - \tilde{n}_{\uparrow}^d)(1 - \tilde{n}_{\downarrow}^d) + \sum_{\delta} U_{pp}(1 - \tilde{n}_{\delta, \uparrow}^p)(1 - \tilde{n}_{\delta, \downarrow}^p). \quad (9)$$

Expanding the last two terms gives

$$\tilde{H} = - \sum_{\sigma} (\epsilon_d + U) \tilde{d}_{\sigma}^{\dagger} \tilde{d}_{\sigma} - \sum_{\delta, \sigma} (\epsilon_p + U_{pp}) \tilde{p}_{\delta, \sigma}^{\dagger} \tilde{p}_{\delta, \sigma} + U \tilde{n}_{\uparrow}^d \tilde{n}_{\downarrow}^d + \sum_{\delta} U_{pp} \tilde{n}_{\delta, \uparrow}^p \tilde{n}_{\delta, \downarrow}^p, \quad (10)$$

where some constant terms have been omitted. By comparison to Eq. 1 we can associate $\tilde{\epsilon}_d = -(\epsilon_d + U)$, $\tilde{\epsilon}_p = -(\epsilon_p + U_{pp})$, $\tilde{U} = U$, and $\tilde{U}_{pp} = U_{pp}$. This follows the expectation that a particle-hole transformation leaves the

Coulomb interactions unchanged but shifts the on-site energies by the value of the local Hubbard repulsion, reflecting a change in the vacuum state. Our result in hole language, $\Delta = \epsilon_p - \epsilon_d$, can then be recast as $\Delta = -(\tilde{\epsilon}_p + U_{pp}) + (\tilde{\epsilon}_d + U)$ in electron language, which is the same as $\tilde{\Delta} = E(d^{10}\underline{L}) - E(d^9)$. This transformation shows that when comparing with first principles calculations, care needs to be taken about how the correlations and many body effects are handled. To do so, one must take into account possible double counting errors [2, 3], which will effectively change the meanings and values of ϵ_d and ϵ_p .

III. THE CHOICE OF MODEL PARAMETERS IN ED CALCULATIONS

Here we provide the details about how the parameters are determined/chosen in the exact-diagonalization (ED) calculations. Although there are many parameters in the original Hamiltonian, most of them are constrained by the physical considerations described below so that they can be effectively fixed with our quoted accuracy of 1 eV. We categorize the parameters in four parts.

1. **Coulomb interactions.** Since we work in the hole language, the on-site Coulomb repulsion for O is not crucial since double hole occupation on the O sites is unlikely. Therefore, F_{pp}^0 and F_{pp}^2 do not influence our conclusions and are fixed to standard Hartree-Fock values throughout the calculations [4]. The inter-site Coulomb interaction U_{dp} is also fixed since the distance between Ni and O atoms means that it is expected to be much smaller than the Ni on-site Coulomb interactions and thus plays a negligible role [5]. The ratio between F_{dd}^4 and F_{dd}^2 is known to be approximately 5/8, independent of solid-state screening [6, 7]. The Hund's exchange in transition-metal (TM) materials is known empirically to vary between 0.4 and 1.2 eV [6, 7]. Hence, it is safe to fix it with an estimated uncertainty much smaller than 1 eV. By doing so, the only tunable parameter with the largest uncertainty is the Ni intra-orbital Coulomb repulsion U . Once U is chosen, F_{dd}^0 , as well as the inter-orbital Coulomb interactions, is uniquely determined through our procedure.
2. **Hopping integrals.** Making use of the Slater-Koster scheme, all the hopping integrals can be derived from two parameters, $V_{pd\sigma}$ and $V_{pp\sigma}$. The other two parameters are set as $V_{pd\pi} = -V_{pd\sigma}/2$ and $V_{pp\pi} = -V_{pp\sigma}/4$ based on the known scaling of the hopping for TM-O octahedra of this type [8]. This fixes these two parameters with an accuracy better than our estimated error bar. An additional parameter, η , is used for the Cu_2O_{11} cluster, since it has apical O bonds, and this is fixed to the standard value [9].
3. **Point charge crystal field splitting.** The crystal electric field (CEF) splitting is primarily inferred from the low energy dd excitations and has less of an effect on the charge transfer ones. It has two contributions. The major one is the $p - p$ and $p - d$ hoppings and the minor one is the point charge CEF. Therefore, once the hopping integrals are chosen, the point charge CEF parameters can be confidently determined to match the dd excitations seen at both the O K and Ni L edges with an uncertainty much smaller than 1 eV.
4. **Other parameters.** The core-hole potential U_q only modifies the peak intensities but not the peak positions since it is not involved in the ground states and the excited states. So it is fixed to a standard value for the O K -edge of 6 eV [10]. The charge transfer energy Δ is the most important quantity we want to extract, so we treat this as fully tunable.

Points 1-4 leave U , Δ , $V_{pd\sigma}$, and $V_{pp\sigma}$, as the only free parameters. These have distinct effects on the Resonant Inelastic X-ray Scattering (RIXS) spectra, allowing them to be determined by comparison with the RIXS spectra. The width of feature A along the energy loss axis is primarily determined by $V_{pp\sigma}$ while its position is a correlated combination of U , Δ , and $V_{pd\sigma}$, which is further constrained by the superexchange interaction J . We also need to consider the relative intensities of features within the manifold of feature A as well as the ratio between features A and B along with their angular dependence. With these constraints, we search the parameter space to match our RIXS data [Fig. S1], and the results are presented in Fig. 3 and Fig. S2. The primary factor limiting the accuracy is a range of different Δ and U values that produce reasonable agreement with the data and which gives us our estimated error bar of 1 eV. We test our approach by measuring and applying the same analysis to a cuprate. As explained in the main text, the fact that we obtain values in good accord with the literature validates the accuracy of our approach within our quoted error bar.

IV. PARAMETER DEPENDENCE OF THE SPECTRA

To test the accuracy of our derived parameters, we investigated the variation of the spectra when changing the input parameters. Table S1 and Fig. S2 show the range of different $\Delta = \epsilon_{p_\sigma}$ values that produce a satisfactory fit

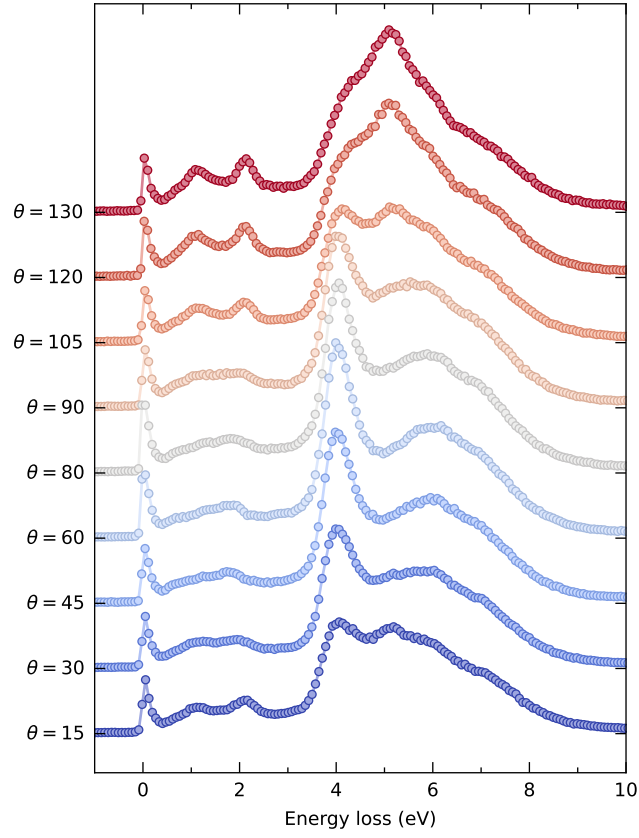


FIG. S1. Self-absorption corrected RIXS spectra of $\text{La}_4\text{Ni}_3\text{O}_8$ collected at 40 K. The same set of data produce Fig. 4(a) in the main text.

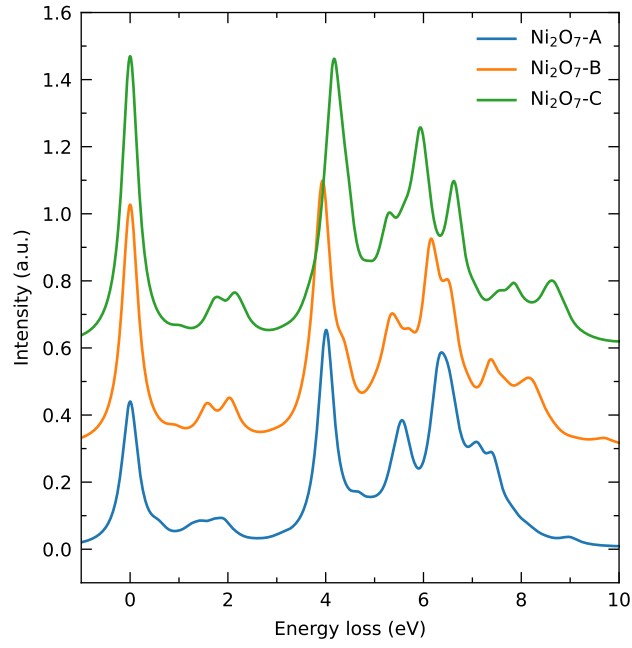


FIG. S2. Calculated RIXS spectra of Ni_2O_7 cluster using the parameters listed in Table S1. The calculations are performed with $\theta = 60^\circ$ and σ polarization. The spectra are shifted along the y axis for clarity.

TABLE S1. List of parameters used for the Ni_2O_7 ED calculations in Fig. S2. All parameters are listed in units of eV.

Label	$\epsilon_{d_{x^2-y^2}}$	$\epsilon_{d_{3z^2-r^2}}$	$\epsilon_{d_{xy}}$	$\epsilon_{d_{xz/yz}}$	ϵ_{p_σ}	ϵ_{p_π/p_z}	$V_{pd\sigma}$	$V_{pp\sigma}$	F_{dd}^0	F_{dd}^2	F_{dd}^4	F_{pp}^0	F_{pp}^2	U_{dp}	U_q	J_{calc}
A	0	0.2	0.3	0.5	5.8	5.8	1.55	0.6	4.58	6.89	4.31	3.3	5	1	6	0.083
B	0	0.2	0	0.2	6	6.5	1.63	0.7	6.58	6.89	4.31	3.3	5	1	6	0.085
C	0	0.2	0	0.2	5.9	6.9	1.65	0.7	7.58	6.89	4.31	3.3	5	1	6	0.085

of the spectra. We conclude that $\Delta \approx 6$ eV within an error bar of about 1 eV, such that $\text{La}_4\text{Ni}_3\text{O}_8$ can be robustly classified as a mixed charge-transfer/ Mott-Hubbard system with $\Delta \sim U$. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, we were able to further constrain our values using literature O K -edge RIXS measurements of the undoped sample [11], so the values for this material are constrained to $\lesssim 1$ eV. This approach is currently impractical for nickelates as efforts to electron dope $\text{La}_4\text{Ni}_3\text{O}_8$ have so far not been successful, and infinite-layer nickelate films are inhomogeneous due to spatial variability in the oxygen reduction [12–18].

V. ANGULAR DEPENDENCE OF O K -EDGE SPECTRA

In this section we explain the angular dependence of the spectra. Figure 4 in the main text was taken at a fixed scattering angle of $2\Theta = 150^\circ$ while varying the incident angle θ . In this way, the angle between the outgoing beam and the sample surface is $\theta_{\text{out}} = \theta + 30^\circ$. The incident x-ray polarization was σ and therefore parallel to the sample b -axis at all θ , whereas the emitted x-ray polarization was not analyzed such that both π and σ polarizations are detected. To understand the overall angular dependence we calculate the transition probability out of the p_σ , p_π , and p_z orbitals at different θ , which captures the main transitions, even though this leaves out some detailed structure that is present in the full calculations in Fig. 4. Excitations involving p_π are maximized when $\theta_{\text{out}} = 90^\circ$ (equivalent to $\theta = 60^\circ$) such that all emitted photons are polarized in the ab plane of the sample. Excitations involving p_z are largest as θ_{out} gets close to 180° such that the π polarized emitted photons are along the sample c -axis.

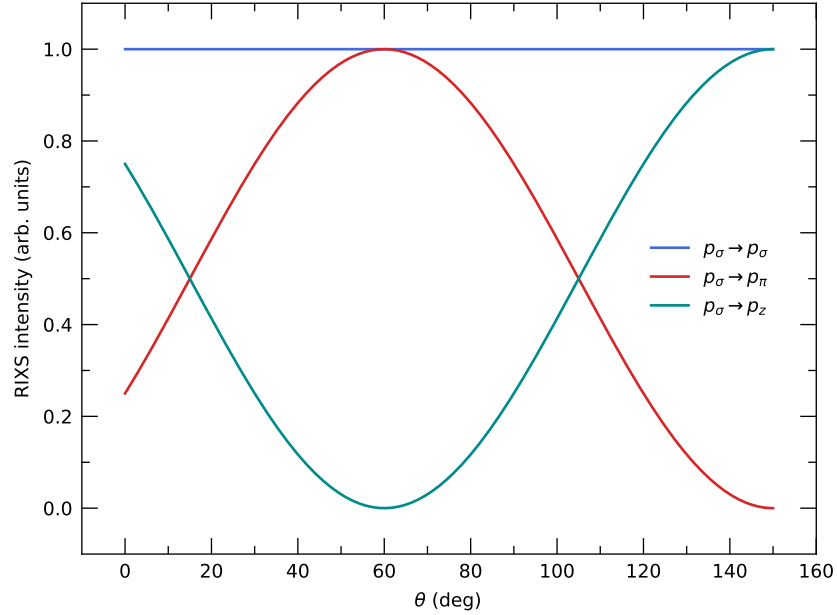


FIG. S3. Calculated RIXS intensities for transitions between different combinations of p_σ , p_π , and p_z as a function of incident angle θ with σ polarized incident x-rays.

-
- [1] J. Zaanen, G. A. Sawatzky, and J. W. Allen, “Band gaps and electronic structure of transition-metal compounds,” *Physical Review Letters* **55**, 418–421 (1985).
 - [2] Hung T. Dang, Andrew J. Millis, and Chris A. Marianetti, “Covalency and the metal-insulator transition in titanate and vanadate perovskites,” *Phys. Rev. B* **89**, 161113 (2014).
 - [3] Kristjan Haule, “Exact double counting in combining the dynamical mean field theory and the density functional theory,” *Phys. Rev. Lett.* **115**, 196403 (2015).
 - [4] Y.L. Wang, G. Fabbri, M.P.M. Dean, and G. Kotliar, “EDRIXS: An open source toolkit for simulating spectra of resonant inelastic x-ray scattering,” *Computer Physics Communications* **243**, 151–165 (2019).
 - [5] Kozo Okada and Akio Kotani, “Intersite coulomb interactions in quasi-one-dimensional copper oxides,” *Journal of the Physical Society of Japan* **66**, 341–344 (1997).
 - [6] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, “2p x-ray absorption of 3d transition-metal compounds: An atomic multiplet description including the crystal field,” *Phys. Rev. B* **42**, 5459–5468 (1990).
 - [7] Frank De Groot and Akio Kotani, *Core level spectroscopy of solids* (CRC press, 2008).
 - [8] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, “Electronic states and magnetic properties of edge-sharing Cu-O chains,” *Physical Review B* **57**, 5326–5335 (1998).
 - [9] H. Eskes, L. H. Tjeng, and G. A. Sawatzky, “Cluster-model calculation of the electronic structure of CuO: A model material for the high- T_c superconductors,” *Physical Review B* **41**, 288–299 (1990).
 - [10] Kozo Okada and Akio Kotani, “Copper K and oxygen K resonant inelastic x-ray scattering of one-dimensional cuprates,” *Journal of the Physical Society of Japan* **75**, 044702 (2006).
 - [11] V. Bisogni, M. Moretti Sala, A. Bendounan, N. B. Brookes, G. Ghiringhelli, and L. Braicovich, “Bimagnon studies in cuprates with resonant inelastic x-ray scattering at the O K edge. II. Doping effect in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,” *Physical Review B* **85**, 214528 (2012).
 - [12] H. Lu, M. Rossi, A. Nag, M. Osada, D. F. Li, K. Lee, B. Y. Wang, M. Garcia-Fernandez, S. Agrestini, Z. X. Shen, E. M. Been, B. Moritz, T. P. Devereaux, J. Zaanen, H. Y. Hwang, Ke-Jin Zhou, and W. S. Lee, “Magnetic excitations in infinite-layer nickelates,” *Science* **373**, 213 (2021).
 - [13] M. Rossi, H. Lu, A. Nag, D. Li, M. Osada, K. Lee, B. Y. Wang, S. Agrestini, M. Garcia-Fernandez, J. J. Kas, Y.-D. Chuang, Z. X. Shen, H. Y. Hwang, B. Moritz, Ke-Jin Zhou, T. P. Devereaux, and W. S. Lee, “Orbital and spin character of doped carriers in infinite-layer nickelates,” *Phys. Rev. B* **104**, L220505 (2021).
 - [14] Ying Fu, Le Wang, Hu Cheng, Shenghai Pei, Xuefeng Zhou, Jian Chen, Shaoheng Wang, Ran Zhao, Wenrui Jiang, Cai Liu, *et al.*, “Core-level x-ray photoemission and Raman spectroscopy studies on electronic structures in Mott-Hubbard type nickelate oxide NdNiO_2 ,” *arXiv:1911.03177* (2019).
 - [15] Matthias Hepting, Danfeng Li, CJ Jia, Haiyu Lu, E Paris, Y Tseng, X Feng, M Osada, E Been, Y Hikita, *et al.*, “Electronic structure of the parent compound of superconducting infinite-layer nickelates,” *Nature Materials* **19**, 381–385 (2020).
 - [16] Qiangqiang Gu, Yueying Li, Siyuan Wan, Huazhou Li, Wei Guo, Huan Yang, Qing Li, Xiyu Zhu, Xiaoqing Pan, Yuefeng Nie, and Hai-Hu Wen, “Single particle tunneling spectrum of superconducting $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ thin films,” *Nature Communications* **11**, 6027 (2020).
 - [17] Berit H. Goodge, Danfeng Li, Kyuho Lee, Motoki Osada, Bai Yang Wang, George A. Sawatzky, Harold Y. Hwang, and Lena F. Kourkoutis, “Doping evolution of the mott-hubbard landscape in infinite-layer nickelates,” *Proceedings of the National Academy of Sciences* (2021), 10.1073/pnas.2007683118.
 - [18] Zhuoyu Chen, Motoki Osada, Danfeng Li, Emily M. Been, Su-Di Chen, Makoto Hashimoto, Donghui Lu, Sung-Kwan Mo, Kyuho Lee, Bai Yang Wang, Fanny Rodolakis, Jessica L. McChesney, Chunjing Jia, Brian Moritz, Thomas P. Devereaux, Harold Y. Hwang, and Zhi-Xun Shen, “Electronic structure of superconducting nickelates probed by resonant photoemission spectroscopy,” *arXiv:2106.03963* (2021).