

Continuum Charge Excitations in High-Valence Transition-Metal Oxides Revealed by Resonant Inelastic X-Ray Scattering

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We present a theoretical investigation of the origin of Raman-like and fluorescence-like (FL) features of resonant inelastic x-ray scattering (RIXS) spectra. Using a combination of local-density approximation + dynamical mean-field theory and a configuration interaction solver for Anderson impurity model, we calculate the L -edge RIXS and x-ray absorption spectra of high-valence transition-metal oxides LaCuO_3 and NaCuO_2 . We analyze in detail the behavior of the FL feature and show how it is connected to the details of electronic and crystal structure. On the studied compounds we demonstrate how material details determine whether the electron-hole continuum can be excited in the L -edge RIXS process.

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The excitation spectrum is a fundamental characteristic that determines properties of a physical system. While the excitations of weakly correlated electrons can be built out of elementary ones and therefore different spectroscopic experiments show the similar spectra, e.g., the same gap for charge, spin, and optical excitations, correlated materials such as transition metal oxides (TMO) are different [1,2]. Here, the connection between various types of excitations is buried deep in the experimentally unobservable wave function and different techniques are necessary to probe specific excitations.

Following the remarkable improvements of energy resolution in the past decade resonant inelastic x-ray scattering (RIXS) became a popular tool to study diverse materials [3]. Its sensitivity to a range of two-particle excitations enables observation of low-energy spin, orbital, and charge excitations (~ 100 meV) [4–7] together with high-energy excitations (~ 1 – 10 eV), such as atomic multiplets or charge-transfer (CT) excitations [8–10]. The versatility of RIXS is paid for complicated interpretation of the resonant spectra which requires theoretical modeling.

Two features have been observed in the L -edge RIXS ($2p \rightarrow 3d \rightarrow 2p$) of TMO when scanning the incident photon energy ω_{in} across the x-ray absorption spectra (XAS): a Raman-like (RL) signal with a constant energy loss $\omega_{\text{loss}} = \omega_{\text{in}} - \omega_{\text{out}}$ and a fluorescence-like (FL) signal with a constant emission energy ω_{out} , i.e., a linear dependence of ω_{loss} on ω_{in} [3,9,11–14]. The analysis of material specific behavior of these features shows a potential for addressing questions concerning itinerancy of charge carriers and localization of charge excitations [12,14,15]. While several experimentally motivated interpretations were put forward, a unified description of the atomiclike RL and itinerant FL features poses a theoretical challenge [16,17].

The L -edge RIXS spectrum of the CT Mott insulator NiO [8,9] exhibits a RL behavior at ω_{in} of the main absorption peak well separated from the FL feature at ω_{in} of the CT satellite. A different behavior was reported in the negative-CT compound NdNiO_3 , where Bisogni *et al.* [15] observed merging of the low- ω_{loss} RL and FL features in $\text{Ni } L_3$ RIXS. Moreover, the details of the low- ω_{loss} FL feature exhibit distinct temperature dependence connected to opening of charge gap at low temperatures. Bisogni *et al.* interpreted the low- ω_{loss} FL feature as a signature of unbound particle-hole pairs in the RIXS final state. Zhou *et al.* [12] studied L -edge RIXS in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures and interpreted the relative intensity of the FL feature as a measure of itinerant carrier concentration. This conclusion was recently questioned by Pfaff *et al.* [14], who suggested that either RL or FL signals reflect the nature of the intermediate state of the RIXS process.

The commonly used cluster model with the TM $3d$ and the neighboring O $2p$ orbitals misses the FL feature completely due to the lack of continuum (delocalized) particle-hole excitations. This is remedied by the Anderson impurity model (AIM); however, the use of simple *ad hoc* bath densities of states [8–10,15] does not allow us to capture the important material details. To overcome this limitation we employ the local-density approximation (LDA) + dynamical mean-field theory (DMFT) [18,19] approach. The AIM with material specific hybridization density is then extended to include the core orbitals [20]. This approach, which we recently applied to study nonlocal screening effects in L -edge x-ray photoemission spectroscopy (XPS) [20], is here extended to analyze RIXS.

In order to focus on the physics of RIXS excitations, we avoid the uncertainties brought about by structural phase transition in nickelates and choose two isoelectronic Cu^{3+} compounds LaCuO_3 and NaCuO_2 as model systems for

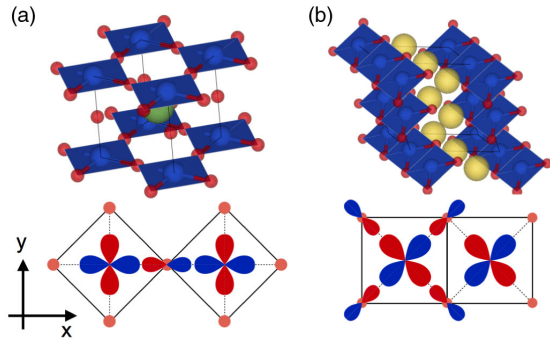


FIG. 1. The crystal structures of (a) LaCuO_3 with $P4/m$ and $C2/m$ space groups in paramagnetic and antiferromagnetic states, respectively [26] (b) NaCuO_2 [28] visualized by VESTA [29]. The blue, red, green, and yellow circles represent Cu, O, La, and Na atoms, respectively. The sketch of the xy plane is shown together.

high-valence TMO. Both share a tiny CT energy [21–25] leading to small or no gap [21,23,24,26,27]. As we show later the key difference between the two compounds is the lattice geometry with corner-sharing CuO_6 octahedra in LaCuO_3 , but edge-sharing ones in NaCuO_2 ; see Fig. 1.

The calculation proceeds in two steps. First, a standard LDA + DMFT calculation is performed as follows. The LDA band structure obtained with WIEN2K [30] is projected [31,32] onto a dp tight-binding model spanning the Cu $3d$ and O $2p$ orbitals and augmented with the electron-electron interaction within the Cu $3d$ shell, giving the Hamiltonian

$$H = \sum_{\mathbf{k}} \begin{pmatrix} \mathbf{d}_{\mathbf{k}}^{\dagger} & \mathbf{p}_{\mathbf{k}}^{\dagger} \end{pmatrix} \begin{pmatrix} h_{\mathbf{k}}^{dd} - \mu_{dc} & h_{\mathbf{k}}^{dp} \\ h_{\mathbf{k}}^{pd} & h_{\mathbf{k}}^{pp} \end{pmatrix} \begin{pmatrix} \mathbf{d}_{\mathbf{k}} \\ \mathbf{p}_{\mathbf{k}} \end{pmatrix} + \sum_i W_i^{dd}.$$

Here, $\mathbf{d}_{\mathbf{k}}$ ($\mathbf{p}_{\mathbf{k}}$) is an operator-valued vector whose elements are Fourier transforms of d_{ai} ($p_{\gamma i}$), that annihilate the Cu $3d$ (O $2p$) electron in the orbital α (γ) in the i th unit cell. The on-site Coulomb interaction W_i^{dd} is parametrized in the usual way [33,34] with $U = 7.5$ and $J = 0.98$ eV, typical for Cu systems [35]. The double-counting term μ_{dc} , which corrects for the d - d interaction present in the LDA step, renormalizes the p - d splitting and thus the CT energy. While several *ad hoc* schemes exist to compute μ_{dc} (with somewhat different results), we treated μ_{dc} as an adjustable parameter fixed by comparison to the available L -edge XAS and valence XPS data; see the Supplemental Material (SM) [36]. The strong-coupling continuous-time quantum Monte Carlo method [40–42] with density-density approximation to the on-site interaction was used to solve the auxiliary AIM.

In the second step, we compute the RIXS spectra for AIM with DMFT hybridization density and Cu $2p$ core states using the configuration interaction method [20]. The hybridization function, which encodes the information of

how a given Cu orbital γ exchanges electrons with the rest of the crystal, can be written as

$$V_{\gamma}^2(\varepsilon) = \sum_{\alpha} \frac{V_{\alpha,\gamma}^2}{\varepsilon - \varepsilon_{\alpha,\gamma}}.$$

Here, $V_{\alpha,\gamma}$ is the hopping amplitude between the Cu ion and auxiliary orbitals at energies $\varepsilon_{\gamma,\alpha}$ [43], which represent the effect of the nearest-neighbor oxygen ligands as well as the more distant atoms [18,20]. In practice, $V_{\gamma}^2(\varepsilon)$ obtained in the LDA + DMFT calculation is represented by 25 discretized bath states α for each Cu orbital γ [20]. The RIXS intensity at finite temperature T is given by [9,10,44]

$$F_{\text{RIXS}}(\omega_{\text{out}}, \omega_{\text{in}}) = \sum_n F_{\text{RIXS}}^{(n)}(\omega_{\text{out}}, \omega_{\text{in}}) e^{-E_n/k_B T} / Z,$$

where

$$\begin{aligned} F_{\text{RIXS}}^{(n)}(\omega_{\text{out}}, \omega_{\text{in}}) &= \sum_f \left| \sum_m \frac{\langle f | T_e | m \rangle \langle m | T_i | n \rangle}{\omega_{\text{in}} + E_n - E_m + i\Gamma_L} \right|^2 \\ &\times \delta(\omega_{\text{in}} + E_n - \omega_{\text{out}} - E_f) \\ &= \sum_f \left| \langle f | T_e \frac{1}{\omega_{\text{in}} + E_n - H_{\text{imp}} + i\Gamma_L} T_i | n \rangle \right|^2 \\ &\times \delta(\omega_{\text{in}} + E_n - \omega_{\text{out}} - E_f). \end{aligned} \quad (1)$$

Here, $|n\rangle$, $|m\rangle$, and $|f\rangle$ are the initial, intermediate, and final states with energies E_n , E_m , and E_f , respectively, and $e^{-E_n/k_B T} / Z$ is the Boltzmann factor with the partition function Z . Γ_L is the lifetime width of the intermediate state, and T_i (T_e) describes the dipole transition for the incident (emitted) photon. H_{imp} is the AIM Hamiltonian augmented by the core orbitals and their interaction with Cu $3d$ orbitals; see Eq. (3) in Ref. [20]. In the actual calculation the resolvent formulation on the second line of Eq. (1) is used. We also compute L -edge XAS spectra since the intermediate state $|m\rangle$ (corresponding to the final state of XAS) provides an important clue for interpretation of RIXS spectra. Details of the calculation can be found in the Supplemental Material [36].

In Figs. 2(a),2(b) we show the one-particle (1P) density of states of LaCuO_3 and NaCuO_2 . The μ_{dc} in the range of 55.64–57.64 eV yields results consistent with Cu L -edge XAS studies [23,45,46]; see Figs. 3(a),3(c). The μ_{dc} values provide also the best match with earlier valence XPS studies [23,25] shown in Figs. 2(a),2(b). The deviations from the experimental XPS spectra may be due to the uncertainty of the relative $\text{Cu}3d:\text{O}2p$ cross section and the surface sensitivity of XPS. In NaCuO_2 , in particular, the surface is prone to contamination leading to the appearance of Cu^{2+} ions [45,47]. Varying μ_{dc} within the above range has only a minor impact on the RIXS spectra for both

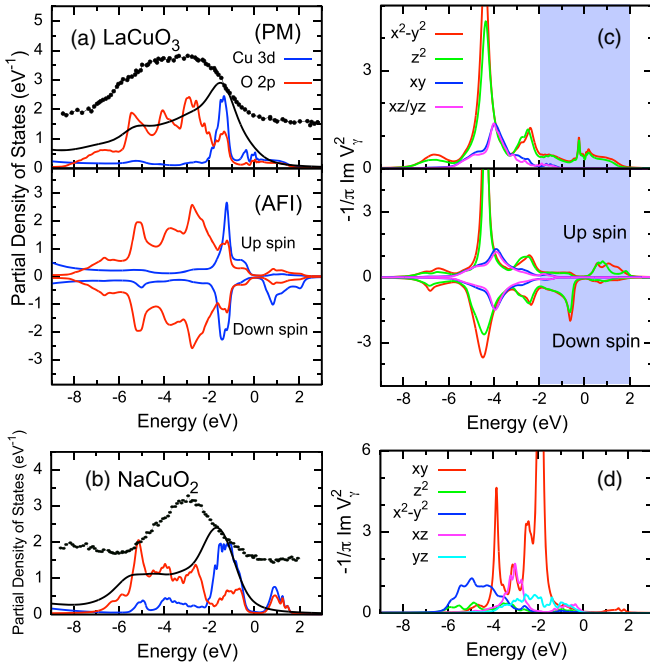


FIG. 2. LDA + DMFT 1P density of states for (a) LaCuO₃ in the PM and AFI phases and (b) NaCuO₂. The hybridization function $V_\gamma^2(\epsilon)$ of LaCuO₃ (c) in the PM and AFI phases and NaCuO₂ (d). The energy origin is taken at E_F . The experimental XPS data (symbols) of LaCuO₃ [23] and NaCuO₂ [25] are compared to the theoretical ones (black line) [50]. $\mu_{dc} = 55.64$ eV is employed in the calculation.

materials and does not affect our conclusions [36]. For LaCuO₃, paramagnetic metal (PM) and antiferromagnetic insulator (AFI) solutions can be stabilized, similar to LDA + U studies [24], indicating the Slater nature of the gap. Reflecting the unclear experimental situation

[23,24,26,27], we proceed with both states and use them later to demonstrate the effect of the small gap on RIXS. NaCuO₂ ($E_{\text{gap}} \approx 0.5$ eV) has a band-insulator character with a gap present already in the LDA solution [47,48]. Overall, the 1P density of states suggest existing phase space for the continuum of p - p excitations in the few eV range. The calculated Cu L_3 -edge XAS and RIXS spectra are shown in Fig. 3. The XAS spectrum of NaCuO₂ has a single-peak (A), while that of LaCuO₃ exhibits an additional shoulder (B), enhanced in the PM phase, observed also in experiment for NaCuO₂ [45] and LaCuO₃ [23]. The shoulder B is missing in the calculations on the CuO₆ cluster model [23,49], see Fig. 3(e), indicating that the shoulder is not of d - d or CT origin but due to a final state delocalized beyond the CuO₆ cluster. Such a nonlocal charge excitation is captured by the present approach [20].

The RIXS spectra of NaCuO₂ and LaCuO₃ are strikingly different. Tuning ω_{in} to the peak A of the XAS, two distinct d - d transitions with RL behavior are found in both compounds, similar to another Cu³⁺ material Zn_{1-x}Cu_xO [52], followed by CT transitions with higher ω_{loss} . However, at higher ω_{in} the RIXS of LaCuO₃ yields a linear FL feature, with little difference between the AFI and PM phase. The FL feature is suppressed in NaCuO₂, resembling the spectrum of the cluster model [36]. The calculated RIXS spectra of LaCuO₃ reminds one of the experimental observation on NdNiO₃ [15] with the FL feature starting at the ω_{in} on the L_3 main edge and not far above it as in NiO. The continuum of unbound particle-hole pairs in the manner of Ref. [15] explains the FL feature in LaCuO₃.

Why is the FL feature missing in NaCuO₂ then? The small NaCuO₂ gap cannot explain the absence of visible

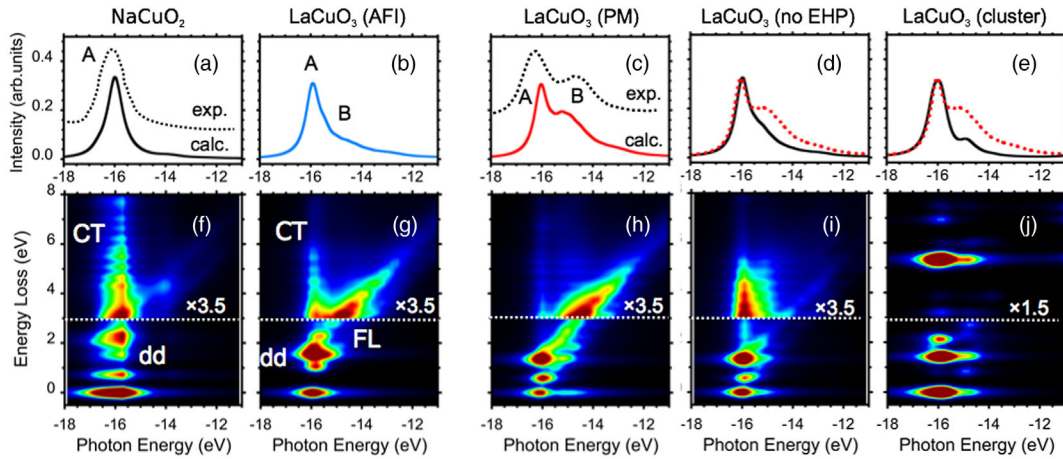


FIG. 3. The calculated L_3 -edge XAS and RIXS spectra for (a),(f) NaCuO₂ and LaCuO₃ in the (b),(g) AFI phase, (c),(h) PM phase, (d),(i) no EHP, and (e),(j) CuO₆ cluster model. The RIXS intensity with $\omega_{\text{loss}} \geq 3.0$ eV (horizontal dashed line) are magnified by 3.5 times [1.5 times for (e)]. $\mu_{dc} = 55.64$ eV is employed in the calculation. The LDA + DMFT spectrum for LaCuO₃ (PM) is shown by a dotted curve in (d) and (f), for comparison. The cluster-model results for NaCuO₂ are found in the Supplemental Material [36]. The experimental XAS data (dashed line) for LaCuO₃ (PM) and NaCuO₂ are taken from Refs. [23] and [45]. The spectral broadening is considered using a Gaussian of 150 meV for RIXS and a Lorentzian 300 meV for XAS (HWHM).

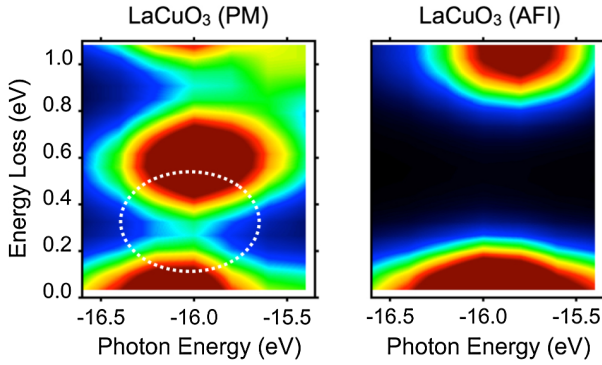


FIG. 4. Low ω_{loss} region (< 1.0 eV) of the RIXS map in the PM and AFI phases of LaCuO_3 . The FL feature continues to zero energy loss in the PM phase.

particle-hole excitations at ω_{loss} in the 3–4 eV range. In fact, the experiment on NdNiO_3 [15] and the calculations in the PM and AFI phases of LaCuO_3 in Fig. 4 show that the gap opening affects the FL feature only at low ω_{loss} . Moreover, the NaCuO_2 1P density of states, Fig. 2(b), exhibits noticeably higher density of states above and below the gap than LaCuO_3 , Fig. 2(a), suggesting a larger phase space for particle-hole excitations. To answer this question we show, in Figs. 2(c), 2(d), the hybridization intensities $V_\gamma(\epsilon)$. It is instructive to consider the $V_\gamma(\epsilon)$ of the cluster model first [36]. Here, $V_\gamma(\epsilon)$ is a single Dirac δ function peaked at the energy ϵ_p of the ligand orbital, while the O $2p$ density of states exhibits two peaks corresponding to the bonding and antibonding states.

A prominent peak in $V_\gamma(\epsilon)$ (for the e_g orbitals) due to hybridization to nearest-neighbor O ligands is found in both LaCuO_3 and NaCuO_2 . The continuum part of $V_\gamma(\epsilon)$ in the two materials reveals the difference. While in LaCuO_3 a substantial hybridization intensity exists in the low-energy region of -2 to 2 eV [blue shadow in Fig. 2(c)], the $V_\gamma(\epsilon)$ of NaCuO_2 resembles that of the cluster model with a weak continuum background. This is how the local quantity $V_\gamma(\epsilon)$, relevant for description of the core-level excitation, encodes the information about bonding and lattice geometry. In LaCuO_3 , the corner-sharing network of CuO_6 octahedra allows electrons and holes to propagate through the strong Cu–O σ bonds and thus gives rise to the continuum of $V_\gamma(\epsilon)$. This is not possible in the chains of edge sharing CuO_4 plaquettes in NaCuO_2 , where the neighboring Cu ions form σ bonds with orthogonal O $2p$ orbitals, see Fig. 1, and the crystal resembles a collection of weakly coupled CuO_4 clusters.

How does the hybridization intensity affect the RIXS spectra? In Eq. (1), all intermediate states accessible in the XAS process contribute to RIXS in principle. We estimate that the intermediate states with $|E_m - E_n - \omega_{\text{in}}| \lesssim \Gamma_L$, which approximately conserve energy in the partial XAS process, dominate while those outside this range cancel approximately out due to the varying sign of the

denominator. Such a claim cannot be directly confirmed with the resolvent formulation of Eq. (1). It is, nevertheless, supported by the diagonal shape of the FL feature in the $\omega_{\text{in}} - \omega_{\text{loss}}$ plane, suggesting that a narrow range of intermediate states are “excited” that “decay” into a narrow range of final states with matching electron-hole excitation. The small hybridization intensity for $\epsilon > 0$ in NaCuO_2 implies that (intermediate) states with different numbers of conduction electrons hybridize only weakly with one another. In LaCuO_3 a RIXS process that we schematically write as $d^8 + d^9 \underline{v} \rightarrow \underline{C}d^{10} \underline{v} + \underline{C}d^9 c \underline{v} \rightarrow d^8 c \underline{v}$ ends up in a final state that can be characterized as the ground state plus an electron-hole pair in the continuum, see Fig. 5(a), where \underline{C} , \underline{v} , and c correspond to a hole in $2p$ core level, in valence bands, and an electron in conduction bands, respectively. Such processes in NaCuO_2 are strongly suppressed since states of the type $\underline{C}d^{10} \underline{v}$ and $\underline{C}d^9 c \underline{v}$ hybridize only weakly. This is a local expression of the fact that in NaCuO_2 a hole transferred from Cu to O has a small probability to escape the CuO_4 cluster.

To test this interpretation, we switched off the hybridization to the conduction band in the intermediate states for the PM phase of LaCuO_3 ; see Fig. 3(i). In practice, we have set $V_\gamma(\epsilon > 0) = 0$ in the H_{imp} of Eq. (1) while keeping $V_\gamma(\epsilon)$ unrestricted in the initial and final states. In Fig. 5(b) the hybridization to the conduction band is sketched. The intensity of the FL feature is dramatically suppressed and the structure of the RIXS spectrum resembles that of NaCuO_2 . Although (unchanged) final states with excited electron-hole pairs exist, they cannot be resonantly excited by the RIXS process. This result supports the interpretation of the FL feature in Ti L -edge spectra by Pfaff *et al.* [14] and shows that the nature of hybridization in intermediate states is the dominant factor affecting the intensity of FL feature. Cutting hybridization to the conduction states affects also the XAS spectrum, Fig. 3(d), which loses

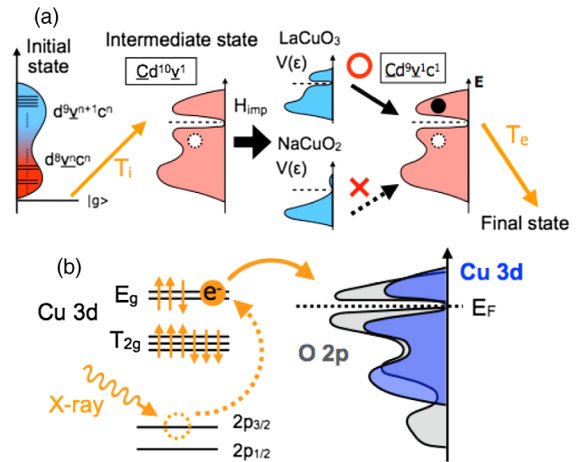


FIG. 5. Schematic of (a) electron-hole pair creation in the RIXS process of LaCuO_3 and NaCuO_2 , and (b) CT to the conduction states in the intermediate state.

the shoulder B and overlaps with that of the cluster model, Fig. 3(e). This shows that intermediate states with localized and delocalized character coexist in this ω_{in} region, which leads to coexistence of FL and RL features in the RIXS spectrum.

In conclusion, we have studied the coexistence of RL and FL features in RIXS spectra of high-valence transition-metal oxides. We have shown how the AIM hybridization function encodes the information about the lattice environment and that it is the hybridization function rather than one-particle spectral density that determines the presence of FL feature. We predict that FL feature is present in the L -edge RIXS spectra of LaCuO_3 both in the PM and AFM phases, while it is absent in the isoelectronic NaCuO_2 , experimental verification of which is highly desirable. We have interpreted this numerical observation in terms of crystal geometry. Comparing the RIXS spectra of PM and AFM LaCuO_3 , we have shown that the low- ω_{loss} details of the FL feature are sensitive to opening of a small gap similar to the experimental observation on NdNiO_3 [15]. The present results show that the FL component of the RIXS spectra is rather material specific and its interpretation requires advanced many-body calculations.

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