

Resonant inelastic x-ray scattering investigation of Hund's and spin-orbit coupling in $5d^2$ double perovskites

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B site ordered $5d^2$ double perovskites ($A_2BB'O_6$, $B' = 5d^2$) display a remarkable range of physical properties upon variation of the chosen B and B' site ions. This sensitivity to chemical substitution reflects the delicate balance and profound impact of strong electronic correlation and spin-orbit coupling in such systems. We present rhenium L_2 and L_3 resonant inelastic x-ray scattering (RIXS) measurements of two such physically dissimilar materials, Mott-insulating Ba_2YReO_6 and semiconducting Sr_2CrReO_6 . Despite these differences, our RIXS results reveal similar energy scales of Hund's (J_H) and spin-orbit coupling (ζ) in the two materials, with both systems firmly in the intermediate Hund's coupling regime where $J_H/\zeta \sim 1$. However, there are clear differences in their RIXS spectra. The conductive character of Sr_2CrReO_6 broadens and obfuscates the atomic transitions within an electron-hole continuum, while the insulating character of Ba_2YReO_6 results in sharp atomic excitations. This contrast in their RIXS spectra despite their similar energy scales reflects a difference in the itinerancy-promoting hopping integral and illustrates the impact of the local crystal environment in double perovskites. Finally, L_2 and L_3 edge analyses of the atomic excitations in Ba_2YReO_6 reveal that the ordering of the low lying excited states is inverted compared to previous reports, such that the appropriate energy scales of Hund's and spin-orbit coupling are significantly modified. We present exact diagonalization calculations of the RIXS spectra at both edges which show good agreement with our results for new energy scales of $\zeta = 0.290(5)$ eV and $J_H = 0.38(2)$ eV [$J_H/\zeta = 1.30(5)$].

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I. INTRODUCTION

Fascination with unconventional materials that do not fit the conventional band theory of solids remains a core thread that connects condensed matter physics research past and present. These so-called strongly correlated materials typically possess partially filled electronic bands and thus would conventionally be expected to be standard metals, however, they defy this fate and instead develop unconventional metallic or even insulating properties due to strong electronic

correlations [1]. While these concepts are no longer new, correlated metals and Mott insulators still garner significant attention due to the plethora of material archetypes with novel physical properties that they contain. One example which has drawn extensive interest is the ordered double perovskites (DPs) of unit formula $A_2BB'O_6$, which have gained tremendous popularity as a highly customizable playground to realize exotic and diverse physical properties [2–4]. Key to this customizability is their crystal structure, which takes the standard ABO_3 perovskite structure and doubles its unit cell by replacing half of the B site transition metal (TM) ions with different B' TM ions. The resulting crystal structure features a checkerboard pattern of corner-sharing $B(B')O_6$ octahedra that surround alkali, alkaline-earth, or rare-earth A site ions, shown in Fig. 1(a). The choice of B , B' , and A site ions each has a profound impact on the resulting physical properties. In fact, the diversity of DPs is such that widely varied states emerge even within the subset where the A site is restricted to be a nonmagnetic alkaline-earth ion and the B' site to be a $5d^2$ ion. Indeed, this subset includes phases as differ-

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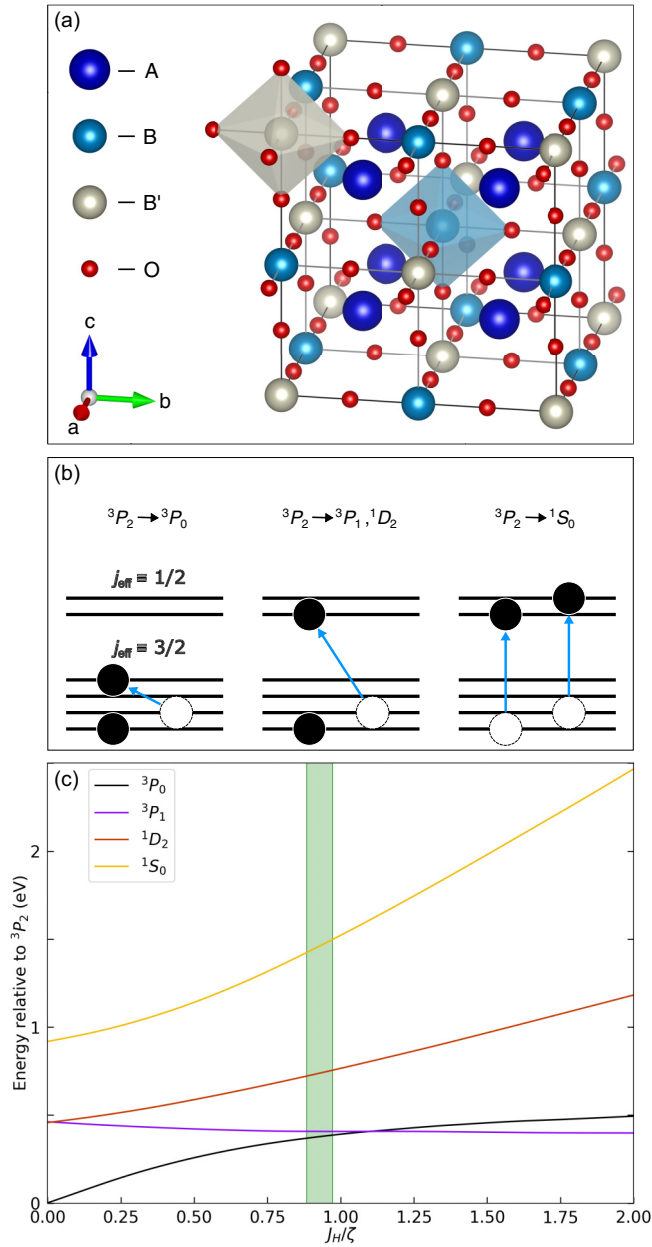


FIG. 1. (a) Ideal cubic crystal structure of the B site ordered double perovskites. (b) Schematic of $5d^2$ excitations from the single-particle perspective. (c) $5d^2$ excited state energy level diagram as a function of J_H for $\zeta = 0.29$ eV, calculated using exact diagonalization (see Sec. III C for details). The noninteracting limit is represented at $J_H/\zeta = 0$. The highlighted region corresponds to Yuan *et al.* chosen parameters for Ba_2YReO_6 [13].

ent as “hidden” multipolar-ordered Mott-insulating states, so dubbed because of their renowned difficulty to observe experimentally, and correlated high- T_c ferrimagnetic half-metals well suited for spintronic applications [4–10].

The first of these phases can be manifested when the B site possesses a closed electronic shell, leaving the B' site as the only electronically active ion. This arrangement quashes nearest neighbor (NN) hopping between B and B' sites, leaving only next-nearest neighbor (NNN) hopping between B' sites.

The NNN hopping occurs across $\sqrt{2}$ times the NN distance and is consequently much weaker, promoting Mott-insulating phases [4,10]. Within this Mott-insulating regime, then, we consider an atomic description of the electronic ground state and excited levels, starting from a $5d^1$ occupation following Refs. [3,4,8,9]. The first and largest energy scale we consider is the crystalline electric field (CEF) exerted by the ligand oxygens, which in the ideal case of a cubic crystal structure splits the tenfold degenerate $5d$ levels by an energy Δ into a lower energy t_{2g} sextet and higher energy e_g quartet. Working in the t_{2g} manifold, which possesses threefold orbital degeneracy, it is convenient to describe its constituent microstates as possessing an effective orbital angular momentum $l_{\text{eff}} = 1$. This l_{eff} description is subsequently converted to a j_{eff} description when spin-orbit coupling (SOC) is applied, splitting the t_{2g} sextet into a ground state quartet carrying effective total angular momentum $j_{\text{eff}} = 3/2$ and an excited state doublet with $j_{\text{eff}} = 1/2$. In the large CEF limit, these levels are separated by $3/2$ times the SOC strength ζ and are inverse-ordered to maximize j_{eff} as a result of a sign change incurred within the l_{eff} scheme. More generally, $t_{2g} - e_g$ mixing weakly splits the $j_{\text{eff}} = 3/2$ levels and increases the separation between the ground state and the $j_{\text{eff}} = 1/2$ doublet by $\frac{3}{2} \frac{\zeta^2}{\zeta/2 + \Delta}$ to $\frac{3}{2} \zeta (1 + \frac{\zeta}{\zeta/2 + \Delta}) = \frac{3}{2} \zeta_{\text{eff}}$, where Δ is the CEF strength [11]. Previous studies have often used schemes disregarding the e_g orbitals ($\Delta = \infty$) which consequently enforces $\zeta = \zeta_{\text{eff}}$ [12]. In the case of two electrons occupying the spin-orbit coupled $5d$ levels, the introduction of electronic correlation, in the form of the Hund’s coupling J_H , necessitates that we balance two limiting-case descriptions: (i) a noninteracting system with $J_H/\zeta = 0$ and (ii) a strongly interacting one with $J_H/\zeta \gg 1$.

We begin with the large SOC limit in which two one-electron states are combined after SOC is considered, which thus connects directly to the $5d^1$ description above. In the absence of Hund’s coupling, these states can be combined in three ways: a ground state manifold with both electrons in a $j_{\text{eff}} = 3/2$ state, an excited manifold at $3\zeta_{\text{eff}}/2$ above the ground state with one electron in a $j_{\text{eff}} = 3/2$ state and the second in a $j_{\text{eff}} = 1/2$ state, and an excited state at $3\zeta_{\text{eff}}$ above the ground state with both electrons in a $j_{\text{eff}} = 1/2$ state. These combinations are illustrated graphically as transitions from the ground state configuration in Fig. 1(b). The ground state manifold contains $\binom{4}{2} = 6$ states, five with total effective angular momentum $J_{\text{eff}} = 2$ and one with $J_{\text{eff}} = 0$, respectively described by the combined angular momentum terms symbols $^{2S+1}L_J = ^3P_2$ and 3P_0 . The first excited manifold contains $4 \times 2 = 8$ states, five with $J_{\text{eff}} = 2$ (1D_2) and three with $J_{\text{eff}} = 1$ (3P_1). The second excited manifold contains $\binom{2}{2} = 1$ state, which possesses $J_{\text{eff}} = 0$ (1S_0).

The second limit, with $J_H/\zeta \gg 1$, fittingly uses Hund’s rules to determine the electronic ground state. In order to impose dominance of Hund’s coupling over SOC while simultaneously requiring $J_H < \Delta$, we pick up from the pre-SOC one-electron $l_{\text{eff}} = 1$ description of the t_{2g} manifold. Within the t_{2g} manifold, Hund’s rules dictate that the two-electron ground state possesses $S = 1$ and $L_{\text{eff}} = 1$, and effective total angular momentum $J_{\text{eff}} = 2$ due to SOC, maximized as in the single-electron case. This ground state, the same 3P_2 manifold

as in the noninteracting scheme, is stabilized compared to the lowest excited states (the 3P_1 triplet and 3P_0 singlet) by SOC, and from the subsequent 1D_2 quintet and 1S_0 singlet and 1S_0 singlet excited states by Hund's coupling in combination with SOC. The evolution of the $5d^2$ levels between these extrema is shown in Fig. 1(c) as a function of J_H/ζ , which reveals that the 3P_2 manifold is stabilized as the unique ground state for any $J_H > 0$. The resulting 3P_2 ground state phase space is very rich, supporting novel multipolar ordered states, including reduced moment dipolar, quadrupolar, and octupolar orders [4,8,9]. Indeed, recent measurements have revealed that Ba_2YReO_6 orders magnetically below $T_m \sim 31$ K with a heavily reduced ordered moment of $<0.5 \mu_B$ and with strong indications of underlying quadrupolar order [14,15]. Moreover, the two transitions observed in the specific heat at $T_q \sim 37$ K and $T_m \sim 31$ K match theoretical predictions of a two-step quadrupolar-to-dipolar ordering transition [4,15,16]. Earlier work has sought to improve our understanding of these electronic ground state properties using resonant inelastic x-ray scattering (RIXS), establishing that Ba_2YReO_6 belongs in the intermediate Hund's coupling regime where $J_H/\zeta \sim 1$ [13,17].

The second aforementioned class of $5d^2$ DPs, the high- T_c ferrimagnetic half-metals, can be manifested in $3d$ - $5d$ ordered DPs where an electronically active $3d$ ion resides on the B site. Here, the $3d$ and $5d$ ions typically order magnetically well above room temperature, forming antiferromagnetically coupled ferromagnetic sublattices and leaving a remnant net moment (spin up by convention) due to a larger $3d$ ion magnetic moment [7]. Unfortunately, B/B' antisite disorder often significantly impacts their magnetic and electronic properties [18–21], making it difficult to reach a clear understanding. Therefore the synthesis of fully ordered $\text{Sr}_2\text{CrReO}_6$ thin films has rightly drawn attention and positioned $\text{Sr}_2\text{CrReO}_6$ as a model $3d$ – $5d$ DP system that can help us understand this class of materials more broadly [20,22,23].

In $\text{Sr}_2\text{CrReO}_6$, the B sites are occupied by $3d^3$ Cr ions and the B' sites by $5d^2$ Re ions respectively possessing $S = 3/2$ and $S = 1$ due to Hund's coupling. Given the antiferromagnetic coupling of the two moments, a net ferrimagnetic moment of $1 \mu_B$ is anticipated within the ionic picture. The half-metallicity of this archetype is also borne due to Hund's coupling, illustrated nicely in $\text{Sr}_2\text{CrReO}_6$ as follows [5,24]. Because the Cr site electron configuration is $3d^3$ and is also split into t_{2g} and e_g levels, the t_{2g} spin-up levels are completely filled and the lowest energy empty state is a spin down t_{2g} level. On the other hand, because the Re site configuration is $5d^2$, the spin-down levels are only partially filled and the lowest energy empty state is the remaining spin down t_{2g} level due to Hund's coupling. This means that the minority down spins may hop between Re and Cr sites and become itinerant while the majority up spins become localized on the Cr sites. Correlation effects thus induce near complete spin-polarization at the fermi level, such that this archetype of materials is highly promising for spintronic applications [5–7]. Experimentally, ferrimagnetic ordering in $\text{Sr}_2\text{CrReO}_6$ occurs below $T_c = 508$ K in fully ordered thin films with a saturated moment of $\sim 1.29 \mu_B$ [20]. This enhancement from the ionic picture prediction of $1 \mu_B$ has been attributed to the presence of strong SOC, which theoretically should lead to

a saturated moment of $1.28 \mu_B$ [25]. Supporting the notion of strong SOC in $\text{Sr}_2\text{CrReO}_6$, which further promotes Mott-insulating phases, updated measurements of fully ordered $\text{Sr}_2\text{CrReO}_6$ reveal that it is in fact a small band gap semiconductor rather than a true half-metal [20,25–27]. Moreover, recent RIXS measurements of $\text{Sr}_2\text{CrReO}_6$ reveal features believed to represent Hund's coupling spin-orbit excitations, pointing to both strong SOC and Hund's coupling [28].

In this paper, we present Re L_2 and L_3 edge RIXS measurements of $\text{Sr}_2\text{CrReO}_6$ and Ba_2YReO_6 that reveal intermediate Hund's coupling and strong SOC in both materials. Moreover, we use the contrast between L_2 and L_3 edge RIXS spectra to directly identify the SOC features in these materials by way of single-particle RIXS selection rules which forbid SOC excitations at the L_2 edge. Remarkably, the L_2 – L_3 edge contrast also reveals the crossover from a single-particle description to a many-body description as correlation effects partially relax this strict selection rule and SOC excitations appear, though significantly suppressed, at the L_2 edge. In Ba_2YReO_6 , this L_2 edge suppression of SOC features furthermore reveals that the order of the 3P_1 and 3P_0 levels is inverted relative to earlier parametrizations, necessitating a description with decreased SOC and increased Hund's coupling [13,17]. In order to refine the specific energy scales of the SOC and Hund's coupling we employed exact diagonalization methods to calculate the L_2 and L_3 edge RIXS spectra of Ba_2YReO_6 using the EDRIXS program. We report that values $\zeta = 0.290(5)$ eV and $J_H/\zeta = 1.30(5)$ ($J_H = 0.38(2)$ eV) successfully reproduce the energy scales and spectral weight characteristics of the L_2 and L_3 edge RIXS features in Ba_2YReO_6 . This newly refined value of ζ is more in line with that found in other Re-based Mott insulators [29–31]. Our measurements of Ba_2YReO_6 additionally reveal low energy features plausibly explained by the presence of a dynamic Jahn-Teller effect either in isolation or in conjunction with an e - h continuum. The presence of a dynamic Jahn-Teller effect could moreover help to explain the asymmetric, edge dependent lineshape of the atomic multiplet excitations [32]. In $\text{Sr}_2\text{CrReO}_6$, our measurements reveal the presence of previously unresolved excitations characteristic of intermediate Hund's coupling [28]. Moreover, we observe a strong e - h continuum at energy transfer under ~ 2.5 eV, which was also not discerned in previous studies and which may explain the low energy feature previously attributed to single-magnon excitations [28]. The e - h continuum also presents with no discernible gap, reflecting $\text{Sr}_2\text{CrReO}_6$'s small band gap nature and furthermore pointing to an indirect gap in line with resistivity estimates and much smaller than optical estimates of the direct gap [20]. Finally, a comparison of the RIXS spectra of Ba_2YReO_6 and $\text{Sr}_2\text{CrReO}_6$ reveals similar energy scales of Hund's coupling and SOC despite their respective Mott-insulating and semiconducting natures, reflecting the crucial role of B site substitution in $5d^2$ DPs.

II. EXPERIMENTAL DETAILS

Our experiments were performed with a high quality powder Ba_2YReO_6 sample and an unstrained 319 nm thick $\text{Sr}_2\text{CrReO}_6$ thin film sample grown on a SrTiO_3 substrate. The growth and characterization of Ba_2YReO_6 and $\text{Sr}_2\text{CrReO}_6$ have been previously reported [16,20].

RIXS measurements were conducted at the Advanced Photon Source at the 27-ID-B beamline. The experiments were performed at the Re L_2 and L_3 x-ray absorption edges ($2p_{1/2} \rightarrow 5d$, $E_i = 11.960$ keV and $2p_{3/2} \rightarrow 5d$, $E_i = 10.531$ keV, respectively). The incident optics consist of a high heat load monochromator and a high resolution monochromator used to select the incident photon energy as well as a set of focusing optics to focus the beam at the sample surface. The high heat load monochromator is a two-bounce diamond (111) crystal monochromator, while the high resolution monochromator is a four-bounce Si crystal monochromator with variable reflection condition. The four-bounce arrangement is chosen so that the beam position does not change with a change in incident energy. The experiment utilized the Si(440) reflection condition of the high resolution monochromator. The incident energy was calibrated by measuring the total fluorescence yield x-ray absorption (TFY-XAS) of the powder Ba_2YReO_6 sample using a pin diode and setting the inflection point of the absorption to a reference value.

The receiving optics are arranged in the typical Rowland circle geometry to discriminate between emitted photon energies, with a diced, spherically-bent crystal analyzer of bending radius 2 m and a Spectrum Lambda60k two-dimensional pixelated strip detector. The crystal analyzer used for the Re L_3 edge measurements had a Si(119) reflection condition, while the one used at the Re L_2 edge had a Si(773) condition.

In order to minimize the elastic background due to Thomson scattering, the experiments were conducted with horizontally polarized light in a horizontal four-circle geometry (ensuring polarization $\pi \rightarrow \pi', \sigma'$) with 2θ close to 90° . The total energy resolution was ~ 95 meV (FWHM) at the Re L_2 edge and ~ 65 meV at the Re L_3 edge. A closed cycle cryostat was used for temperature control. The $\text{Sr}_2\text{CrReO}_6$ sample was aligned with the (HHL) crystallographic plane in the scattering plane. Because the thickness of the thin-film $\text{Sr}_2\text{CrReO}_6$ sample is significantly less than the x-ray penetration depth, measurements were conducted at grazing incidence ($\theta = 1^\circ$) to increase the sample volume probed. This helps maximize the RIXS signal to noise ratio.

III. Ba_2YReO_6 RESULTS

A. General features

RIXS maps of excitations in Ba_2YReO_6 up to 2.5 eV in energy transfer (E_t) are shown in Fig. 2. The Re L_2 and L_3 edge RIXS maps were measured at a temperature of $T = 18$ K. Limited measurements as a function of temperature at the Re L_2 edge do not show significant temperature dependence, see Supplemental Material Ref. [33] (see also Refs. [34,35] therein). The two RIXS maps display the same primary features in addition to the elastic line: two strong features at ~ 0.5 and ~ 0.9 eV and a third, weaker feature at ~ 2 eV. The Re L_2 data have higher statistics but the features are also visually broader than their Re L_3 counterparts due to the coarser resolution. The sub 1 eV features resonate at an incident photon energy of 10.532–10.533 keV at the Re L_3 edge and at 11.961 keV at the Re L_2 edge. In comparison, the 2 eV feature resonates at a slightly higher incident photon

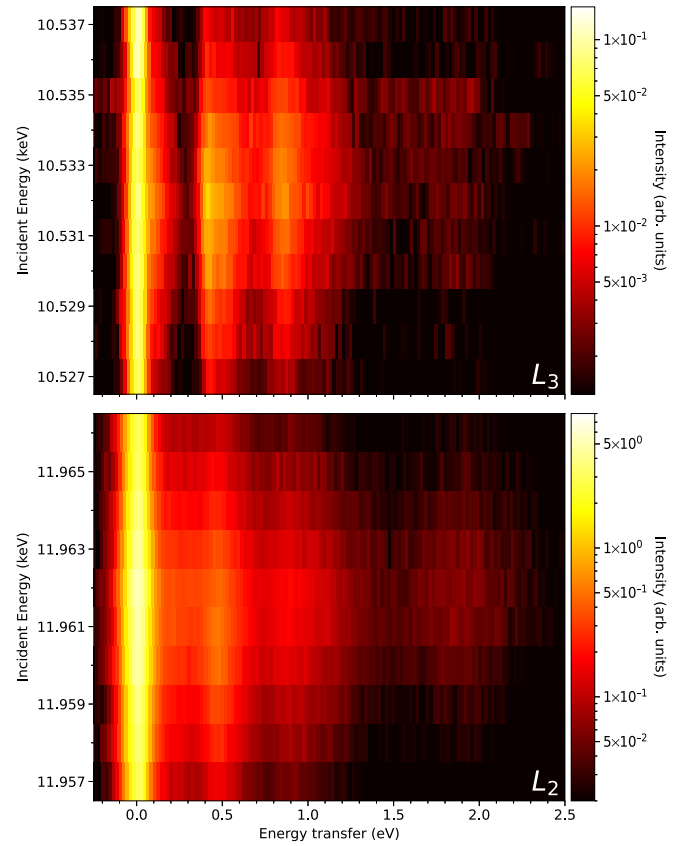


FIG. 2. Top (bottom) Ba_2YReO_6 Re L_3 (L_2) edge RIXS map with E_i up to 2.5 eV collected at $T = 18$ K.

energy of 11.962 keV at the Re L_2 edge, however this trend is unfortunately not distinguishable at the Re L_3 edge due to the poorer statistics. The higher incident energy resonance of the excitation indicates that the feature represents a dd excitation, i.e. an excitation in which the incident photon promotes a core electron to an excited $5d$ state and a ground state electron de-excites to annihilate the induced core-hole. The end result is the transition of an electron from the ground state to an excited $5d$ state, and this process resonates at an incident photon energy that increases linearly with the energy of the excited state. Thus, a 2 eV dd excitation will resonate at an E_i 1 eV above the resonance of a 1 eV dd excitation, precisely as we have observed. The energy scale of the features and identification of these features as dd excitations generally agrees with prior Re L_2 and L_3 edge RIXS measurements and theory of Ba_2YReO_6 shown in Fig. 1(c) [13,17]. These theoretical calculations identified the 0.5 eV feature as a doublet excitation composed of one sub-level (3P_0) primarily reflective of the Hund's coupling J_H and a second sub-level (3P_1) primarily reflective of the SOC ζ , shown schematically in Fig. 1(b). Meanwhile, the 0.9 eV feature was theorized to reflect J_H and ζ combined. Finally, the 2 eV feature was identified as a 'two-particle' SOC excitation to the 1S_0 level of nominal energy $3\zeta_{\text{eff}}$ which increases with J_H . This excitation to the 1S_0 level is dubbed a "two-particle" excitation because it corresponds to an excitation of two electrons from the $j_{\text{eff}} = 3/2$ manifold to the $j_{\text{eff}} = 1/2$ doublet from a single-particle perspective, though it is more accurately described as occurring due to

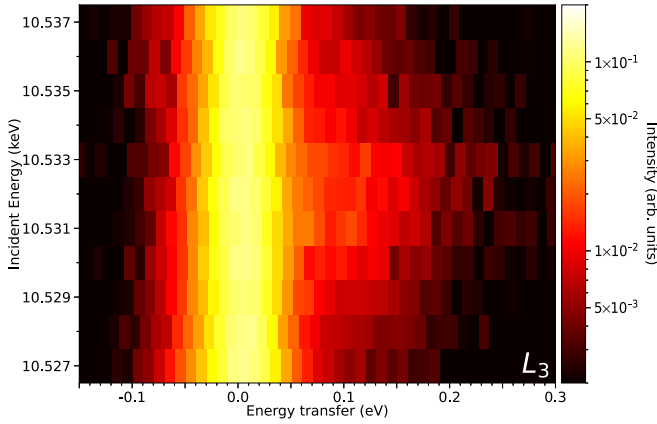


FIG. 3. Re L_3 edge RIXS map of Ba_2YReO_6 with E_i up to 0.3 eV obtained at $T = 18$ K.

correlation-driven mixing of the $j_{\text{eff}} = 3/2$ and $j_{\text{eff}} = 1/2$ levels in the multiparticle regime with $J_H > 0$ [13,17]. The low spectral weight of the 2 eV feature is also in agreement with prior results and theory, which predicts the intensity of the “two-particle” excitations to be suppressed compared to the single-particle excitations [13,17].

Besides these three primary features, and not as obvious in Fig. 2, is a resonant low energy excitation that presents as a shoulder in the quasielastic line at both edges, which was not resolved in the aforementioned prior measurements. In order to better resolve this low energy feature, we collected a RIXS map of the quasielastic region at the Re L_3 edge at $T = 18$ K, shown in Fig. 3. The increased detail of this RIXS map clearly shows the presence of a resonant low energy excitation that extends up to E_i of ~ 0.25 eV. The maximum of resonance occurs at an incident photon energy of $E_i \sim 10.532$ – 10.533 keV, matching the excitations at 0.5 eV and 0.9 eV, indicating that this feature either represents a low energy dd excitation, implying a splitting of the $J_{\text{eff}} = 2$ ground state, or represents some low energy non- dd excitation of the ground state. The possible origins of this feature are discussed at greater length in Sec. V.

B. L_2 and L_3 edge comparison

In order to gain a better understanding of the excitations in Ba_2YReO_6 we compare the Re L_2 and L_3 edge spectra obtained at resonance ($E_i = 11.961$ and 10.533 keV), shown in Fig. 4 normalized by the 0.5 eV feature maximum. Normalization by the 0.5 eV feature is done for easier comparison as the 0.5 eV and 0.9 eV features are much weaker relative to the elastic line at the L_2 edge, a phenomenon which relates to the overall differences between L_2 and L_3 edges which will be discussed shortly. This closer comparison of the Re L_2 and L_3 edge spectra reveals notable differences in the spectra even after the overall scale difference is accounted for.

The first and most stark difference is a shift in the maximum of the first feature, with the Re L_3 data peaked around 0.41 eV and the Re L_2 data peaked around 0.47 eV. This difference becomes more remarkable when we analyze the physical meaning of the excitations in the spectra. As discussed in Sec. I, the $5d^2$ ground state for intermediate Hund’s coupling

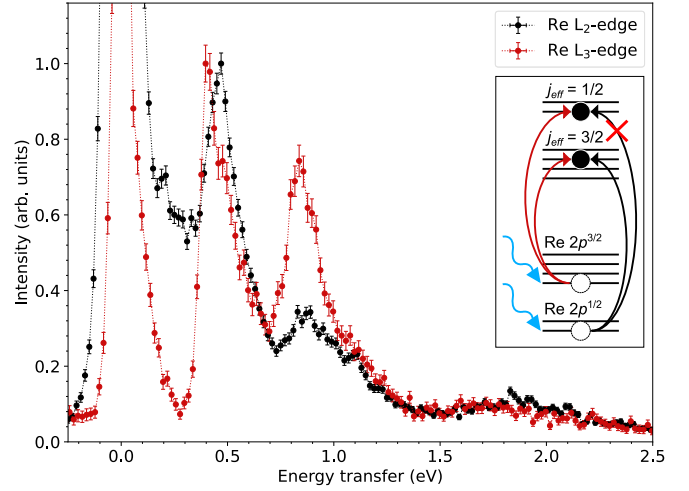


FIG. 4. Ba_2YReO_6 RIXS spectra at the Re $L_2(L_3)$ edge resonances up to 2.5 eV in E_i collected at $T = 18$ K and $E_i = 11.961(10.533)$ keV. The RIXS spectra are normalized by the maximum intensity of the 0.5 eV feature. The right inset schematically shows the allowed and forbidden single-particle RIXS transitions at the L_2 and L_3 edges.

is the fivefold degenerate 3P_2 manifold, which is stabilized compared to the 3P_1 , 3P_0 , 1D_2 , and 1S_0 excited levels by a combination of Hund’s coupling and SOC. The energy levels of these excited states relative to the ground state depends on both ζ and J_H/ζ as shown in Fig. 1(c). The levels evolve fairly smoothly and with preserved hierarchy as a function of J_H/ζ , with the notable exception being the 3P_1 and 3P_0 levels. These states approach each other, forming the doublet peak observed by Yuan et al., and ultimately cross around $J_H/\zeta = 1.1$ before the 3P_0 state further elevates in the large J_H limit. Yuan et al. modelled the spectra using a Kanamori parametrization restricted to the t_{2g} levels, such that $\Delta = \infty$ and $\zeta = \zeta_{\text{eff}}$, and conclude the Kanamori J_H^{eff} ($\sim 5/7J_H$) to be 0.26 eV and the t_{2g} ζ_{eff} to be 0.38 eV [12]. Within a full d level parametrization with a physical CEF strength of $\Delta \sim 4.5$ eV these values become $J_H \sim 0.34$ eV and $\zeta \sim 0.35$ eV, giving a ratio of $J_H/\zeta \sim 0.95$, that places the 3P_0 level below the 3P_1 level as highlighted in Fig. 1(c). The differences in the L_2 and L_3 edge spectra, however, tell a different story when L_2 and L_3 edge selection rules are considered. As discussed in Sec. I and as illustrated in Fig. 1(b), from a single-particle perspective a transition to the 3P_1 level corresponds to promoting one electron from the $j_{\text{eff}} = 3/2$ level to the $j_{\text{eff}} = 1/2$ level, which is derived from $J = 5/2$ as illustrated in the study of iridates [36,37]. Thus, the atomic $j_{\text{eff}} = 1/2$ level cannot be probed at the L_2 edge since this would require a dipole forbidden transition with $\Delta J = 2$ ($2p_{1/2} \rightarrow 5d_{5/2}$), shown schematically in the inset of Fig. 4. While the strict selection rule is relaxed by the introduction of Hund’s coupling, we nevertheless anticipate this transition to be suppressed at the L_2 edge. Thus, if the 3P_0 state were to lie lower in energy than the 3P_1 manifold we would expect the L_2 RIXS spectrum to have a lower spectral weight in the high energy region of the doublet feature, whereas the opposite trend is clearly observed. It stands to reason then that the spectral differences

between the L_2 and L_3 edges inform us that the 3P_1 manifold lies below the 3P_0 state, i.e., $J_H/\zeta \gtrsim 1.1$ based on Fig. 1(c). Moreover, this increase in J_H necessitates a decrease in ζ from 0.35 eV to maintain the overall excited state energy levels, which would in fact put it more in line with other Re-based Mott insulators that display $\zeta \sim 0.3$ eV [29–31].

With the edge dependence trend of the doublet feature explained, we now apply this single-particle selection rule lens to other differences between the L_2 and L_3 edge spectra. To this end we start with the aforementioned question of overall scale, i.e., why the L_2 edge features are so much weaker relative to the elastic. This follows easily using the same argument as for the 3P_1 manifold: both the 0.9 eV transition to the 1D_2 level and 1.8 eV (refined from the rough estimate of 2 eV from the RIXS map) transition to the 1S_0 level involve the L_2 -forbidden single-particle $j_{\text{eff}} = 1/2$ state, and will thus also be suppressed compared to the L_3 edge. Next, we turn to the suppression of the 0.9 eV feature at the L_2 edge beyond the overall scale factor. Its suppression compared to the 0.5 eV feature can be naturally explained: whereas the 0.5 eV feature contains the L_2 -allowed 3P_0 sublevel, the 0.9 eV feature is only composed of the L_2 -forbidden 1D_2 level and should therefore be more suppressed compared to the doublet 0.5 eV feature. On the other hand, its suppression compared to the 1.8 eV 1S_0 feature is less easy to reconcile, given that it is also solely composed of L_2 suppressed transitions. Speculatively, the answer may lie in the fact that the 1S_0 transition is, as aforementioned, a “two-particle” excitation mediated by correlation effects, weakening the validity of edge-based selection rules taken from the single-particle picture. Indeed, the “two-particle” excitation nature of the 1S_0 feature appears to be manifest in the fact that it is much broader than the single-particle excitation features, which we interpret as lifetime broadening that indicates the unstable nature of the “two-particle” excitation in the final state. Overall, then, the application of single-particle selection rules does an impressive job in explaining the $L_2 - L_3$ edge discrepancies of the atomic dd excitations within the standard $J_{\text{eff}} = 2$ ground state theory. While this general description indeed fits our results, we are interested to provide a more quantitative one below.

C. RIXS calculations

In order to quantitatively estimate the energy scales of J_H and ζ , we calculate the Re L_2 and L_3 edge RIXS spectra of Ba_2YReO_6 with exact diagonalization computational methods using the EDRIXS program [38]. In order to refine appropriate values of J_H and ζ , we calculated the RIXS spectra of a $5d^2$ ion at both Re L_3 and L_2 edges for variable $\zeta \in [0.25, 0.33]$ eV and $J_H/\zeta \in [0, 2]$, and fixed $\Delta = 4.5$ eV (see Sec. IV A, Ref. [13]). The calculated spectra were measured against the experimental spectra, resulting in optimized values of $\zeta = 0.290(5)$ eV and $J_H/\zeta = 1.30(5)$. The optimization process and other details of the EDRIXS calculations are discussed in Ref. [33].

The calculated RIXS spectra with $\zeta = 0.29$ eV are shown in heatmap form as a function of J_H/ζ and E_t in Fig. 5 with intensity corresponding to the RIXS signal. The spectra are only moderately broadened to 15 meV FWHM to more clearly show the sublevels of the $^3P_0 + ^3P_1$ doublet feature. Figure 5

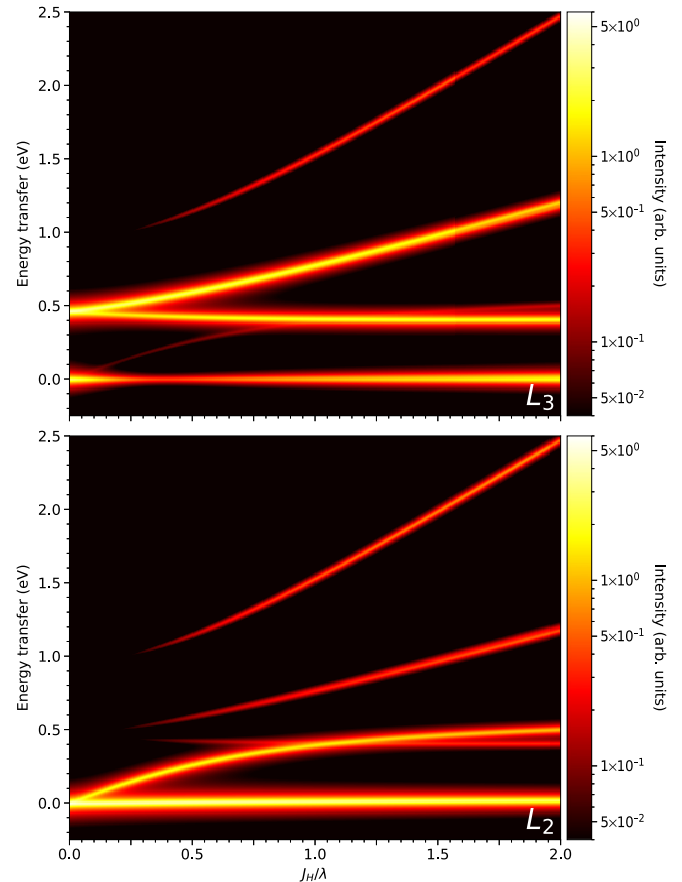


FIG. 5. Top (bottom) EDRIXS calculated Re L_3 (L_2) edge RIXS heatmap of a $5d^2$ system as a function of J_H/ζ and E_t . The heatmaps are calculated for fixed $\zeta = 0.29$ eV at a temperature $T = 18$ K.

clearly replicates the Hund’s coupling dependent trends of the atomic energy levels shown in Fig. 1(c) with added information of the edge-dependent RIXS signal intensity. The intensity profile of the spectra reflect and substantiate several key points discussed in Sec. III B. First, we observe that at both edges the intensity of the “two-particle” 1S_0 excitation disappears in the noninteracting limit of $J_H/\zeta = 0$ as anticipated. Next, we see that the 3P_1 and 1D_2 SOC excitations also vanish in this limit at the L_2 edge in correspondence with the aforementioned selection rule in the noninteracting case. Finally, we observe that this selection rule is gradually relaxed as a function of J_H/ζ but that these excitations remain suppressed at the L_2 edge compared to the L_3 edge, reflecting a smooth crossover from single-particle to many-body physics. Correspondingly, the calculation also corroborates our earlier speculation that the ~ 0.5 eV doublet would be spectrally biased to higher energy at the Re L_3 edge for $J_H/\zeta \lesssim 1.1$ and at the Re L_2 edge for $J_H/\zeta \gtrsim 1.1$. This is reflected in the optimized value of $J_H/\zeta = 1.30(5)$, for which we show the RIXS spectra in Fig. 6.

The optimized spectra shown in Fig. 6 are normalized by the $^3P_0 + ^3P_1$ doublet intensity and are broadened to the instrumental resolutions, with the exception of the 1S_0 excitation. Since this excitation has a “two-particle” origin in the single particle picture, we expect that it may be unstable (more so than other dd excitations), showing the lifetime broadening

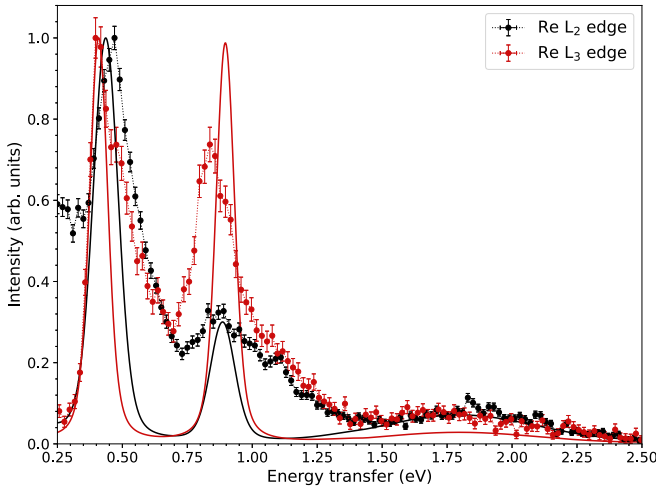


FIG. 6. Experimental and EDRIXS calculated Re L_3 (red) and L_2 (black) edge RIXS spectra of Ba_2YReO_6 at $T = 18$ K. The spectra are calculated with the optimized values of $J_H/\zeta = 1.30$ and $\zeta = 0.290$ eV.

effect. Figure 6 reveals a good overall agreement between the EDRIXS calculations and the experimental spectra both in terms of the energy levels of the excitations and their relative intensities at each edge. In particular, the calculated spectra reproduce the shifting of the $^3P_0 + ^3P_1$ doublet to higher energy from the L_3 to L_2 edge, the greater suppression of the 1D_2 excitation at the L_2 edge compared to the other two features, and the low intensity of the 1S_0 excitation at both edges. Despite this broad agreement, we take note of the fact that the shifting of the $^3P_0 + ^3P_1$ doublet is underestimated for this value of J_H/ζ and that the 1D_2 excitation energy is slightly overestimated. These characteristics are not independent and reflect a balance that must be struck to achieve the greatest overall agreement, where the shifting of the doublet can be matched by increasing J_H/ζ but at the direct cost of further overestimating the energy of the 1D_2 transition and additionally overestimating the energy of the 1S_0 transition. The reason for this slight quantitative deviation from the experimental results is not well understood, but could for instance be caused by the energy-level-shifting vibronic coupling effects seen in several related Re-based DPs and whose suspected presence in Ba_2YReO_6 is further discussed in Sec. V [29,30,32]. Overall, the atomic EDRIXS calculations do a good job in qualitatively and quantitatively replicating the RIXS spectra of Ba_2YReO_6 and, moreover, demonstrate the applicability of our preceding single-particle selection-rule based analysis.

IV. $\text{Sr}_2\text{CrReO}_6$ RESULTS

A. High energy features

A RIXS map of the $\text{Sr}_2\text{CrReO}_6$ excitations up to 11 eV was measured at the Re L_2 edge at $T = 300$ K, shown in Fig. 7. Three broad features are observed in Fig. 7: a continuum extending from the elastic line up to ~ 2.5 eV in E_i , a feature centered at ~ 4.5 eV in E_i , and a feature centered at ~ 8 eV in E_i . The first of the features resonates at $E_i = 11.961$ keV and appears to decrease monotonically in intensity with E_i . The resonance energy of this feature and its extended na-

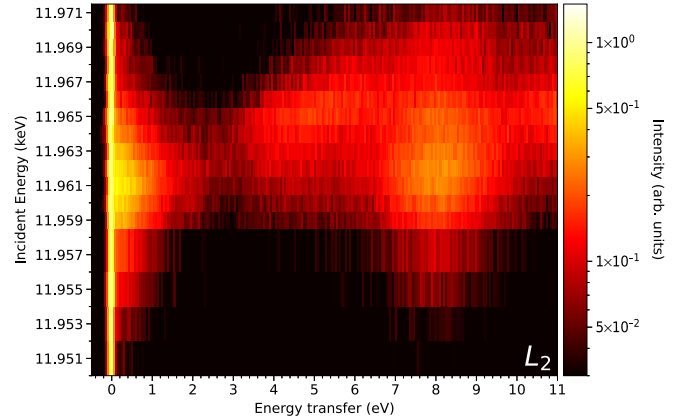


FIG. 7. $\text{Sr}_2\text{CrReO}_6$ Re L_2 edge RIXS map up to 11 eV in E_i . The spectra were collected at $T = 300$ K and are normalized by the elastic line.

ture likely indicate that it corresponds to excitations to the conduction levels directly above the ground state, i.e., into the electron-hole ($e-h$) continuum. Indeed, similar excitations were previously observed and so-diagnosed in the related $3d-5d$ DPs $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ [13]. The breadth of the feature may therefore give an rough measure of the conduction band width and points to a small or nonexistent band gap, both in line with the small band gap semiconducting nature of $\text{Sr}_2\text{CrReO}_6$. The second of the aforementioned features resonates at a higher incident photon energy of $E_i = 11.965-11.966$ keV, marking it as dd excitation as described in Sec. III A. The energy of the excitation further identifies it as the transition between the t_{2g} ground state and e_g excited states, whose nominal energy $\Delta \sim 4.5$ eV defines the ligand CEF strength. Contrastingly, the third feature resonates at the same incident photon energy as the low energy $e-h$ continuum, marking it instead as charge-transfer excitations from the ligand oxygens rather than a dd excitation. Charge-transfer excitations refer to the process in which hybridized Re-O states (O $2p$ states in the atomic picture) de-excite to annihilate the Re site core-hole during the RIXS process. The lowest energy charge-transfer excitations share the same t_{2g}^3 intermediate state as the lowest energy dd excitations and $e-h$ continuum, causing them to resonate at the same incident photon energy; however, they occur at a larger energy transfer because the $t_{2g}^3\bar{L}$ final state featuring a ligand hole is more energetic than the corresponding t_{2g}^2 dd excitation/ $e-h$ continuum final state. A hint of a fourth feature is also visible above 10 eV in E_i and extending beyond the limit of 11 eV. The feature appears to resonate at the same energy as the e_g feature, marking it as a charge-transfer + crystal field excitation in which an electron is excited to an empty e_g state and a ligand oxygen electron de-excites to annihilate the core hole.

B. Low energy features

RIXS maps of the low energy continuum in $\text{Sr}_2\text{CrReO}_6$ were measured with greater point density at the Re L_2 and L_3 edges at $T = 300$ K, shown in Fig. 8. The RIXS maps in Fig. 8 both show the aforementioned continuum, however,

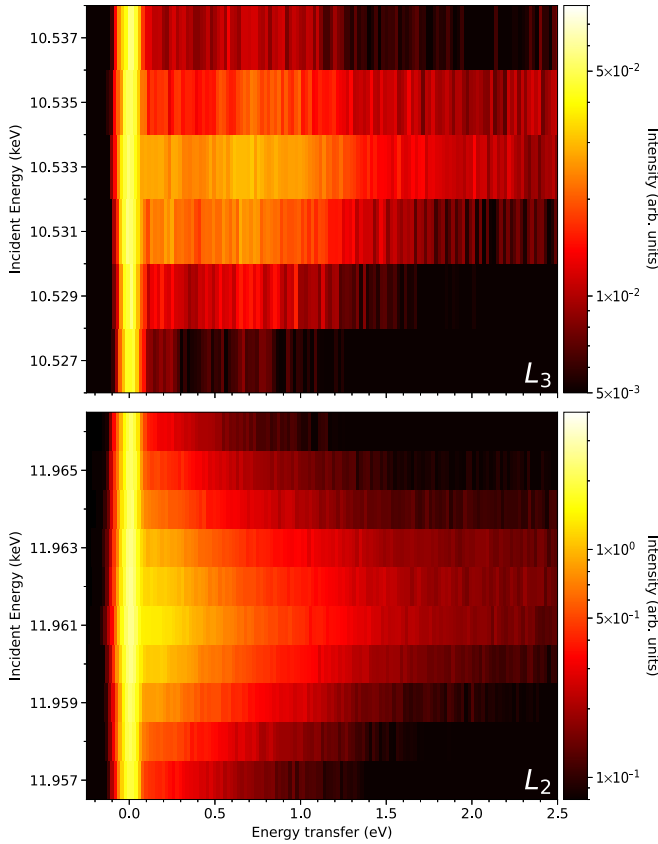


FIG. 8. Top (bottom) $\text{Sr}_2\text{CrReO}_6$ Re $L_3(L_2)$ edge RIXS map up to 2.5 eV in E_t . The data were collected at $T = 300$ K.

there is a clear discrepancy between L_2 and L_3 edges. The L_3 RIXS map clearly shows the presence of a broad feature between ~ 0.5 and 1.25 eV not observed at the L_2 edge. This is seen more easily and in more detail when viewing the line scan cuts at resonance ($E_i = 11.961$ and 10.533 keV), shown in Fig. 9. Moving on now to focus on the broad L_3 edge feature, we note that the energy range of the feature roughly matches that of the spin-orbit excitations in Ba_2YReO_6 , which leads us to believe it shares the same origin, though broadened due to the itinerant nature of $\text{Sr}_2\text{CrReO}_6$ at $T = 300$ K. Besides the matching energy scale, the suppression of the feature at the L_2 edge mirrors that in Ba_2YReO_6 and agrees with its interpretation as spin-orbit coupling excitations involving the L_2 -forbidden single-particle $j_{\text{eff}} = 1/2$ level. This interpretation of the broad L_3 feature as spin-orbit excitations also agrees with Marcaud et al. recently published L_3 edge RIXS measurements of $\text{Sr}_2\text{CrReO}_6$ [28]. What's more, Marcaud et al. measurements of $\text{Sr}_2\text{CrReO}_6$ reveal two peaks at ~ 0.65 eV and 1 eV which are ascribed to Hund's coupled spin-orbit excitations, placing $\text{Sr}_2\text{CrReO}_6$ in the intermediate Hund's coupling regime along with Ba_2YReO_6 . Upon closer inspection, the broad SOC feature in our measurements of unstrained thin film $\text{Sr}_2\text{CrReO}_6$ is slightly peaked around these energies, suggesting the feature may possess the same underlying doublet structure.

In order to better analyze the SOC feature, we fitted and subtracted off the e - h continuum from the overall spectrum, shown in the zoomed inset of Fig. 9. Because the dd exci-

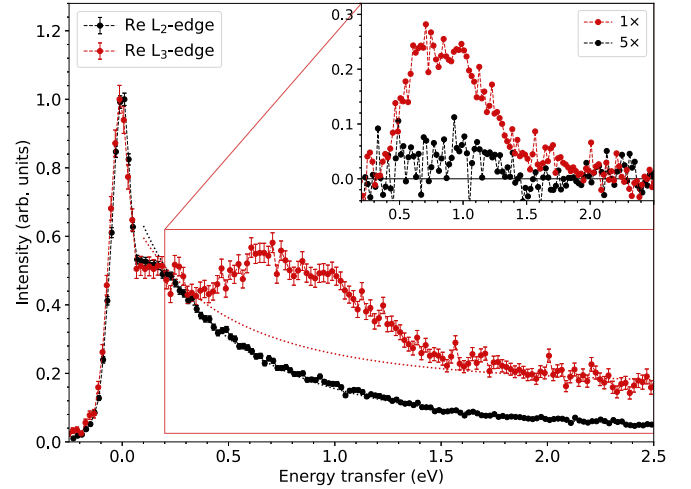


FIG. 9. $\text{Sr}_2\text{CrReO}_6$ RIXS spectra at the Re $L_2(L_3)$ edge resonance of $E_i = 11.961(10.533)$ keV up to 2.5 eV E_t . The data are overlaid with the L_2 and L_3 edge decaying power law fits of the e - h continuum, respectively indicated by the black and red dashed lines. The zoomed inset shows the spectra with the e - h continuum background subtracted. The data were collected at $T = 300$ K and are normalized by the elastic line intensity for greater comparability.

tations are suppressed at the L_2 edge, we used this dataset to fit the e - h continuum using an empirical decaying power law $f(x) = (x - x_0)^b + c$, yielding $b \sim -2.65$, $x_0 \sim -1$ eV. These parameters were then kept fixed when fitting the L_3 edge e - h continuum, with only a constant background term and an overall scale term fitted. The continuum subtracted results more clearly show that the L_3 edge spectrum appears to possess two SOC peaks at ~ 0.65 and 1 eV, and furthermore reveal a third, weaker peak around 1.8 eV not reported by Marcaud et al. Considering the low intensity of this third peak and its similar energy scale, we associate this feature with a “two-particle” excitation to the 1S_0 level as in Ba_2YReO_6 . As described in our discussion of Ba_2YReO_6 , this third feature naturally appears in the intermediate Hund's coupling regime, confirming this same description is accurate for $\text{Sr}_2\text{CrReO}_6$. Moreover, whereas the raw L_2 edge RIXS spectrum shows no apparent trace of the SOC features, the continuum subtracted spectrum appears to show a small bump in the region of the SOC features, suggesting that the excitations do not entirely disappear but are instead highly suppressed. As discussed in Sec. III B, the fact that the SOC excitations do not disappear at the L_2 edge is again owed to the presence of Hund's coupling, which relaxes the strict single-particle L_2 edge selection rule. While we can confidently state that $\text{Sr}_2\text{CrReO}_6$ possesses strong SOC and intermediate Hund's coupling, the breadth of the features and weak L_2 signature makes it impossible to untangle their individual scales and discern whether $\text{Sr}_2\text{CrReO}_6$ should possess $J_H/\zeta < 1$ as reported by Marcaud et al. or whether it should also possess $J_H/\zeta > 1$ as we have shown for Ba_2YReO_6 [28].

V. DISCUSSION

Moving on from the preceding atomic theory analyses, we now discuss the possible origins of the features unaccounted

for within this theory, beginning with the low energy feature in Ba_2YReO_6 . As discussed in Sec. III A, the resonance profile of this feature indicates that it either corresponds to a low energy dd excitation or to a low energy non- dd excitation. The first case implies a splitting of the $J_{\text{eff}} = 2$ ground state, which agrees with theoretical works that propose a splitting δ of the ground state due to either (a) the aforementioned $t_{2g} - e_g$ mixing effects or (b) nonspherical Coulomb interactions allowed within an octahedral local environment [8,9,39]. Moreover, this splitting scheme theoretically helps to stabilize the recently reported charge-quadrupole and magnetic-dipole ordered states in Ba_2YReO_6 [14,15]. On the other hand, δ is not anticipated to be large enough to account for the extent of the feature up to 250 meV in Fig. 3. Some estimates put δ at up to ~ 50 meV, while our RIXS calculations incorporating only the $t_{2g} - e_g$ mixing aspect show a splitting of only ~ 15 meV, see Refs. [9,15,33].

Moving on to the second case of a low energy non- dd excitation, one notable possibility due to visual similarity is that the feature represents ground state Jahn-Teller active phonon excitations (vibronic excitations) as seen in the $5d^1$ A_2MgReO_6 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) DPs [29]. Indeed, $5d^2$ DPs such as Ba_2YReO_6 are theorized to also be subject to this so-called dynamic Jahn-Teller effect, and their RIXS spectra are expected to display a series of low energy excitations fitting the appearance of this feature [32]. Beyond a theoretical possibility, recent O K edge RIXS measurements of the Os-based $5d^2$ DP $\text{Ba}_2\text{CaOsO}_6$ clearly show a low energy phonon sideband fitting a dynamic Jahn-Teller description [32,40]. Moreover, the feature could potentially be explained as a combination of the prior two options, i.e., the feature corresponds to a dd excitation across δ dressed by vibronic modes akin to the dressed SOC excitations seen in the aforementioned A_2MgReO_6 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) DPs. In this case, the dressed excitation would extend to a significantly higher energy and could easily reconcile the theorized energy scale of δ with that of the feature observed here.

In order to further elucidate the origin of the feature we scrutinize the edge-dependence of the feature shown in Fig. 4, which reveals that the low energy region is significantly enhanced at the L_2 edge and appears to possess a different lineshape than at the L_3 edge. We first note that this enhancement is not an illusory result of our normalization scheme and persists, though less dramatic, when the data are instead normalized by the elastic line, see Ref. [33]. As for the apparent difference in lineshape between the two edges, we perform an elastic background subtraction to gain further insight, shown in Fig. 10. While the background subtracted spectra at both edges show a rise in inelastic intensity of a similar scale that begins around 100 meV, the feature at the L_2 edge extends continuously to the 3P_1 feature and does not decay unlike the feature at the L_3 edge. The lineshape at the L_2 edge is moreover reminiscent of the continuum in $\text{Sr}_2\text{CrReO}_6$, and a fit to the same form of decaying power law appears to isolate the atomic features well, shown in the upper right inset of Fig. 10. The exact origin of this continuum is unclear; it may reflect an e - h continuum as in $\text{Sr}_2\text{CrReO}_6$, or else could represent multi phonon processes as in a dynamic Jahn-Teller effect. The former explanation is somewhat at odds with the supposedly insulating character of Ba_2YReO_6 according to

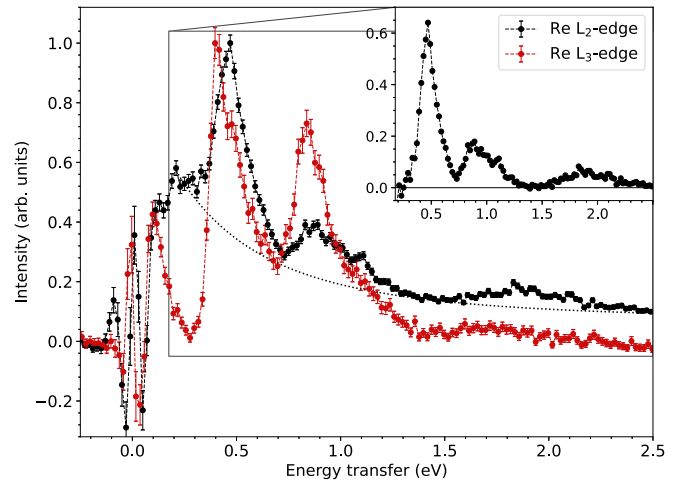


FIG. 10. Ba_2YReO_6 RIXS spectra at the Re $L_2(L_3)$ edge resonance of $E_i = 11.961(10.533)$ keV up to 2.5 eV E_t with the elastic line subtracted. The data are overlaid with an L_2 edge decaying power law fit of the continuum background. The zoomed inset shows the L_2 spectrum with the continuum background subtracted.

first principle calculations [41]; however, we note that there is no experimental report of insulating behavior for Ba_2YReO_6 . We also note that the insulating nature of Ba_2YReO_6 may be manifest in the fact that the continuum is much less prominent than in semiconducting $\text{Sr}_2\text{CrReO}_6$. Unfortunately, both of these explanations also appear to be consistent with the observed edge dependence, making it difficult to draw any decisive conclusions. In the case of an e - h continuum, we observed similar edge dependence in $\text{Sr}_2\text{CrReO}_6$ where the continuum was much stronger at the L_2 edge due to the partial suppression of the atomic features. In the case of multi phonon excitations, recently presented theory results have also shown an enhancement of low energy vibronic excitations at the L_2 edge compared to the L_3 edge [42]. Due to the lack of clarity as to the nature of the continuum, it is also unclear whether the continuum and the low energy feature at the L_3 edge share the same origin, raising the possibility that there are two separate contributions to the low energy lineshape.

Besides its potential applicability to the low energy features, the presence of a dynamic Jahn-Teller effect may also explain some of the as-of-yet unaddressed quirks of our spectra that deviate from the theory to date. In particular, both the 0.5 eV and 0.9 eV features appear distinctly asymmetric with additional spectral weight in the high energy region of the features reminiscent of the SOC excitations in the A_2MgReO_6 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) $5d^1$ DPs well described by vibronic coupling [29]. Cementing this notion, vibronic theory for $5d^2$ DPs indeed predicts that such phonon sidebands should dress both the 0.5 eV and 0.9 eV features [32]. Additionally, we observe that the 0.9 eV feature is not only enhanced between L_2 and L_3 edges, but also changes in lineshape. While the enhancement is understood, the change in lineshape does not mesh well with its explanation as a single dd transition. Conversely, if the high energy region instead corresponds to a phonon sideband then the change in lineshape can be explained by edge dependence of the

vibronic excitations. Thus, to summarize, the RIXS spectra of Ba_2YReO_6 and their edge dependence are well described by an atomic multiplet theory with $\zeta = 0.290(5)$ eV and $J_H/\zeta = 1.30(5)$ and by the presence of a dynamic Jahn-Teller effect possibly supplemented by an e - h continuum.

Now shifting our focus to $\text{Sr}_2\text{CrReO}_6$ and its deviation from the atomic theory, we expand on our preliminary discussion of the e - h continuum with the additional detail provided by the line scans in Fig. 9. This additional detail immediately reveals the presence of a low energy shoulder between the elastic region and ~ 200 – 300 meV which does not follow the otherwise smooth trend of the e - h continuum. Notably, this feature is mirrored in Re L_2 edge RIXS measurements of the related $3d$ - $5d$ high- T_c ferrimagnets $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, leading us to believe that the feature may simply indicated to the beginning of the e - h continuum [13]. Moreover, in comparison to the spectra of $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, we note that the L_2 edge continuum is far more similar to that in metallic $\text{Ba}_2\text{FeReO}_6$ than that in the larger band gap semiconductor $\text{Ca}_2\text{FeReO}_6$ [43,44]. In particular, the shoulder feature in $\text{Ba}_2\text{FeReO}_6$ merges with the elastic line as in $\text{Sr}_2\text{CrReO}_6$, whereas in $\text{Ca}_2\text{FeReO}_6$ the shoulder feature becomes a true peak separated from the elastic. Thus, if shoulder feature indeed represents the beginning of the e - h continuum, merging versus separation of the feature from the elastic should correspondingly reflect a gapless versus gapped (or small gap versus large gap) e - h continuum. This fits naturally with the respective transport properties of $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, and should additionally reflect a near-metallic nature in $\text{Sr}_2\text{CrReO}_6$. Qualitatively, this is supported by the fact that $\text{Sr}_2\text{CrReO}_6$ is much more conductive than the already semiconducting $\text{Ca}_2\text{FeReO}_6$ [20,43,44]. More quantitatively, this is also in line with the resistivity-estimated activation gap of 9.4 meV found in 200 nm thick $\text{Sr}_2\text{CrReO}_6$ films, considering both that a temperature of $T = 300$ K would be sufficient to thermally populate the conduction band ($k_B T \sim 26$ meV) and that this small of a gap would likely not be visible even at $T = 0$ K given our resolution of 65/95 meV FWHM. On the other hand, our results agree less well with optical estimates of a 0.2 eV band gap which should be visible at room temperature and with our resolution [20]. This latter point may indicate an indirect nature of the band gap given that optical probes typically only probe the direct gap due to the negligible momentum they can impart. Conversely, hard x rays can impart significant momentum and therefore probe an indirect band gap.

While we believe that the shoulder feature in $\text{Sr}_2\text{CrReO}_6$ indeed corresponds to the beginning of the e - h continuum, we now address other possibilities. The first of these, which the reader may already have pondered, is that feature may be explained as multiphonon excitations to match the low energy feature in Ba_2YReO_6 . Indeed, we are initially encouraged by this possibility considering the energy scale and overall appearance of the feature is fairly similar to that of the feature in Ba_2YReO_6 . Looking deeper, however, this option loses some plausibility as we do not observe any L_2 edge enhancement of the feature as we did in Ba_2YReO_6 , nor is it possible to look for hints in the lineshape of the SOC excitations given their broadness and overall lack of detail. Thus, while we cannot reject this possibility with certainty, we do not think there is

sufficient evidence to consider this the most likely origin of the feature.

Next, we discuss Marcaud et al. attribution of the feature to magnon excitations [28]. Specifically, Marcaud et al. calculations predict a zone boundary energy of a Re(Cr) magnon mode extending up to $\sim 200(300)$ meV. However, this energy scale far outstrips that of zone-boundary magnons measured by inelastic neutron scattering in the related high- T_c ferrimagnets $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ which extend up to a maximum energy of 50 meV [28,45,46]. Adding to this, both $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ order ferrimagnetically at temperatures on the same order of magnitude as $\text{Sr}_2\text{CrReO}_6$ ($T_c \sim 305$ and 520 K respectively), such that we anticipate their exchange couplings to be similar [24,43,45,46]. Finally, we note that $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ possess B site spin moments of $S = 5/2$ rather than $S = 3/2$ as in $\text{Sr}_2\text{CrReO}_6$ and thus possess significantly larger ferrimagnetic moment than $\text{Sr}_2\text{CrReO}_6$ [24]. Thus, on both counts of the moment size and exchange coupling, we believe that it is unlikely that $\text{Sr}_2\text{CrReO}_6$ should possess single-magnon bands 4–8 times more energetic than those in $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$. Moreover, regardless of the true magnon energy scale in $\text{Sr}_2\text{CrReO}_6$, we emphasize that $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ share similar low energy RIXS features to $\text{Sr}_2\text{CrReO}_6$ that are decidedly incompatible with the energy scales of single magnons in these materials. Thus, given this comparison, we are compelled to conclude that the low energy shoulder in $\text{Sr}_2\text{CrReO}_6$ does not represent single-magnon excitations. Although in principle multimagnon modes can appear in RIXS [47], we do not consider this a plausible origin for the feature because we would then correspondingly expect to see separate signatures of single-magnon excitations in the RIXS spectra of $\text{Sr}_2\text{CrReO}_6$, $\text{Ba}_2\text{FeReO}_6$, and $\text{Ca}_2\text{FeReO}_6$ in the form of greater spectral weight in the region below 200 meV.

VI. CONCLUSION

In summary, we have presented Re L_2 and L_3 edge RIXS measurements of the Re-based DPs Ba_2YReO_6 and $\text{Sr}_2\text{CrReO}_6$ and have extracted powerful information from the differences between the two edges using simple single-particle selection rules. In Mott-insulating Ba_2YReO_6 , these differences allowed us to discern that the hierarchy of the lowest excited states is in fact the inverse of what has previously been theorized, reflecting a need to revisit the appropriate energy scales of the Hund's coupling and SOC. We used exact diagonalization methods to estimate said new energy scales and found that the values of $J_H = 0.38(2)$ eV and $\zeta = 0.290(5)$ eV describe our data well, which in particular puts ζ more in line with that found in other Re-based Mott insulators.

Our RIXS measurements of Ba_2YReO_6 also for the first time reveals the presence of edge dependent resonant low energy features which we conclude most plausibly represent Jahn-Teller active excitations, which have been predicted to occur in Ba_2YReO_6 and which have been observed in other Re-based DPs, and which may also be supplemented by an e - h continuum. The presence of a dynamic Jahn-Teller effect in Ba_2YReO_6 also helps explain the observed asymmetry and edge dependent lineshape of the 0.5 eV and 0.9 eV

features. Future RIXS experiments with higher resolution and expanded temperature dependence will be invaluable in refining our understanding of vibronic physics in Ba_2YReO_6 .

In the correlated small band gap semiconductor $\text{Sr}_2\text{CrReO}_6$, the difference between L_2 and L_3 edge RIXS measurements confirms that the broad features between 0.5 and 1.5 eV correspond to Hund's coupled spin-orbit excitations. Additionally, we have newly resolved the presence of "two-particle" spin-orbit excitations anticipated within the intermediate Hund's coupling regime. Unfortunately, the presence of a strong e - h continuum masks and broadens the dd excitations in $\text{Sr}_2\text{CrReO}_6$, such that the individual scales of J_H and ζ cannot be discerned. Our measurements also reveal a near-metallic character in $\text{Sr}_2\text{CrReO}_6$ as no discernible band gap exists in the e - h continuum excitations. A comparison with other works suggests the presence of an indirect band gap smaller than our instrumental resolution, in good agreement with prior estimates of a 9.4 meV activation gap. Finally, the RIXS spectra of Ba_2YReO_6 and $\text{Sr}_2\text{CrReO}_6$ reveal similar energy scales of Hund's coupling and SOC despite their respective Mott-insulating and semiconducting natures, reflecting the crucial role of B site substitution in $5d^2$ DPs.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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