

Charge ordering in Ir dimers in the ground state of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$

Vamshi M. Katukuri^{1,*}, Xingye Lu^{2,3,†}, D. E. McNally², Marcus Dantz², Vladimir N. Strocov², M. Moretti Sala^{4,5}, M. H. Upton⁶, J. Terzic⁷, G. Cao⁷, Oleg V. Yazyev¹, and Thorsten Schmitt^{2,‡}

¹*Institute of Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

²*Swiss Light Source, Photon Science Division, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

³*Center for Advanced Quantum Studies and Department of Physics, Beijing Normal University, Beijing 100875, China*

⁴*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France*

⁵*Dipartimento di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, I-20133 Milano, Italy*

⁶*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

⁷*Department of Physics, University of Colorado at Boulder, Boulder, Colorado 80309, USA*



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It has been well established experimentally that the interplay of electronic correlations and spin-orbit interactions in Ir^{4+} and Ir^{5+} oxides results in insulating $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 0$ ground states, respectively. However, in compounds where the structural dimerization of iridium ions is favorable, the direct Ir d - d hybridization can be significant and takes a key role. Here, we investigate the effects of direct Ir d - d hybridization in comparison with electronic correlations and spin-orbit coupling in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, a compound with Ir dimers. Using a combination of *ab initio* many-body wave-function quantum chemistry calculations and resonant inelastic x-ray scattering experiments, we elucidate the electronic structure of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$. We find excellent agreement between the calculated and the measured spin-orbit excitations. Contrary to expectations, the analysis of the many-body wave function shows that the two Ir (Ir^{4+} and Ir^{5+}) ions in the Ir_2O_9 dimer unit in this compound preserve their local J_{eff} character close to $1/2$ and 0 , respectively. The local point group symmetry at each of the Ir ions plays an important role, significantly limiting the direct d - d hybridization. Our results emphasize that minute details in the local crystal field environment can lead to dramatic differences in the electronic states in iridates and $5d$ oxides in general.

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I. INTRODUCTION

Dimerization or clustering of transition metal (TM) atoms is observed in many TM compounds, e.g., in vanadium oxides [1,2], and titanates [3], when the t_{2g} orbitals of the TM d manifold form partially filled singlet states of dimers akin to the Peierls state in one dimension [4]. In these systems, the TM ions tend to have a strong direct (intradimer) d - d overlap that results in molecularlike orbitals with appreciable bonding-antibonding splitting. Consequently, the local electronic structure depends on the intradimer hopping integral (t_d), intra-atomic Hund's coupling (J_H), and interatomic (U) Coulomb interactions and electron filling of the orbitals localized at TM clusters. Alternatively, dimerization of TM ions can also be favorable from crystallographic considerations, particularly in compounds with heavy TM ions, e.g., $5d$ ions, where the d orbitals are more spread out. A number of dimerized or cluster $4d$ and $5d$ compounds [5–8] with intriguing properties have been synthesized recently. Novel physical phenomena have been observed in these compounds, e.g.,

the inelastic x-ray scattering analog of Young's double-slit experiment has been realized in $\text{Ba}_3\text{CeIr}_2\text{O}_9$ [9], where the molecular orbital formation within the Ir dimers is crucial. In lacunar spinels $\text{Ga}M_4X_8$ ($M = \text{Nb, Mo, Ta, and W}$ and $X = \text{S, Se, and Te}$), spin-orbit coupled molecular J_{eff} states [10,11] and topological superconductivity [12] have been proposed where molecular orbital formation within the tetrahedral cluster of M ions is the key.

The interplay of intersite electron hopping (t), J_H , U , and the strong atomic spin-orbit coupling (SOC) in $5d$ and in some $4d$ compounds result in intriguing J_{eff} physics [13–17]. For instance, in compounds with an Ir^{4+} (d^5) configuration in an octahedral environment, e.g., in Sr_2IrO_4 [13,14], the strong SOC leads to completely filled $J_{\text{eff}} = 3/2$ and half-filled $J_{\text{eff}} = 1/2$ levels. Similarly, in Ba_2YIrO_6 and NaIrO_3 , the Ir^{5+} ions realize completely filled $J_{\text{eff}} = 3/2$ and empty $J_{\text{eff}} = 1/2$ submanifolds [18,19], resulting in a nonmagnetic $J_{\text{eff}} = 0$ ground state [20]. In dimerized systems, t_d can be much larger and successively may play a dominant role compared to other local interactions, which could result in the breakdown or a significant modification of the J_{eff} physics. Thus, it is crucial to identify the role of these multiple interactions in Ir dimer systems to gain a better understanding of the electronic and magnetic properties of these materials.

In this paper, we illustrate how subtle crystal structure details are extremely important to precisely understand the electronic structure of $5d$ compounds where structural

*Present address: Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569, Stuttgart Germany; V.Katukuri@fkf.mpg.de

[†]luxy@bnu.edu.cn

[‡]thorsten.schmitt@psi.ch

dimerization or clustering is prevalent. Using state-of-the-art *ab initio* many-body electronic structure methods in combination with high-resolution resonant inelastic x-ray scattering (RIXS) experiments, we present a detailed analysis of the electronic structure of Ir_2O_9 dimers in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ and unravel the nature of the electronic ground and excited states of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$. While we find an excellent agreement between the RIXS spectra and the calculated excitations, analysis of the many-body wave functions reveals a nearly complete charge separation— Ir^{4+} and Ir^{5+} —within the dimers in the ground state, in contrast to an earlier report describing the formation of molecular orbitals in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ [21]. The strong SOC of the Ir^{4+} and Ir^{5+} ions results in $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 0$ local configurations, respectively, and thus we conclude that a localized J_{eff} picture is more appropriate in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$.

$\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ contains dimers composed of crystallographically inequivalent Ir cations encaged in face-sharing O_6 octahedra [22,23] [see Figs. 3(a) and 3(b), and Supplemental Material (SM) Fig. S1 [24]]. At 210 K, a lattice distortion is believed to lower the symmetry of the crystal and enhance the charge disproportionation leading to charge ordering that corresponds to Ir^{4+} and Ir^{5+} valence configurations [23]. However, an analysis of the previously measured RIXS spectrum of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ using density functional theory and model Hamiltonian calculations [21] has proposed the formation of hybridized dimer orbitals, debunking the charge disproportionation phenomenon. Nevertheless, given the complex low-symmetry crystal environment and the interplay of spin and orbital degrees of freedom in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, it is unclear if the dimer orbitals are actually realized in the ground state.

II. RESULTS

The RIXS spectra shown in Fig. 1 were measured on single crystals grown by the flux method [23] at the ID20 beamline of the European Synchrotron Radiation Facility (ESRF) with ~ 25 meV resolution [25] and the 27-ID-B beamline with ~ 30 meV resolution at the Advanced Photon Source (APS), with π polarization at a scattering angle close to $2\theta = 90^\circ$. The incident-energy dependence of RIXS spectra across the Ir L_3 edge ($E_i = 11.215$ keV) at the zone center $Q = (23.5, 0, 2.5)$ is shown in Fig. 1(a). While the same E_i as determined from previous measurements on iridates such as Sr_2IrO_4 and Ba_2YIrO_6 [20,26] was chosen, we find that the maximum of the resonance is not at E_i in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ as the precise crystal field (CF) environment around Ir ions and the mixing of the valence states influences the resonance energy. However, we see that the energies of the modes remain unchanged in a broad range around E_i .

The features marked by A-K in Fig. 1(b) are incident-energy independent Raman modes as shown in Fig. 1(a). These modes correspond to intrinsic electronic transitions between various occupied and unoccupied states, and therefore provide direct information about the low-energy electronic structure. To resolve all the Raman modes and determine the low-energy electronic structure, we show in Figs. 1(b) and 1(c) the high-statistic energy spectra collected at E_i [white dashed line in Fig. 1(a)]. In Fig. 1(b), several sharp Raman modes below 1 eV and a broad peak at 1.2 eV, named A-K,

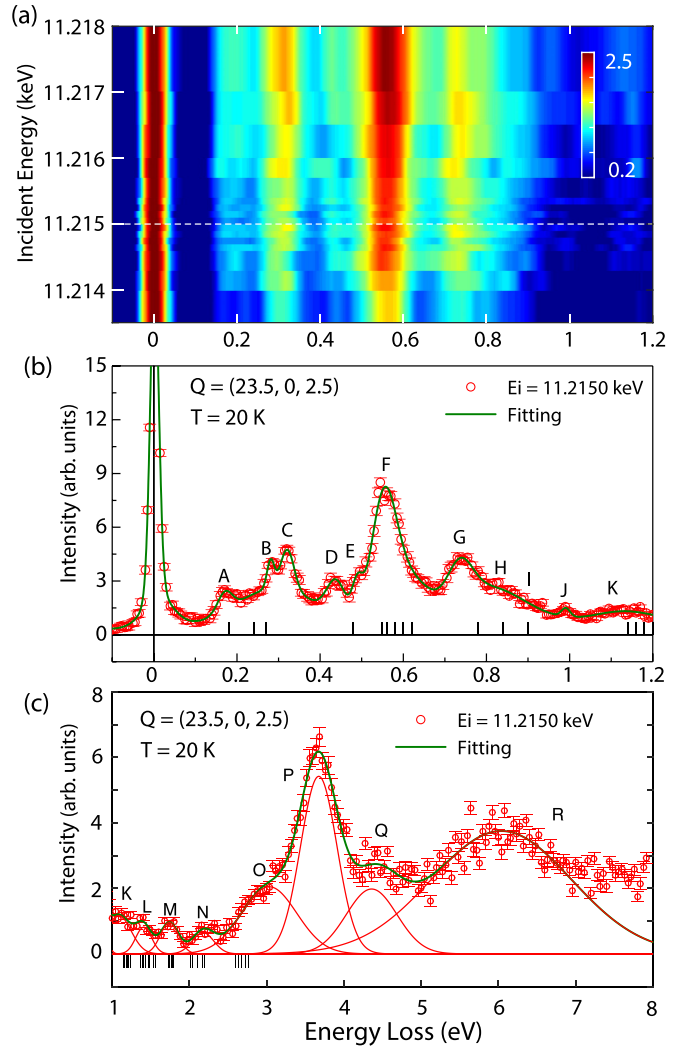


FIG. 1. (a) Incident-energy dependence of elementary excitations below 1.2 eV for $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ measured around the Ir L_3 edge with $Q = (23.5, 0, 2.5)$ at 20 K. (b) RIXS spectra (below 1.2 eV) measured at $E_i = 11.215$ keV [marked as a white dashed line in (a)]. (c) High-energy excitations (1–8 eV) measured with the same setup as that for (b). The green line is a multi-Gaussian fitting of the raw data in red open circles (with error bars).

are determined by fitting the spectra using multiple Gaussians. The sum of the fitting curves is shown as a green solid curve. In Fig. 1(c), higher-energy excitations up to 8 eV are shown. This spectrum is decomposed into several peaks and interestingly, these modes show very little momentum dependence (see SM Fig. S6 [24]), indicating that all of them correspond to local spin-orbital ($d-d$) excitations and are reflecting the low-energy electronic structure.

We now turn to the RIXS results measured using the O K edge (Fig. 2 and Fig. S2 in SM [24]) carried out at the ADDRESS beamline of the Swiss Light Source at the Paul Scherrer Institut, with ~ 70 meV energy resolution for both σ and π polarizations at a scattering angle of $2\theta = 130^\circ$ [27,28] (see SM Fig. S1). With the presence of strong hybridization between the O $2p$ orbitals and Ir $5d$ orbitals, O K RIXS is sensitive to various elementary excitations of iridates [29]. Figures 2(a) and 2(b) are RIXS maps collected at the O K edge

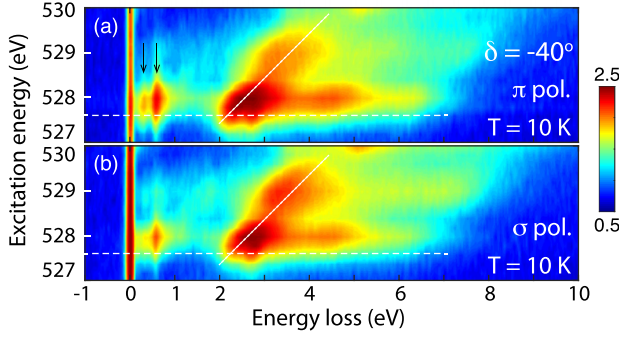


FIG. 2. RIXS results of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ as measured at the O K edge. (a), (b) Energy dependence of RIXS spectra for $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ taken around the O K edge with $\delta = -40^\circ$ [$Q = (0.93, 0, 0.65)$].

with π and σ polarizations at 25° grazing incidence. Besides the sharp spin-orbital excitations ($E \approx 0.26, 0.57$ eV) below 1 eV consistent with those measured with the Ir L_3 edge, two high-energy excitations at $E \approx 2.26$ and 2.71 eV have also been observed. Note the RIXS maps in Fig. 2 contain substantial fluorescence which is absent in the results collected at the Ir L_3 edge (Fig. 1), indicating a complex Ir $5d$ -O $2p$ hybridization between the energy bands of the oxygen ions. In addition, a significant polarization dependence of the excitations has also been observed, which we attribute to the overlap between light polarization (electric field $\mathbf{E}$) and the different O $2p$ orbitals hybridized with different Ir $5d$ orbitals (for details, see SM [24]).

To decipher the nature of the rich excitation spectrum observed in the RIXS spectra and to examine the formation of dimer orbitals in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, we performed many-body *ab initio* cluster-in-embedding quantum chemistry (QC) calculations, starting from the crystal structure reported in Refs. [22,23]. These are based on the construction of the exact wave function for a cluster of atoms, embedded in a potential that represents the solid-state environment, using complete active space self-consistent field (CASSCF) and multireference perturbation methods [30]. The calculations were performed on a cluster containing one Ir_2O_9 dimer unit, two neighboring AlO_4 tetrahedra, and the surrounding 15 Ba^{2+} ions. The ORCA quantum chemistry program [31] was used for all calculations (see SM [24] for all the computational details, which includes Refs. [29,31–36]).

The relative energies of the multiplet structure of the Ir_2O_9 dimer unit obtained from CASSCF + NEVPT2 (N -electron valence perturbation theory) [37] calculations are shown in Table I. An active space of nine electrons in six orbitals (three t_{2g} orbitals on each iridium) was considered in the CASSCF calculation which sufficiently captures the important static correlations (i.e., near degeneracies) in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$. In the NEVPT2 calculation, the correlations involving all the neighboring occupied oxygen $2p$ and iridium $5s, 5p$ orbitals as well as all the unoccupied orbitals are accounted for, accurately describing the O $2p$ to Ir d charge transfer effects and other dynamic correlation effects. It is important to note that the intrasite (Hund's coupling J_H) and intersite (U) Coulomb interactions and the hybridization between different orbitals are included in the calculation, accurate within the basis-set limit.

TABLE I. Relative energies (eV) of the excitation levels obtained from CASSCF+NEVPT2 calculations. The first column contains the nonrelativistic multiplet structure, and the multiplet symbols on the left correspond to the octahedral (O_h) symmetry. The degeneracy of the states is split in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ due to the lowered symmetry in the two octahedra due to the anisotropic crystal fields (see text). The spin-orbit coupled multiplet structure is shown in the second column. Note that each state is doubly degenerate (Kramers doublet). The corresponding peaks in the RIXS data in Fig. 1(a) are shown in column 3.

	CASSCF+NEVPT2	+ SOC ($\times 2$)	Ir L -edge RIXS
4A_1	0.00	0.00	0.00
2T_1	0.03, 0.08, 0.10	0.18	0.18 (A)
2A_1	0.14	0.24, 0.27	0.28 (B) 0.33 (C)
4T_1	0.16, 0.17, 0.17		0.44 (D)
2E_1	0.18, 0.23	0.48, 0.62	0.50 (E)
4E_1	0.25, 0.28	0.55, 0.56, 0.58	0.56 (F)
2T_2	0.77, 0.80, 0.94	0.60, 0.78	0.75 (G)
4T_2	0.84, 0.86, 0.95	0.84, 0.90	0.82 (H)
2T_3	0.86, 0.86, 0.90	1.14–1.20 (4)	0.98 (I), 1.00 (J)
2A_2	0.91	1.21, 1.24	1.20 (K)
2E_2	1.00, 1.01	1.37–1.43 (4)	1.4 (L)
2A_3	1.03	1.47	
2T_4	1.10, 1.10, 1.12	1.48, 1.53, 1.56	
2E_3	1.60, 1.63	1.73–1.80 (5)	1.77 (M)
2T_5	1.68, 1.78, 1.81	2.02, 2.04	
		2.11, 2.17, 2.20	2.17 (N)
		2.59	
		2.63–2.77 (4)	2.70 (O)

The lowest nine quartet ($s = \frac{3}{2}$) and 24 doublet ($s = \frac{1}{2}$) scalar relativistic states (first column in Table I) are first computed and then are allowed to admix via the SOC, resulting in 84 states (see the second column of Table I). It can be seen that the excitation energies obtained from CASSCF + NEVPT2 + SOC calculations are in excellent agreement with the peaks observed in RIXS experiments, except for peak D. This peak is related to the electron-hole exciton which is also observed in other iridate materials such as Sr_2IrO_4 [29,38,39] and Na_2IrO_3 [40]. Such excitations are not considered in the current QC calculations [41]. Further, our calculations reveal excitations from the t_{2g} to e_g manifold starting at 3.4 eV which correspond to RIXS peaks P and Q.

To elucidate the origin of these excitations, we first analyze the scalar-relativistic multiplet structure. When the two iridium ions in the dimer unit are in a cubic environment (O_h symmetry), the low-energy multiplet structure is a result of the interaction of the ground state $^2T_{1g}$ multiplet of the Ir^{4+} ion [42] and the $^3T_{1g}$ ground state term of the Ir^{5+} ion. In addition, the lowest $^1T_{1g}$ and $^1E_{1g}$ [20] singlet states contribute significantly to the low-energy spin-orbit excitations [20]. The resulting spectrum contains $^4T_{1g}, ^4T_{2g}, ^4A_{1g}, ^4E_{1g}$ quartets and 11 doublet terms, $^2T_{1g,2g,3g,4g,5g}, ^2A_{1g,2g,3g}, ^2E_{1g,2g,3g}$ [43]. However, in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ the Ir ions are enclosed in distorted octahedra, resulting in low-symmetry CFs and splitting of the t_{2g} levels at each Ir ion [44]. Further, the small Ir-Ir intradimer distance of 2.73 Å in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ (2.698 Å in elemental iridium) may result in a direct overlap of the Ir d orbitals

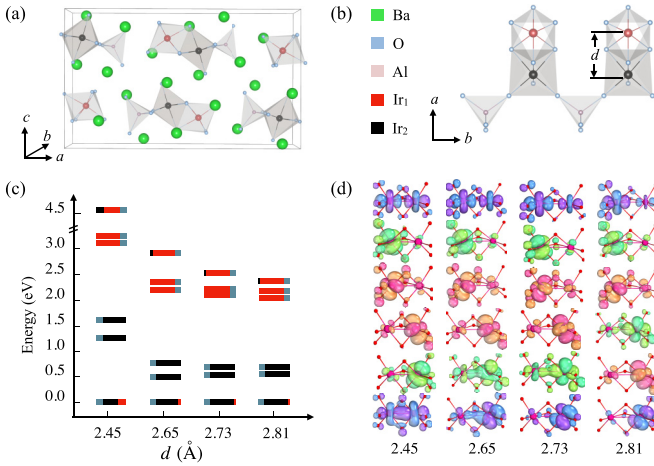


FIG. 3. Crystal structure of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$: (a) Unit cell, (b) Ir_2O_9 dimer units connected along the b axis, and d is the intradimer Ir_1 - Ir_2 distance. (c) Orbital (relative) energy-level diagram of the six t_{2g} orbitals, shown in (d), for different d , where the lowest-energy orbital is set to zero. The lengths of the red, black, and blue colors of each level are proportional to the percentage contributions from Ir_1 , Ir_2 , and O ions, respectively.

and the formation of bonding and antibonding states [45]. Consequentially, the multiplet degeneracies in the spectrum are split.

To understand the formation of bonding and antibonding dimer orbitals in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, we plot the evolution of orbital energies as a function of Ir_1 - Ir_2 intradimer distance (d) in Fig. 3(c). The six levels for each d correspond to the CASSCF canonical orbital [46] energies of the six t_{2g} -like orbitals in the Ir_2O_9 dimer unit. The color variations of the energy levels represent the orbital compositions [47] from Ir_1 , Ir_2 , and O ions. Interestingly, for $d \geq 2.73$ Å, we find 20% and 13% hybridization for Ir_1 $5d$ -O $2p$ and Ir_2 $5d$ -O $2p$, respectively, while there is negligible direct Ir_1 - Ir_2 d -orbital hybridization. The a_{1g} orbital of Ir_1 contains a 4.5% contribution from the a_{1g} orbital of Ir_2 and vice versa. For $d = 2.65$ Å, a significant direct Ir_1 - Ir_2 d -orbital hybridization is observed. We find this hybridization increasing up to 25% for $d = 2.45$ Å, resulting in a large bonding-antibonding energy separation, as seen in the corresponding orbital plots in Fig. 3(d). Note that for $d = 2.73$ Å orbitals with a predominantly Ir_1 character are at higher energies than those of Ir_2 character, reflecting different on-site orbital energies. This is a direct consequence of the difference in the valence configurations of Ir_1 and Ir_2 ions and the $\text{Ir}_{1,2}$ $5d$ -O $2p$ hybridization.

The effect of the low CF symmetry at two different Ir ions can be estimated by computing the t_{2g} splittings δ at each of the Ir ions from restricted active space (RAS) [48] calculations where the d orbital occupation at the other Ir ion is constrained. We find considerably large t_{2g} splittings of $\delta_1 = 0.58$ and $\delta_2 = 0.60$ eV for Ir_1 and Ir_2 , respectively. Such large values compete with the SOC strength of ~ 0.5 eV of the Ir ions to considerably reduce the effect of SOC, thus resulting in the modification of the local spin-orbit multiplet structure.

The scalar-relativistic ground state realized in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ is the double-exchange $^4A_{1g}$ multiplet [49], an orbitally nondegenerate high-spin quartet, with wave function $^4\psi_0 = \alpha|d_1^4, d_2^5\rangle + \beta|d_1^3, d_2^6\rangle + \gamma|d_1^5, d_2^4\rangle$ with $\alpha^2 = 0.89$, $\beta^2 = 0.09$, and $\gamma^2 = 0.02$, where d_i^n corresponds to n electrons in Ir_i d orbitals. The lowest 2T_1 doublet state is 40 meV higher with wave-function weights $\alpha^2 = 0.85$, $\beta^2 = 0.11$, and $\gamma^2 = 0.02$. We further find that the weight of the $|d_1^4, d_2^5\rangle$ configuration in all the excited multiplet wave functions is greater than 95%. It is interesting to note that excluding all the configurations involving the hopping of electrons from Ir_1 to Ir_2 and vice versa in the wave function preserve the spin-orbit spectrum except for an overall shift ≤ 50 meV. The double-exchange ground state as well as the dominant contribution of the $|d_1^4, d_2^5\rangle$ configuration imply charge separation within the dimer units. Further, the natural orbital occupations obtained from the CASSCF calculations are close to 4 and 5 for Ir_1 and Ir_2 ions, respectively. Thus, we conclude that the two Ir ions in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ host different ionic states— Ir_1^{5+} and Ir_2^{4+} —which results in charge ordering within the dimers and the low-energy excitations are strictly local to individual Ir ions and not among dimer orbitals.

The SOC results in the admixture of all the 15 nonrelativistic multiplet terms shown in Table I. The addition of angular momenta of two $l_{\text{eff}} = 1$ ($l_{\text{eff},1} = l_{\text{eff},2} = 1$) sites with spins $s_1 = 1/2$ and $s_2 = 1$ gives rise to 84 effective total angular momentum (J_{eff}) states. In $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, due to the noncubic CFs, all degeneracies are removed except for the Kramers doublet degeneracy. From the analysis of the wave functions, we assign the peaks A-C to excitations from the Ir_1 $J_{\text{eff}} = 0$ to $J_{\text{eff}} = 1$ states. Peak F and satellite feature H consist of excitations from Ir_1 $J_{\text{eff}} = 0$ to $J_{\text{eff}} = 2$ and Ir_2 $J_{\text{eff}} = 1/2$ to $J_{\text{eff}} = 3/2$ states that are split due to noncubic CFs. Peak G originates from excitations involving Ir_1 $J_{\text{eff}} = 0$ and $J_{\text{eff}} = 2$ states as well. Peaks I-K are the result of simultaneous on-site excitations at Ir_1 and Ir_2 ions (see Fig. S5 in SM [24]).

At first sight, an insignificant Ir-Ir intradimer d -orbital hybridization in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ might be surprising, even though the distance between the Ir sites is close to that of Ir metal. However, due to the crystallographic inequivalence of the two Ir ions in the dimer unit and the different O_6 arrangement, the symmetry of split t_{2g} orbitals at each of the Ir ions is very different and subsequently little direct overlap is realized. In fact, for dimer systems with structurally equivalent ions such as $\text{Ba}_3\text{InIr}_2\text{O}_9$ [7], we find a considerable hybridization resulting in delocalized dimer orbitals [50]. It would be interesting to characterize the local electronic structure in other face-sharing Ir dimer compounds such as $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ and $\text{Ba}_3\text{ZrIr}_2\text{O}_9$ [51] where the Ir dimer unit occupancy is eight and ten, respectively.

III. CONCLUSION

In conclusion, we have measured both Ir L_3 - and O K -edge RIXS spectra and observed multiple spin-orbit excitations. Our *ab initio* QC calculations reproduce very well the excitation spectrum up to 3.5 eV observed in the RIXS measurements. We find charge ordering within the Ir dimers with $\text{Ir}_1^{5+}(d^4)$ and $\text{Ir}_2^{4+}(d^5)$ configurations. We have established a direct connection between the excitations in Ir_2O_9

dimer units and those at individual Ir ions. The appearance of multiple peaks is a direct consequence of strong noncubic CFs originating from the distorted octahedral environment around the Ir ions. In spite of the small intradimer Ir-Ir distance, the direct d - d hybridization is relatively weak and the bonding-antibonding splitting is negligible compared to the noncubic CF splittings. Alternatively, we find increased intradimer configuration mixing due to strong electron-electron interactions, particularly the $|d_1^3, d_2^6\rangle$ configuration stabilizing the ground state. This strongly supports nearly complete charge ordering within the Ir dimers in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ and refutes the suggested formation of dimer orbitals [21]. Our results highlight the importance of minute details of the crystal structure to understand the electronic and magnetic properties of clustered iridates and TM magnets in general and calls for reinvestigating several already studied materials with accurate *ab initio* many-body calculations. Finally, we emphasize that the combination of RIXS and quantum chemistry calculations is an excellent tool to unambiguously decipher complicated electronic structures.

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