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

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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 isolating $J_{\text{eff}}=1/2$ and $J_{\text{eff}}=0$ ground states, respectively. However, in compounds where the structural dimerization of iridium ions is favourable, the direct Ir $d-d$ hybridisation can be significant and takes a key role. Here, we investigate the effects of direct Ir $d-d$ hybridisation in comparison with electronic correlations and spin-orbit coupling in Ba$_5$AlIr$_2$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 (RIXS) experiments, we elucidate the electronic structure of Ba$_5$AlIr$_2$O$_{11}$. We find excellent agreement between the calculated and the measured spin-orbit excitations. Contrary to the expectations, the analysis of the many-body wave function shows that the two Ir (Ir$^{4+}$ and Ir$^{5+}$) ions in the Ir$_2$O$_9$ dimer unit in this compound preserve their local $J_{\text{eff}}$ character close to 1/2 and 0, respectively. The local point group symmetry at each of the Ir sites assumes an important role, significantly limiting the direct $d-d$ hybridisation. Our results emphasize that minute details in the local crystal field (CF) environment can lead to dramatic differences in electronic states in iridates and 5$d$ oxides in general.

Dimerization or clustering of TM atoms is observed in many TM compounds, e.g. in vanadium oxides [1, 2] and titanates [3] where dimers of spin singlets akin to the Peierls state in one dimension [4] are stabilized when the $t_{2g}$ orbitals of the TM $d$-manifold are partially filled. In these systems, the TM ions tend to have a strong direct (intra-dimer) $d-d$ overlap that result in molecular-like orbitals with appreciable bonding-antibonding splitting. Consequently, the local electronic structure depends on the intra-dimer hopping integral $(t_d)$, intra-atomic Hund’s coupling $(J_H)$ and inter-atomic $(U)$ Coulomb interactions and electron filling of the orbitals localized at TM clusters. Alternatively, dimerization of TM ions can also be favourable from crystallographic considerations, particularly in compounds with heavy TM ions, e.g. 5$d$ ions, where the $d$ orbitals are more spread out. A number of dimerized or cluster 4$d$ and 5$d$ 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 analogue of Young’s double slit experiment has been realized in Ba$_3$CeIr$_2$O$_9$ [9], where the molecular orbital formation within the Ir dimers is crucial. In lacunar spinels Ga$_M$$_2$X$_9$ ($M=$Nb, Mo, Ta and W and X=S, Se and Te), spin-orbit coupled molecular $J_{\text{eff}}$ states [10, 11] and topological superfucnductivity [12] have been proposed where molecular orbital formation within the tetrahedral cluster of $M$ ions is the key.

The interplay of inter-site electron hopping $(t)$, $J_H$, $U$ and the strong atomic spin-orbit coupling (SOC) in 5$d$ and in some 4$d$ compounds result in the $J_{\text{eff}}$ physics [13, 14]. For instance, in compounds with Ir$^{4+}$ $(d^2)$ configuration in an octahedral environment, e.g. in Sr$_2$IrO$_4$ [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$_2$YIrO$_6$ and NaIrO$_3$, the Ir$^{5+}$ ions realise a completely filled $J_{\text{eff}}=3/2$ and empty $J_{\text{eff}}=1/2$ sub-manifolds [15, 19], resulting in a non-magnetic $J_{\text{eff}}=0$ 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 $J_{\text{eff}}$ physics. Thus, it is crucial to identify the role of these multiple physical interactions in Ir dimer systems to gain a better understanding of the electronic and magnetic properties of these materials.

In this letter, we illustrate how subtle crystal structure details are extremely important to precisely understand the electronic structure of 5$d$ compounds where structural 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$_2$O$_9$ dimers in Ba$_5$AlIr$_2$O$_{11}$ and unravel the nature of electronic ground and excited states of Ba$_5$AlIr$_2$O$_{11}$. While we find an excellent agreement between the RIXS spectra and the calculated excitations, analysis of the many-body
wave functions reveal a nearly complete charge separation – Ir\(^{4+}\) and Ir\(^{5+}\) – within the dimers in the ground state, in contrary to an earlier report of formation of molecular orbitals in Ba\(_5\)AlIr\(_2\)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 \(J_{\text{eff}}\) picture is more appropriate in Ba\(_5\)AlIr\(_2\)O\(_{11}\).

Ba\(_5\)AlIr\(_2\)O\(_{11}\) contains dimers composed of crystallographically inequivalent Ir cations encaged in face sharing O\(_6\) octahedra [22, 23], see Fig. 3k and 3l, and Supplementary 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 correspond to Ir\(^{4+}\) and Ir\(^{5+}\) valence configurations [23]. However, analysis of RIXS spectrum of Ba\(_5\)AlIr\(_2\)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 Ba\(_5\)AlIr\(_2\)O\(_{11}\), it is unclear if the dimer orbitals are actually realised in the ground state.

**Results:** The RIXS spectra shown in Fig. 1 was measured on single crystals grown by flux method [23] at the ID20 beam line of the European Synchrotron Radiation Facility (ESRF) with \(\sim 25\) meV resolution [25] and the 27-ID-B beamline with \(\sim 30\) meV resolution at the Advanced Photon Source (APS), with \(\pi\) 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\(_2\)IrO\(_4\) and Ba\(_2\)YIrO\(_6\) [20, 24] was chosen, we find that the maximum of the resonance is not at \(E_i\) in Ba\(_5\)AlIr\(_2\)O\(_{11}\) as the precise 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 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) 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 \(A\) to \(K\) 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. 6 [24]), indicating that all of them correspond to local spin-orbital (\(d-d\)) excitations and reflecting the low energy electronic structure.

We now turn to the RIXS results measured using O-\(K\) edge (Fig. 2 and Fig. S2 in SM [24]) carried out at the ADRESS beamline of the Swiss Light Source at the Paul Scherrer Institut, with \(\sim 70\) meV energy resolution for both \(\sigma\) and \(\pi\) polarizations at a scattering angle of \(2\theta=130^\circ\) [27, 28], see SM, Fig. S1. With the presence of strong hybridization between O 2\(p\) orbitals and Ir 5\(d\) orbitals, O-\(K\) RIXS is sensitive to various elementary excitations of iridates [23]. Figs. 2(a) and 2(b) are RIXS maps collected at O-\(K\) edge with \(\pi\) and \(\sigma\) polarizations at 25\(^\circ\) grazing incidence. Besides the sharp spin-orbital excitations (\(E \approx 0.26, 0.57\) eV) below 1 eV consistent
with those measured with 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 contains substantial fluorescence which is absent in the results collected at Ir L$_3$ edge (Fig. 1), indicating complex energy levels/bands of oxygen ions. In addition, significant polarization dependence of the excitations have also been observed, which we attribute to the overlap between light polarization (electric field $E$) and the different O 2p orbitals hybridized with different Ir 5d orbitals (for details, see [24]).

To decipher the nature of the rich excitation spectrum observed in RIXS spectra and to examine the formation of dimer orbitals in Ba$_5$AlIr$_2$O$_{11}$, we performed many-body $ab$ initio cluster-in-embedding quantum chemistry (QC) calculations, starting from the crystal structure reported in Ref. [22,23]. These are based on the construction of the exact wave function for the atoms in the cluster using configuration interaction wave function theory –

| Energy Loss (eV) | Excitation energy (eV) |
|-----------------|------------------------|
| 528             | 529                    |
| $\pi$ pol.      | $\delta = -40^\circ$   |
| $\sigma$        | $\pi$                  |
| = 0.0           | $\sigma$               |
| 1               | $\pi$                  |

$\delta = -40^\circ \times 1.0$  
$\delta = -40^\circ \times 0.95$  
$\delta = -40^\circ \times 1.25$  

(c) (d)  
(e) (f)  
c  
a  
b  
$\sigma$  
$\pi$  
c  
a  
b  
$\sigma$  
$\pi$  
c  
a  
b  
$\sigma$  
$\pi$  
c  

T = 10 K  
Energy Loss (eV)  
0 -1  
(c) (d)  
(e) (f)  
c  
a  
b  
$\sigma$  
$\pi$  
c  
a  
b  
$\sigma$  
$\pi$  
c  

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

complete active space self-consistent field (CASSCF) and multireference perturbation methods [30]. The calculations were performed on a cluster containing one Ir$_2$O$_9$ dimer unit, two neighboring AlO$_4$ tetrahedra and the surrounding 15 Ba$^{2+}$ ions. All the calculations were performed using ORCA quantum chemistry program [31], see SM [24] for all the computational details.

Relative energies of the multiplet structure of the Ir$_2$O$_9$ dimer unit obtained from CASSCF + NEVPT2 (N-electron valence perturbation theory) [32] 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 Ba$_5$AlIr$_2$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 intra- (Hund’s coupling $J_H$) and inter-site ($U$) Coulomb interactions and the hybridization between different orbitals are included in the calculation, accurate within the basis set limit.

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 excitation which is also observed in other iridate materials such as Sr$_2$IrO$_4$ [29] [33] and Na$_2$IrO$_3$ [34]. Such excitations are not considered in the current QC calculations [35]. 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

| CASSCF+NEVPT2 + SOC (x 2) | Ir L-edge RIXS |
|---------------------------|---------------|
| $^1A_1 - 0.00$            | 0.00          |
| $^2T_1 - 0.03, 0.08, 0.10$ | 0.18          |
| $^2T_1 - 0.14$            | 0.24 , 0.27   |
| $^4T_1 - 0.16, 0.17, 0.17$| 0.44          |
| $^2E_1 - 0.18, 0.23$      | 0.48 , 0.62   |
| $^4E_1 - 0.25, 0.28$      | 0.55 , 0.56 , 0.58 |
| $^2T_2 - 0.77, 0.80, 0.94$| 0.60 , 0.78   |
| $^4T_2 - 0.84, 0.86, 0.95$| 0.84 , 0.90   |
| $^2T_3 - 0.86, 0.86, 0.90$| 1.14 – 1.20 (4) |
| $^2A_2 - 0.91$            | 1.21 , 1.24   |
| $^2E_2 - 1.00, 1.01$      | 1.37 – 1.43 (4) |
| $^2A_3 - 1.03$            | 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) |
| $^2T_5 - 1.68, 1.78, 1.81$| 2.02 , 2.04   |
|                        | 2.11, 2.17, 2.20 |
|                        | 2.59          |
|                        | 2.63 – 2.77 (4) |
|                        | 2.70 (O)      |
analyze the scalar-relativistic multiplet structure. When
the two iridium ions in the dimer unit are in cubic envi-
ronment (Oh symmetry), the low energy multiplet struc-
ture is a result of the interaction of the ground state
$^{2}T_{1g}$ multiplet of the Ir$^{4+}$ ion [36] and the $^{3}T_{1g}$ ground
state term of the Ir$^{5+}$ ion. In addition, the lowest $^{1}T_{1g}$
and $^{1}E_{g}$ [20] singlet states contribute significantly to
the low energy spin-orbit excitations [20]. The resulting
spectrum contains $^{4}T_{1g}, ^{4}T_{2g}, ^{4}A_{1g}, ^{5}E_{g}$, quartets and 11
doublet terms – $^{2}T_{1g,2g,3g,4g,5g,2^{2}A_{1g,2g,3g},2^{2}E_{g,2g,3g,4g,5g}}$ [37].
However, in Ba$_{5}$AlIr$_{2}$O$_{11}$, the Ir ions are enclosed in dis-
torted octahedra resulting in low symmetry CFs and
splitting of the $t_{2g}$ levels at each Ir ion [35]. Further, the
small Ir-Ir intra-dimer distance of 2.73 Å in Ba$_{5}$AlIr$_{2}$O$_{11}$
(2.698 Å in elemental iridium) may result in direct over-
lap of the Ir $d$ orbitals and the formation of bonding and
antibonding states [39]. Consequently, the multiplet
degeneracies in the spectrum are split.

To understand the formation of bonding and antibond-
ing dimer orbitals in Ba$_{5}$AlIr$_{2}$O$_{11}$, we plot the evolution
of orbital energies as a function of Ir$_{1}$-Ir$_{2}$ intra-dimer dis-
tance (d) in Fig. 3(c). The six levels for each d correspond
to the CASSCF canonical orbital [30] energies of the six
t$_{2g}$-like orbitals in the Ir$_{2}$O$_{6}$ dimer unit. The colour vari-
ations of the energy levels represent the orbital compo-
sitions [41] from Ir$_{1}$, Ir$_{2}$ and O ions. Interestingly, for
d $\geq$ 2.73 Å, we find 20% and 13% hybridization for Ir$_{1}$
5$d$ – O 2$p$ and Ir$_{2}$ 5$d$ – O 2$p$, respectively, while there is
negligible direct Ir$_{1}$-Ir$_{2}$ $d$-orbital hybridization. The $a_{1g}$
orbital of Ir$_{1}$ contains 4.5% contribution from $a_{1g}$ 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, re-
sulting in 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 predominantly Ir$_{1}$
character are at higher energies than those of Ir$_{2}$ char-
acter, 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 Ir$_{1,2}$ 5$d$ – O 2$p$
hybridization.

The effect of the low crystal filed symmetry at two
different Ir ions can be estimated by computing the $t_{2g}$
 splittings, $\delta$, at each of the Ir ions from restricted active
space (RAS) [42] calculations where the $d$ orbital occu-
pation at the other Ir ion is constrained. We find consid-
erably 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 $\sim$ 0.5 eV of the Ir ions to con-
siderably reduce the effect of SOC, thus resulting in the
modification of the local spin-orbit multiplet structure.

The scalar-relativistic ground state realized in
Ba$_{5}$AlIr$_{2}$O$_{11}$ is the double exchange $^{4}A_{1g}$ multiplet [34],
an orbitally non-degenerate high-spin quartet, with wave
function $^{4}\psi_{0} = \alpha |d_{1}^{4}, d_{2}^{4}\rangle + \beta |d_{1}^{3}, d_{2}^{3}\rangle + \gamma |d_{1}^{5}, d_{2}^{5}\rangle$, with
$\alpha^{2} = 0.89, \beta^{2} = 0.09$ and $\gamma^{2} = 0.02$, where $d_{i}^{n}$ cor-
responds to $n$ electrons in Ir$_{i}$ $d$ orbitals. The lowest
$^{2}T_{1}$ doublet state is 40 meV higher with wave function
weights $\alpha^{2} = 0.85, \beta^{2} = 0.11$ and $\gamma^{2} = 0.02$. We fur-
ther find that the weight of $|d_{1}^{5}, d_{2}^{5}\rangle$ configuration in all the ex-
cited multiplet wave functions is greater than 95%. It is
interesting to note that excluding all the configurations
involving hopping of electrons from Ir$_{1}$ to Ir$_{2}$ and vice
versa in the wave function preserve the spin-orbit spec-
trum except for an overall shift $\leq 50$ meV. The double
exchange ground state as well as the dominant contribu-
tion of $|d_{1}^{5}, d_{2}^{5}\rangle$ configuration imply charge separation
within the dimer units. Further, the natural orbital occu-
pations 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 Ba$_{5}$AlIr$_{2}$O$_{11}$ host
different ionic states – Ir$_{1}^{5+}$ and Ir$_{2}^{5+}$ – which results in
charge ordering within the dimers and the low energy ex-
citations are strictly local to individual Ir ions and not
among dimer orbitals.

The SOC results in the admixture of all the 15 non-
relativistic multiplet terms shown in Table I. 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 ($J_{\text{eff}}$) states. In Ba$_{5}$AlIr$_{2}$O$_{11}$,
due to the non-cubic CFs, all degeneracies are removed
except for the Kramers double degeneracy. From the
analysis of the wave functions, we assign the peaks A-C
to excitations from the $^{1}$Ir$_{1}$ $J_{\text{eff}} = 0$ to $J_{\text{eff}} = 1$ states.
The peak F and satellite feature H consists of excitations from
Ir$_{1}$ $J_{\text{eff}} = 0$ to $J_{\text{eff}} = 1 1/2$ and Ir$_{2}$ $J_{\text{eff}} = 1 1/2$ to $J_{\text{eff}} = 3/2$
states that are split due to non-cubic CFs. The peak
G originates from excitations involving Ir$_{1}$ $J_{\text{eff}} = 0$ and
Ir$_{2}$ $J_{\text{eff}} = 2$ states as well. The 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 the first sight, an insignificant Ir-Ir intra-dimer d-orbital hybridization in Ba$_3$AlIr$_2$O$_{11}$ might be surprising, even though the distance between Ir sites is close to that of Ir metal. However, due to the crystallographic in-equivalence 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 a little direct overlap is realized. In fact, for dimer systems with structurally equivalent ions such as Ba$_3$InIr$_2$O$_9$ 21, we find a considerable hybridization resulting in delocalized dimer orbitals 24. It would be interesting to characterize the local electronic structure in other face-sharing Ir-dimer compounds such as Ba$_3$ZnIr$_2$O$_9$ and Ba$_3$ZrIr$_2$O$_9$ 14 where the Ir dimer unit occupancy is eight and ten respectively.

In conclusion, we have measured both Ir $L_3$ and O $K$-edge RIXS spectra and observed multiple spin-orbital excitations. Our \textit{ab initio} quantum chemistry 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 $t_{2g}^4 (d^8)$ and $t_{2g}^2 (d^5)$ configurations. We have established a direct connection between the excitations in Ir$_2$O$_9$ dimer unit and those at individual Ir ions. The appearance of multiple peaks is a direct consequence of strong non-cubic CFs originating from the distorted octahedral environment around the Ir ions. In spite of small intra-dimer Ir-Ir distance, the direct $d$-$d$ hybridization is relatively weak and the bonding–antibonding splitting is negligible compared to the non-cubic CF splittings. Alternatively, we find increased intra-dimer configuration mixing due to strong electron-electron interactions, particularly the $|d^1, d^8 \rangle$ configuration stabilizing the ground state. This strongly supports nearly complete charge ordering within the Ir dimers in Ba$_3$AlIr$_2$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 to understand the electronic and magnetic properties of these materials.

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