Nearly itinerant electronic groundstate in the intercalated honeycomb iridate Ag$_3$LiIr$_2$O$_6$

A. de la Torre,†† B. Zager,†† F. Bahrami,† M. DiScala,† J. R. Chamorro,†,‡ M. H. Upton,§ G. Fabbris,∥ D. Haskell,∥ D. Casa,∥ T. M. McQueen,†,‡,¶ F. Tafti,∥ and K. W. Plumb†,⊥,*

††Department of Physics, Brown University, Providence, Rhode Island 02912, United States
‡‡Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
∥∥Department of Chemistry, The Johns Hopkins University, Baltimore, MD, USA
¶¶Institute for Quantum Matter, The Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD, USA
∥∥Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
⊥⊥Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD, USA

(Dated: June 11, 2021)

We use x-ray spectroscopy at Ir L$_3$/L$_2$ absorption edge to study powder samples of the intercalated honeycomb magnet Ag$_3$LiIr$_2$O$_6$. Based on x-ray absorption and resonant inelastic x-ray scattering measurements, and exact diagonalization calculations including next-neighbour Ir-Ir electron hoping integrals, we argue that the intercalation of Ag atoms results in a nearly itinerant electronic structure with enhanced Ir-O hybridization. As a result of the departure from the local relativistic $j_{\text{eff}}=1/2$ state, we find that the relative orbital contribution to the magnetic moment is increased, and the magnetization density is spatially extended and asymmetric. Our results confirm the importance of metal - ligand hybridization in the magnetism of transition metal oxides and provide empirical guidance for understanding the collective magnetism in intercalated honeycomb iridates.

Recognition that the Kitaev model, an exactly solvable quantum spin liquid, may have material realization in heavy transition metal oxides has driven significant research for the past decade [1]. The emergence of this effective quantum compass model depends on a hierarchy of crystal field, spin-orbit coupling, and electronic correlations that act to generate a relativistic atomic orbital with $j_{\text{eff}}=1/2$ effective angular moments. For insulators with edge sharing octahedra coordinating $j_{\text{eff}}=1/2$ ions, isotropic Heisenberg exchange interactions nearly vanish and the magnetism is dominated by spatially anisotropic Kitaev exchange [1]. On the other hand, ab initio calculation find that for many model $j_{\text{eff}}=1/2$ materials, kinetic energy can promote Ir-Ir covalency and the formation of a delocalized quasimolecular orbital (QMO) state [2, 3]. Kitaev models are not obviously applicable in such covalent materials and little is known about the collective magnetism in the itinerant limit.

In the context of Heisenberg-Kitaev magnetism, there has been intensive research on honeycomb iridates [4–6] and α-RuCl$_3$ [7–9]. These compounds have strong Kitaev exchange in addition to Heisenberg and pseudodipolar interactions that result in magnetic order [10, 11]. A successful strategy to reduce Néel temperatures has been to synthesize new versions of these compounds by substitution at the alkali site through intercalation between the honeycomb planes, for example, Ag$_3$LiIr$_2$O$_6$ and H$_3$LiIr$_3$O$_6$ [12–14]. However, the $j_{\text{eff}}=1/2$ state is fragile against structural details [15, 16] while bond disorder and off-stoichiometries can inhibit magnetic order [17, 18]. An empirical understanding of the influence of chemical substitutions on this state is lacking and there does not yet exist a sound starting point to understand collective magnetism in these intercalated materials.

In this letter, we use x-ray spectroscopies to show that the topochemical exchange of interlayer Li atoms with Ag in Ag$_3$LiIr$_2$O$_6$ [19, 20], enhances Ir-O hybridization and fundamentally alters the magnetism. X-ray absorption reveals that the magnetism in Ag$_3$LiIr$_2$O$_6$ is character-
ized by an asymmetric spin density with strong spin-orbit coupling and a larger orbital component than the parent compound \(\alpha\)-Li\(_2\)IrO\(_3\). Resonant Inelastic X-ray Scattering (RIXS) spectra probing the Ir electronic structure of Ag\(_3\)LiIr\(_2\)O\(_6\) is captured by incorporating Ir-O hybridization, demonstrating that the local \(j_{\text{eff}} = 1/2\) picture is not a valid basis. Ag\(_3\)LiIr\(_2\)O\(_6\) must be understood as a new type of nearly itinerant model quantum magnet. We posit that similar effects may be at play in other intercalated honeycomb iridates. Our results provide an empirical foundation to develop suitable effective Hamiltonians in these next-generation frustrated magnets.

High crystalline quality powder samples of Ag\(_3\)LiIr\(_2\)O\(_6\), \(T_N = 8\) K, and \(\alpha\)-Li\(_2\)IrO\(_3\) were from the same clean batch as in [19]. Samples of Sr\(_3\)CaIr\(_2\)O\(_9\) were prepared as described in [21]. RIXS was performed at Sector 27 (MERIX) at the Advanced Photon Source (APS) of the Argonne National Laboratory [22]. We used a horizontal \(290^\circ\) scattering geometry, with a 2 m radius spherically diced Si(844) analyzer to give a 33 meV overall energy resolution (full width at half maximum, FWHM). Powder diffraction was conducted at APS 11-ID-B using wavelength of 0.2115 Å and sample to detector distance of 167.335 mm, calibrated with a ceria standard. The 2D diffraction data were integrated using GSAS-II and then corrected and normalized to obtain the atomic pair distribution function (PDF), \(G(r)\) using PDFgetX3 [23]. X-ray absorption near edge structure (XANES), far edge (EXAFS), and x-ray magnetic circular dichroism (XMCD) were performed in transmission at APS 4-ID-D. XAS and EXAFS data were analyzed using the Larch [24] and FEFF [25] software packages. Magnetic field and temperature were controlled using a 6.5 T LHe cooled magnet system. XMCD magnetic circular polarization was generated using a 500 µm diamond phase plate.

In Fig. 1 (a) and (b) we show the normalized absorption intensity at the Ir L\(_3\) and L\(_2\) edge respectively. Both the relative position of the L\(_3\) white line inflection points and the L-edge sum rules provide quantitative information on the oxidation state of a transition metal ion [26–28]. To extract this information, we fit the normalized data to an arctangent step and Lorentzian peak [29]. The results of our analysis are summarized in Table I. The inset of Fig. 1 shows a direct comparison of the white line measured in Ag\(_3\)LiIr\(_2\)O\(_6\), \(\alpha\)-Li\(_2\)IrO\(_3\) (5d\(^6\)), and Sr\(_3\)CaIr\(_2\)O\(_9\) (5d\(^4\)) [21]. In Ag\(_3\)LiIr\(_2\)O\(_6\), we find \(\langle n_h \rangle = 5.5(2)\) by averaging the results obtained from white line inflection points and integrated intensities. This deviates from \(\langle n_h \rangle = 5\) expected for a localized \(j_{\text{eff}} = 1/2\) state [20]. We also find a branching ratio, \(BR = I_{L_3}/I_{L_2} = 5.7(4)\) that is comparable to that of \(\alpha\)-Li\(_2\)IrO\(_3\); confirming that spin-orbit coupling is a dominant energy scale in Ag\(_3\)LiIr\(_2\)O\(_6\) [3, 30, 31].

If the hole concentration extracted from the XAS analysis is interpreted to arise from a Ir\(^{4+}\)/Ir\(^{5+}\) mixture, it implies that 50% of the Ir are in a non-magnetic \(j = 0\) state. Such a large fraction of Ir\(^{5+}\) is not consistent with chemical analysis or the measured paramagnetic moment of \(\mu_{\text{eff}} = 1.8\mu_B/\text{Ir} [19]\) and our XAS measurements at the Ag L\(_3\)-edge, which restrict Ag to the 1+ oxidation state [20]. Moreover, we find a six orders of magnitude reduction in low temperature resistivity of Ag\(_3\)LiIr\(_2\)O\(_6\) compared with \(\alpha\)-Li\(_2\)IrO\(_3\) [20]. Thus, the more plausible explanation is that the increased electronegativity of Ag over Li results in a larger inductive effect on Ir, bringing Ir away from half-filling. This is consistent with an increase in Ir-O hybridization in Ag\(_3\)LiIr\(_2\)O\(_6\) when compared to \(\alpha\)-Li\(_2\)IrO\(_3\) as found by LDA+U calculations [32].

Metal ligand hybridization is known to affect the magnetism in transition-metal oxides [33–36]. We performed XMCMD at the Ir L\(_3\) edges with \(H=5\) T and \(T=1.6\) K in order to understand the influence of the charge redistribution on the magnetism [Fig. 1 (c) – (d)]. XMCMD measures the projection of the magnetic moment along the x-ray helicity, set to be parallel to the magnetic field direction. We find that the XMCMD signal at the L\(_3\) edge is reduced in Ag\(_3\)LiIr\(_2\)O\(_6\) compared with \(\alpha\)-Li\(_2\)IrO\(_3\). This may be related to a reduction in the on-site Ir moment, or to differences in the in-field magnetic structure between these two compounds. We apply XMCMD sum rules to find orbital \(\langle L_z \rangle\) spin \(\langle S_z \rangle\), and intra-atomic magnetic dipole moment \(T_z\) contributions [37–39]. For a single \(j_{\text{eff}} = 1/2\) hole one expects
Int. (cts/s) \[\langle L_z \rangle/2 \langle S_z \rangle = 2 \] \[40\]. Small departures from the ideal values arising from non-cubic crystal fields and covalency are common in iridates \[41–43\], but we find even larger differences for \(\text{Ag}_3\text{LiIr}_2\text{O}_6\). Sum rule analysis using the measured \(\mu(\text{H} = 5\text{T}) \approx 0.05 \mu_\text{B}/\text{Ir} \) moment for \(\alpha\text{-Li}_2\text{IrO}_3 \[44\] gives \(\langle L_z \rangle = -0.028(1) \mu_\text{B}/\text{Ir} \) and \(\langle S_z \rangle = -0.011 \mu_\text{B} \) and \(\langle L_z \rangle/2 \langle S_z \rangle = 1.27 \) and \(7\langle T_z \rangle/2 \langle S_z \rangle = 1\). For \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) we find \(\langle L_z \rangle = -0.018(3) \mu_\text{B}/\text{Ir} \) and \(\langle S_z \rangle = -0.002(3) \mu_\text{B} \), using \(\langle n_b \rangle = 5.5(2)\) and the measured moment of \(\mu(\text{H} = 5\text{T}) = (\langle L_z \rangle + 2 \langle S_z \rangle) = 0.022(5) \mu_\text{B} \) \[19, 20\]. These values lead to \(\langle L_z \rangle/2 \langle S_z \rangle = 2.6 - 4.5\) and \(7\langle T_z \rangle/2 \langle S_z \rangle = 1.85 - 6.15\). The minimum twofold enhancement of the fractional contribution of \(\langle L_z \rangle\) to the total moment in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) further rules out \(\text{Ir}^{5+}\) \(j = 0\) states where \(\langle L_z \rangle/2 \langle S_z \rangle = 0.5\), and establishes the orbital nature of magnetism. Large values of \(T_z\) are associated with aspherical spin density originating from non-cubic fields, spin-orbit coupling, and electron delocalization due to metal-ligand hybridization \[45–47\]. To quantify departures from a cubic Ir environment, we carefully examined the local structures of \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) using x-ray PDF and EXAFS measurements \[Fig. 2\]. Both measurements are independently consistent with the reported \(C2/m\) space group \[14\] over a broad \(r\)-range. We find distortions of the Ir environment, with Ir-O distances ranging from 2.021 to 2.119 Å, and Ir-O-Ir bond angles of 92.38° and 95.72° \[20\]. While the associated trigonal fields in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) are larger than in \(\alpha\text{-Li}_2\text{IrO}_3\), the 5% difference in Ir-O bond distance is not enough to account for the minimum 80% enhancement of \(7\langle T_z \rangle/2 \langle S_z \rangle\). We thus assign differences in the magnetism of \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) to an increased delocalization of the Ir 5d electrons over the ligands \[46\].

Having found that the magnetism in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) is characterized by a more delocalized electron density, we performed RIXS measurements to better understand the Ir electronic structure. \(\text{Fig. 3 (a),}\) shows the \(T = 20\text{ K}\) RIXS signal in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) as a function of incident energy, \(E_i\) and energy transfer, \(E_{\text{loss}}\). Thompson scattering has a vanishing cross-section in our 90 degree scattering configuration, thus any phonon contribution to the RIXS signal is minimal. The broad and intense features centered at \(E_{\text{loss}} \approx 3.8 \text{ eV}\), originate from \(t_{2g} \rightarrow e_g\) transitions, consistent with the strong crystal field limit, \(10Dq > 3 \text{ eV}\) \[16, 48–50\]. For the remainder of this work, we concentrate on the intra-\(t_{2g}\) excitations, \(E_{\text{loss}} \leq 1.5 \text{ eV}\). \(\text{Fig. 3 (b)}\) shows a representative RIXS spectrum of \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) at \(E_i = 11.215 \text{ keV}\). In order to analyze the experimental data, we fit eight Gaussian peaks: \(A = 0.029(25), B = 0.270(37), C = 0.470(60), D = 0.623(69), E = 0.811(58), F = 1.010(109), G = 1.300(153), H = 1.654(150) \text{ eV}\) and include a resolution limited Voigt function for the elastic line \[20\]. The RIXS spectrum of \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) is distinct from an ideal local \(j_{\text{eff}} = 1/2\) state, where only a single excitation between the \(j = 3/2\) quartet and 1/2 doublet appears at \(\Delta E = 3\lambda/2 \approx 0.75 \text{ eV}\), where \(\lambda\) is the spin orbit coupling constant. \(\Delta E_{D-E} = 0.19(4) \text{ eV}\) is larger than the corresponding 0.11(3) \text{ eV} splittings in \(\alpha\text{-Li}_2\text{IrO}_3\) and \(\text{Na}_2\text{IrO}_4\) \[49\], consistent with a more trigonally distorted environment. However, non-cubic crystal fields (CF) cannot reconcile the RIXS spectra with a single-site \(\text{Ir}^{4+}\) model that can at most produce two RIXS features for \(E_{\text{loss}} < 1 \text{ eV}\) \[20\].

The energy of \(A\), \(E_{\text{loss}}^A = 29 \text{ meV}\), is consistent with collective magnetic excitations observed in other iridates \[51–55\]. We find that the intensity of peak \(A\) follows detailed balance; but there is no correlation with the Curie-Weiss temperature \(\theta_{\text{CW}} = -132 \text{ K}\) \[19\], ruling out a spin wave origin \[20\]. Peak \(C\), \(E_{\text{loss}}^C = 470 \text{ meV}\), is suggestive of the electron-hole exciton in \(\text{Na}_2\text{IrO}_3\), \(\alpha\text{-Li}_2\text{IrO}_3\), and \(\text{Sr}_2\text{IrO}_4\) \[49, 56\]. Peak \(B\), \(E_{\text{loss}}^B = 0.279 \text{ eV}\), is more puzzling. A similar feature in other \(\text{Ir}^{4+}\) compounds was associated with \(\text{Ir}^{5+}\) impurities based on qualitative arguments, but the relative intensity of this feature rules out an origin from the \(< 1\% \text{ off-stoichiometries in our sample, as constrained by chemical analysis}\) \[19, 20\].

Our XAS and XMCD measurements indicate strong Ir-O hybridization in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\). Thus, we consider a

\(\text{FIG. 3. (a) Ir L}_3\) RIXS intensity as a function of \(E_i\) and \(E_{\text{loss}}\) in \(\text{Ag}_3\text{LiIr}_2\text{O}_6\) at \(T = 20 \text{ K}\). Vertical dotted lines indicate the \(E_{\text{loss}}\) range for (b). Horizontal dotted lines are color coded according to the RIXS spectrum in (b). (b) Representative RIXS spectrum at \(E_i = 11.215 \text{ keV}(\text{black markers})\) and fit to the data (\(\text{black solid line}\)) with Gaussian peaks (grey shaded) and Voigt elastic line (dotted), as described in the main text. Blue markers show the RIXS spectrum at \(E_i = 11.221 \text{ keV}\). Inset shows the integrated intensity of features \(B, \) \(D\) and \(E\) as a function of \(E_i\).
FIG. 4. Calculated energy spectrum of Ag$_3$LiIr$_2$O$_6$ as a function of (a) $t_O$, (b) $\delta$ and (c) $t_\parallel$ with $\lambda = 0.395$ eV, $U = 2$ eV, $J_H = 0.3$ eV, $t_o = -t_\parallel$, and $t_\perp = -0.05 t_\parallel$. Horizontal dashed line and grey boxes represent the center energy and FWHM of the extracted inelastic peaks. The color map indicates agreement of the calculation with the experimental data as encoded by the quality factor (QF). (d) Simulated RIXS spectrum for the best parameters compared to the measured intensity.

The delocalized magnetic state in Ag$_3$LiIr$_2$O$_6$ has important implications for the magnetism of intercalated iridates. In Ag$_3$LiIr$_2$O$_6$, the paramagnetic moment $\mu_{\text{eff}}$ is 1.87 $\mu_B$/Ir [14, 19] agrees with the expected 1.74 $\mu_B$/Ir for $j_{\text{eff}} = 1/2$. Muon spin resonance measurements also find oscillations characteristic of incommensurate magnetic order, similar to that of $\alpha$-Li$_2$IrO$_3$, hinting at a common origin of the magnetism [19, 36]. Our finding of an asymmetric spin density and large orbital contribution warrants a more nuanced interpretation. The fundamental magnetic unit in Ag$_3$LiIr$_2$O$_6$ is an extended and anisotropic electron density over Ir and O sites [60] that will promote long-range and possibly anisotropic interactions. The result is a greater magnetic frustration with enhanced Curie-Weiss, but similar ordering temperatures to the parent $\alpha$-Li$_2$IrO$_3$ [14, 19]. Thus, itinerancy could-of-
fer another possible route to spin liquids in iridates. The spatially extended spin density also has consequences for neutron scattering measurements, as the magnetic form-factor of such a state will depart significantly from the localized limit. In order to interpret magnetic measurements, more detailed studies of the effective magnetic Hamiltonians for such a delocalized state are needed [18].

In summary, we have used a suite of x-ray spectroscopies to find that intercalation of Ag atoms on inter honeycomb layer sites in α-Li$_2$IrO$_3$ promotes Ir-O hybridization and alters the magnetism. Our data and analysis suggest that the electronic structure Ag$_3$Ir$_2$O$_6$ is nearly itinerant, a result of a more trigonally distorted Ir environment and enhanced hopping integrals. The magnetism is characterized by a delocalized asymmetric spin density and large orbital moment that is drastically different from the parent compound. Magnetic frustration is enhanced indicating itineracy may offer an alternative route to spin liquids in the iridates. This phenomenology may extend to other intercalated versions of the honeycomb iridates and our results provide a foundation to develop effective magnetic Hamiltonians for these compounds.

We thank Mark Dean for helpful discussions and for his critical reading of this manuscript. Work at Brown University was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC002165. The work at Boston College was supported by the National Science Foundation under award No. DMR–1708929. TMM and JC acknowledge support from the Institute for Quantum Matter, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE-SC0019331. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

* kemp_plumb@brown.edu

[1] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. 102, 017205 (2009).
[2] I. I. Mazin, H. O. Jeschke, K. Foyevtsova, R. Valentí, and D. I. Khomskii, Phys. Rev. Lett. 109, 197201 (2012).
[3] K. Foyevtsova, H. O. Jeschke, I. I. Mazin, D. I. Khomskii, and R. Valentí, Phys. Rev. B 88, 035107 (2013).
[4] J. Chaloupka, G. Jackeli, and G. Khaliullin, Phys. Rev. Lett. 105, 027204 (2010).
[5] Y. Singh and P. Gegenwart, Phys. Rev. B 82, 064412 (2010).
[6] Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, and P. Gegenwart, Phys. Rev. Lett. 108, 127203 (2012).
[7] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, Phys. Rev. B 90, 041112 (2014).
[8] A. Banerjee, J. Yan, J. Knolle, C. A. Bridges, M. B. Stone, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, R. Moessner, and S. E. Nagler, Science 356, 1055 (2017).
[9] A. Banerjee, C. A. Bridges, J.-Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yu, J. Knolle, S. Bhattacharjee, D. L. Koprivizin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, Nature Materials 15, 733 (2016).
[10] J. G. Rau, E.-H. Lee, and H.-Y. Kee, Phys. Rev. Lett. 112, 077204 (2014).
[11] J. G. Rau and H.-Y. Kee, “Trigonal distortion in the honeycomb iridates: Proximity of zigzag and spiral phases in Na$_2$IrO$_3$,” (2014), arXiv:1408.4811 [cond-mat.str-el].
[12] M. Abramchuk, C. Ozsoy-Keskinbora, J. W. Krizan, K. R. Metz, D. C. Bell, and F. Tafti, Journal of the American Chemical Society 139, 15371 (2017).
[13] K. Kitagawa, T. Takayama, Y. Matsumoto, A. Kato, R. Takano, Y. Kishimoto, S. Bette, R. Dinnebier, G. Jackeli, and H. Takagi, Nature 554, 341 (2018).
[14] F. Bahrami, W. Lafargue-Dit-Hauret, O. I. Lebedev, R. Movshovich, H.-Y. Yang, D. Broide, X. Rocquefelte, and F. Tafti, Phys. Rev. Lett. 123, 237203 (2019).
[15] I. I. Mazin, S. Manni, K. Foyevtsova, H. O. Jeschke, P. Gegenwart, and R. Valentí, Phys. Rev. B 88, 035115 (2013).
[16] J. P. Clancy, H. Gretarsson, J. A. Sears, Y. Singh, S. Desgreniers, K. Mehlawat, S. Layek, G. K. Rozenberg, Y. Ding, M. H. Upton, D. Casa, N. Chen, J. Im, Y. Lee, R. Yadav, L. Hozoi, D. Efremov, J. van den Brink, and Y.-J. Kim, npj Quantum Materials 3, 35 (2018).
[17] R. Yadav, R. Ray, M. S. Eldeeb, S. Nishimoto, L. Hozoi, and J. van den Brink, Phys. Rev. Lett. 121, 197203 (2018).
[18] Y. Li, S. M. Winter, and R. Valentí, Phys. Rev. Lett. 121, 247202 (2018).
[19] F. Bahrami, E. M. Kenney, C. Wang, A. Berlie, O. I. Lebedev, M. J. Graf, and F. Tafti, Phys. Rev. B 103, 094427 (2021).
[20] “See supplementary information.”.
[21] D. C. Wallace and T. M. McQueen, Dalton Trans. 44, 20344 (2015).
[22] Y. Shvyd’ko, J. Hill, C. Burns, D. Coburn, B. Brasjus’kovic, D. Casa, K. Goetze, T. Gog, R. Khachatriyan, J.-H. Kim, C. Koditwakkulu, M. Ramanathan, T. Roberts, A. Said, H. Sinn, D. Shu, S. Stoupin, M. Upton, M. Wieczorek, and H. Yavas, Journal of Electron Spectroscopy and Related Phenomena 188, 140 (2013).
[23] P. Juhás, T. Davis, C. L. Farrow, and S. J. L. Billinge, Journal of Applied Crystallography 46, 560 (2013).
[24] M. Newville, Journal of Physics: Conference Series 430, 012007 (2013).
[25] J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, and F. Vila, Comptes Rendus Physique 10, 548 (2009).
[26] F. M. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B 42, 5459 (1990).
[27] J. P. Clancy, N. Chen, C. Y. Kim, W. F. Chen, K. W. Plumb, B. C. Jeon, T. W. Noh, and Y.-J. Kim, Phys. Rev. B 86, 195131 (2012).
[28] M. A. Laguna-Marco, P. Kayser, J. A. Alonso, M. J. Martinez-Lope, M. van Veenendaal, Y. Choi, and D. Haskel, Phys. Rev. B 91, 214433 (2015).
[29] C. Donnerer, M. M. Sala, S. Pascazelli, A. D. Rosa, S. N. Plumb@brown.edu
Here we provide additional technical details describing:

1. \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) chemical characterization.
2. Temperature dependent resistivity in \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) and \( \alpha\text{-Li}_2\text{IrO}_3 \).
3. Analysis and fitting of x-ray absorption data.
4. Temperature dependence of XAS spectra.
5. XAS at the \( \text{Ag} L_3 \)-edge in \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \).
6. Additional RIXS data for \( \text{Ir}^{4+} \) and \( \text{Ir}^{5+} \) compounds.
7. Temperature dependence of the RIXS spectra.
8. Details of the EXAFS refinements.
9. Comparison of bulk magnetisation and XMCD signal as a function of field.
10. Structural parameters of \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) refined from pair distribution and EXAFS measurements.
11. The crystal field Hamiltonian used for treatment of crystals field excitations in the RIXS spectra.
12. Details of Slater integrals used for single site calculation.
13. The tight bonding Hamiltonian used to model the RIXS spectra including electron hopping.
14. Role of Hund’s coupling, \( J_H \), and electron-electron correlations, \( U \), in the calculated RIXS spectrum.
15. Details of the quality factor used to optimize parameters of our tight binding model against the measured RIXS spectra.
16. Procedure for computing the powder (spherically) averaged RIXS spectra.

**Ag\(_3\)LiIr\(_2\)O\(_6\) CHEMICAL CHARACTERIZATION**

In Fig. S1, we show the energy-dispersive x-ray spectroscopy (EDX) spectrum averaged from three different spots on a pellet sample of \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) from the same batch of sample used for our RIXS and XAS measurements. This is also the same high quality sample used in [1]. The mol ratio between Ag and Ir is \( \text{Ag/Ir} = 1.486(1) \), as expected from the chemical formula. Although a more precise characterization of this ratio is hindered by the sensitive of the EDX technique, our measurements indicate that to keep charge balance the maximum amount of \( \text{Ir}^{5+} \) is limited to \( 0.2\% \). This is also consistent with the extracted paramagnetic moment of \( \mu = 1.87(2)\mu_B \) from magnetic susceptibility, [1]. The presence of off-stochiometric \( \text{Ir}^{5+} \), would result in a reduced paramagnetic magnetic moment. Within the error bars of our magnetization measurements and assuming \( g \approx 2.4 \) to account for the large moment when compared to that of a pure \( J_{eff} = \frac{1}{2} \) groundstates [2], we can rule out \( \text{Ir}^{5+} > 1\% \).

**RESISTIVITY COMPARISON**

Fig. S2 shows the measured resistivity of pelletized powder samples of \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) and \( \alpha\text{-Li}_2\text{IrO}_3 \). Both compounds are insulating, with room temperature resistivities of the order Ohm · cm. However, below 200 K, the resistivity of \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) becomes six orders of magnitude smaller than \( \alpha\text{-Li}_2\text{IrO}_3 \). The significantly reduced resistivity of \( \text{Ag}_3\text{LiIr}_2\text{O}_6 \) strongly supports the conclusion of a more covalent Ir state, as observed by XAS and RIXS, with a larger Ag-mediated hybridization between Ir and O orbitals.
DETAILS OF THE XAS ANALYSIS

XAS data was analyzed using the Larch software package [3]. Data was normalized using standard protocols by first fitting both the pre-edge region and the post-edge region to a linear term. The step height was found as the difference between the two fitted lines at the edge position. The edge position $E_0$ was found from the inflection point of the data. Following established procedures, the pre-edge fit was subtracted from the data, which was then normalized to step heights of 1 and $\frac{1}{2}$ for the L3 and L2 edges respectively. Finally, a quadratic fit to the post-edge region was subtracted to obtain the fully normalized data. The normalized data was subsequently fitted to an arctangent step and Lorentzian peak to extract the parameters of the white line. This is shown in Fig. S3 the normalized XAS data for Ag$_3$LiIr$_2$O$_6$, α-Li$_2$IrO$_3$ (4+) and Sr$_3$CaIr$_2$O$_9$ (5+).

The number of holes, $\langle n_h \rangle$, in the 5$d$ orbitals can be calculated from the XAS sum rule: $I_{L3} + I_{L2} = \langle n_h \rangle C$, with $C$ a proportionality constant [4]. Additionally, a monotonic trend of the position of the inflection point of the L$_3$ absorption edge towards higher energies with increasing number of holes has been observed in iridates [5]. By fitting the data to a $y = y_0 + Ax$ we find for the sum rule $\langle n_h \rangle = 5.5(2)$ while $\langle n_h \rangle = 5.4(2)$ for the position of the inflection points. We calculated $\langle n_h \rangle = 5.5(2)$ for Ag$_3$LiIr$_2$O$_6$ by averaging the results using these two approaches in Fig. S4 (a) and (b), with α-Li$_2$IrO$_3$ $\langle n_h \rangle = 5$ and Sr$_3$CaIr$_2$O$_9$ $\langle n_h \rangle = 6$.

The branching ratio $BR = I_{L3}/I_{L2}$ extracted from numerical integration and calculated from the fit parameters is shown in Fig. S4 (c) compared to the statistical value (black dashed line). The BR remains larger than the statistical BR signifying the importance of spin-orbit coupling for the three compounds.

XAS TEMPERATURE DEPENDENCE

In Fig. S5, we show the Ag$_3$LiIr$_2$O$_6$ XAS data at $T=300$ K and $T=9$ K at the L$_3$, (a), and L$_2$, (b), absorption edges. We observe no temperature dependence of the BR, (c), and , (d), inflection point of the L$_3$ white line.

Ag L$_3$ EDGE XAS

In Fig. S6 (a), we show $T=300$ K XAS data collected at the Ag L$_3$ edge of our Ag$_3$LiIr$_2$O$_6$ sample. Data were collected in a partial yield fluorescence geometry using a four-element Si-drift diode. The intensity of the white line peak can be related to the number of holes in the Ag 4$d$ orbitals and the degree of covalence of the Ag bonds [6]. The data shows a characteristic absorption peak for
Ag 1+ at $E_1 = 3.349$ keV, with comparable intensity to the post edge features. The XAS spectrum and the intensity of this absorption feature in Ag$_3$LiIr$_2$O$_6$, $I_{L3} = 0.87(3)$, resemble those of Ag$_2$O [7], Fig. S6 (b) and we conclude from this data that Ag is in the 1+ oxidation state in Ag$_3$LiIr$_2$O$_6$, further ruling out Ir$^{5+}$ impurities.

**FIG. S6.** (a) Representative normalized XAS data of Ag$_3$LiIr$_2$O$_6$ at the Ag L$_3$ at $T = 300$ K, (b) compared to that of Ag (0$^+$), Ag$_2$O (1$^+$) and AgO (2$^+$) adapted from [7]. Spectra were vertically shifted for clarity and horizontal to match the white line position.

**FIG. S7.** Direct comparison of the RIXS spectrum at resonance, $E = 11.215$ keV, between Ag$_3$LiIr$_2$O$_6$ (orange), Sr$_3$CaIr$_2$O$_9$ (yellow) measured under the same experimental circumstances, and $\alpha$-Li$_2$IrO$_3$ (blue) adapted from [12]. The data for $\alpha$-Li$_2$IrO$_3$ has been scaled by an arbitrary factor for qualitative comparison.

**FIG. S5.** (a),(b) Representative normalized XAS data of Ag$_3$LiIr$_2$O$_6$ at the L$_{3,2}$ at $T = 300$ K and $T = 9$ K. Temperature dependence of the (c) BR and (d) inflation point of the L$_3$ magnetic species [9]; in an iridium fluoride with two nonequivalent Ir sites, Na$_2$IrF$_6$ [10]; and in the dimer material Ba$_3$AlIr$_2$O$_{11}$ [11]. We note that in each case mentioned above this assignment was based on qualitative comparison and that no previous quantification of this signal has been reported. We now rule out the possibility of an Ir$^{5+}$ RIXS signal in Ag$_3$LiIr$_2$O$_6$ based on a direct comparison of the RIXS cross-section with a known Ir$^{3+}$ standard.

**COMPARISON OF RIXS SIGNAL IN Ir$^{4+}$ AND Ir$^{3+}$ COMPOUNDS**

As discussed in the main text, an inelastic feature near 300 meV has previously been observed and assigned to Ir$^{5+}$ impurities in a highly distorted Ir$^{4+}$ double perovskites Sr$_2$CeIrO$_6$ [8]; Sr$_3$NiIrO$_6$, a compound with two

In Fig. S7, we show RIXS spectrum at $E_{in} = 11.215$ keV for both Ag$_3$LiIr$_2$O$_6$ and Sr$_3$CaIr$_2$O$_9$, a model Ir$^{5+}$ compound. The measurements were collected consecutively under identical experimental conditions and therefore provide a direct quantification of the relative contributions of Ir$^{4+}$ and Ir$^{5+}$ to the RIXS cross-section. As expected for Ir $d^4$ in an IrO$_6$ octahedral environment, the low energy RIXS spectrum of Sr$_3$CaIr$_2$O$_9$ is characterized by an inelastic feature at $E_{loss} = 330(25)$ meV and a broader peak at $E_{loss} = 600(50)$ meV, similar to other Ir$^{5+}$ compound [13, 14]. We note that these RIXS features in Ir$^{5+}$ compounds are not sensitive to distortions of the IrO$_6$ octahedra [14].

The scattering volume is the same between samples and the total cross-section scales with the number of scattering nuclei in the unit cell volume $N = n/V$. In Sr$_3$CaIr$_2$O$_9$, $N = 0.0101$ and in Ag$_3$LiIr$_2$O$_6$ $N = 0.013$. 

Thus, we can use the integrated intensity of the 330 eV peak in Sr₃CaIr₂O₈ to estimate the molar percentage of Ir ⁵⁺ required to produce a corresponding RIXS signal in Ag₃LiIr₂O₆ I(B). We find that $I_{\text{SrCa}}^{\text{300}} = 24(1)$ cts/s and correspondingly $\approx 20\%$ Ir ⁵⁺ in Ag₃LiIr₂O₆ would be required to produce the measured intensity of $I(B) = 4.8(2)$ cts/s. This is two orders of magnitude greater than the Ir⁵⁺ concentration allowed by chemical characterization and magnetic susceptibility measurements. Thus, while we cannot rule out Ir⁵⁺ impurities at the level of 1% or less, such a small impurity concentration will only have a negligible contribution and cannot account for the measured RIXS signal.

Additionally, in Fig. S7 we also reproduce α-Li₂IrO₃ RIXS, adapted from [12]. We remark that the difference in the low energy features with respect to Ag₃LiIr₂O₆ are not restricted to the large splitting between peaks D and E and a clear peak B, but also to much more defined F and G features.

RIXS TEMPERATURE DEPENDENCE

In Fig. S8 (a) – (b) we show a magnified region of the RIXS data near the elastic line for $T = 20$ K and $T = 300$ K. Within the energy range $E_{\text{loss}} \in [-100, 100]$ meV we fit the data to a resolution limited Voigt line (blue line) and a Gaussian peak for feature A constrained by detailed balance (black line). No temperature dependence of the FWHM (c), centroid (d), or intensity (f) is observed for Peak A.

We observe an increase of intensity in the elastic line with decreasing temperature. At $2\theta = 90^\circ$ we are in the proximity of structural Bragg peaks, for example [2, 8, −6] at $2\theta = 89.77^\circ$ at $\lambda = 1.1055$ Å. Thus, it is likely that this increased elastic intensity is a result of lattice parameters contractions which bring the tail of the Bragg peak into the measurement window, but a weak magnetic signal is also a possibility.

We show in Fig. S9 the RIXS intensity of Ag₃LiIr₂O₆ as a function of temperature. We observe a stronger temperature dependence of the intensity of peaks D–E than that of peaks A–C, similar to that of other iridates [10]. The broadening in energy and decrease of intensity with increasing temperature dependence may be related to Debye Waller factors [15]. This does not affect the analysis presented in the main text.

DETAILS OF EXAFS REFINEMENTS

In Fig. S10 (a) – (b) we show the magnitude of the Fourier transform of the EXAFS oscillations measured at $T = 300$ K and $T = 9$ K. The red line is the magnitude of a fit to the Fourier transform of $k^2\chi(k)$. The Fourier Transform was performed in the range $k = 3 − 15$ Å⁻¹ by applying a Kaiser window of width $\Delta k = 12$ Å⁻¹ with tapering $\delta k = 4$ Å⁻¹. The fit was then performed in real space in the range $r = 1.1 − 4.1$ Å using least-squares minimization. The fit parameters are $E_0$, which fixes the $k = 0$ point for all paths, an amplitude reduction factor $S_0^2$, which is an overall scale factor and the respective shift in path length $\delta r$ and mean-square displacement $\sigma^2$ for each each path of nominal length $r$. The fit includes single scattering paths calculated by the FEFF software package [16] using the refined structure from PDF measurements as initial input. The paths include the nearest-neighbor Ir-O bonds, nearest-neighbor Ir-Ir bonds, nearest-neighbor Ir-Ag bonds and next-nearest neighbor Ir-O bonds. We excluded the Ir-Li paths from the fit due to the large mean-square displacement of Li.
FIG. S9. RIXS intensity at $E_i = 11.215$ keV as a function of temperature.

MAGNETIC FIELD DEPENDENCE OF THE NET MOMENT AND XMCD SIGNAL AT BASE TEMPERATURE

In Fig. S11 we compare the extracted net moment from bulk magnetization measurements at $T = 2$ K and the $L_3$ XMCD signal at $T = 1.6$ K as a function of magnetic field. Both magnitudes follow a linear trend with field.

REFINED STRUCTURAL PARAMETERS FROM PDF AND EXAFS

We show in Table S2 the refined atomic positions from the PDF analysis and in and Table S3 local structural parameters from the PDF and EXAFS analysis.

| Atom | Site | x    | y    | z    |
|------|------|------|------|------|
| Ir   | 4g   | 0.000| 0.334(1)| 0.000|
| Li   | 2a   | 0.000| 0.000| 0.000|
| O    | 4i   | 0.404(9)| 0.000| 0.187(8)|
| O    | 8j   | 0.393(9)| 0.323(7)| 0.178(5)|
| Ag   | 4h   | 0.500| 0.336(2)| 0.500|
| Ag   | 2d   | 0.500| 0.000| 0.500|

TABLE S2. Summary of structural parameters from the PDF refinement over the range $1.2 < r < 12$ Å. The room temperature cell was refined in the $C2/m$ space group to give $a=5.344(5)$ Å, $b=9.012(8)$ Å, $c=6.468(3)$ Å , and $\beta = 105.39(8)^\circ$. All sites are fully occupied.

TREATMENT OF THE TRIGONAL FIELDS

For the complete basis of the spherical harmonic $(Y^2_2, Y^1_2, Y^0_2, Y^{-1}_2, Y^{-2}_2)$ the crystal field Hamiltonian including cubic and trigonal can be written as:
TABLE S3. Summary of the local structural parameters from the PDF and EXAFS analysis. The room temperature structural cell was refined in the C2/m spacegroup to give a=5.343, b=9.015, c=6.468, \( \beta = 105.385 \). All sites are fully occupied.

| Bond      | PDF (Å) | EXAFS (Å) |
|-----------|---------|-----------|
| Ir\(_{1}\)-O\(_{1}\) | 2.021   | 1.954     |
| Ir\(_{1}\)-O\(_{2}\) | 2.119   | 2.050     |
| Ir\(_{1}\)-O\(_{3}\) | 2.074   | 2.006     |
| Ir\(_{1}\)-Ag\(_{1}\) | 3.564   | 3.588     |
| Ir\(_{1}\)-Ag\(_{2}\) | 3.580   | 3.605     |
| Ir\(_{1}\)-Ag\(_{3}\) | 3.607   | 3.632     |
| Ir\(_{1}\)-Ir\(_{2}\) | 2.994   | 3.000     |
| Ir\(_{1}\)-Ir\(_{3}\) | 3.071   | 3.078     |

\[ H^{D_{s=0}}_{CF} = \begin{pmatrix} a_{0,0} & 0 & 0 & a_{0,3} & 0 \\ 0 & a_{1,1} & 0 & 0 & a_{1,4} \\ 0 & 0 & a_{2,2} & 0 & 0 \\ a_{3,0} & 0 & 0 & a_{3,3} & 0 \\ 0 & a_{4,1} & 0 & 0 & a_{4,4} \end{pmatrix} \]  

(S1)

with:

\[ a_{0,0} = a_{4,4} = -3C_p P_1(\alpha) + (3/14)D_q P_2(\alpha), \]

(S2a)

\[ a_{0,3} = a_{3,0} = -a_{1,4} = -a_{4,1} = 15D_q \sin \alpha^3 \cos \alpha, \]

(S2b)

\[ a_{1,1} = a_{3,3} = (3/2)C_p P_1(\alpha) - (6/7)D_q P_2(\alpha), \]

(S2c)

\[ a_{2,2} = 3C_p P_1(\alpha) + (9/7)D_q P_2(\alpha), \]

(S2d)

and \( P_1(\alpha) = 3 \cos \alpha^2 - 1 \) and \( P_2(\alpha) = 35 \cos \alpha^4 - 30 \cos \alpha^2 + 3 \). \( \alpha = \arctan(\sqrt{2}\frac{r_{\text{Ir}-\text{O}}}{r_{\text{Ir}-\text{Ir}}}) \) parameterizes the size of the trigonal distortion, with \( \alpha_0 = 54.74^\circ \) for a perfect octahedral environment. \( D_q \) encodes the cubic crystal fields and gives the splitting between \( \epsilon_2 \) and \( t_{2g} \) levels. \( C_p \) is the value of the non-cubic crystal fields due to trigonal distortion and follows \( C_p = \frac{\kappa}{25}D_q \kappa \) with \( \kappa = \sqrt{2}\frac{r_{\text{Ir}-\text{O}}}{r_{\text{Ir}-\text{Ir}}} \). \( ab\text{-initio} \) calculations give a realistic upper bound of \( \kappa = 1 \) [17, 18]. Notice that \( \alpha = \alpha_0 \) cancels the terms proportional to \( C_p \).

We show in Fig. S12 dependence of \( \Delta E_{D-E} \) as a function of \( \frac{r_{\text{Ir}-\text{O}}}{r_{\text{Ir}-\text{Ir}}} \) for different values of \( C_p \) keeping \( D_q = 0.44 \text{ eV} \) and the spin-orbit coupling strength \( \lambda = 0.37 \text{ eV} \) constant. The observed \( \Delta E_{D-E} = 0.19(4) \text{ eV} \) in \( \text{Ag}_3\text{Li}_2\text{Ir}_2\text{O}_6 \) can be reproduced for \( C_p = -0.3 \text{ eV} \). However, this value gives a ratio \( C_p/D_q = 0.68 \) that is much larger than the upper limit from \( ab\text{-initio} \) calculations for \( 5d\text{-electrons} C_p/D_q = 0.17, \) [17, 18]. In general, the magnitude \( \Delta E_{D-E} \) depends strongly on bond length disproportionation and weakly on \( C_p \) and \( D_q \) [19]. Fixing \( C_p = -0.05 \text{ eV}, C_p/D_q < 0.17, \) we find that to account for the experimentally observed \( D-E \) splitting in \( \alpha\text{-Li}_2\text{Ir}_3\text{O}_3 \), \( \Delta E_{\text{trig}} = 0.10(3) \text{ eV} \), we need to consider an artificially large bond disproportionation, twice as large as the reported value [12]. For \( \text{Ag}_3\text{Li}_2\text{Ir}_2\text{O}_6 \) the observed \( D-E \) splitting requires a \( > 10\% \) Ir-O bond disproportionation, exceeding the range admitted by our local structure measurements [(Ir-O\(_2\)-Ir-O\(_1\))/Ir-O\(_1\) = 5.3\%].

In the large crystal field limit, we can consider the effects of the trigonal non-cubic crystal fields only in the \( t_{2g} \) states through the Hamiltonian:

\[ H^{t_{2g}}_{CF} = \begin{pmatrix} 0 & \delta & \delta \\ \delta & 0 & \delta \\ \delta & \delta & 0 \end{pmatrix} \]  

(S3)

in the basis \( (d_{zx}, d_{zy}, d_{xy}) \).

**SINGLE SITE RIXS CALCULATION**

FIG. S12. \( \Delta E_{D-E} \) as a function of \( \frac{r_{\text{Ir}-\text{O}}}{r_{\text{Ir}-\text{Ir}}} \) for different values of \( C_p \).

FIG. S13. Calculated RIXS spectrum for \( \text{Ir}^{4+}(d^5) \) and \( \text{Ir}^{2+}(d^3) \) with non-cubic crystal field splitting.
The inclusion of non-cubic crystal fields (CF) cannot reconcile the RIXS spectra shown in Fig. 3 with a single-site Ir$^{4+}$ model, which can at most produce two RIXS features for $E_{\text{loss}} < 1\text{ eV}$. Indeed, density functional theory calculations have shown that the effects of trigonal distortions on RIXS spectra in the honeycomb iridates are overestimated when direct Ir-Ir hopping terms are neglected [20–22]. To demonstrate this, we show in Fig. S13 calculations for a single site Ir 5d$^5$ and 5d$^4$ ion in a trigonally distorted environment given by $H_{\text{Dir}}$ with $10Dq = 4.4 \text{ eV}$ and $C_p = -0.05 \text{ eV}$, including spin orbit coupling $\lambda$. We find the best agreement with the experimental RIXS data for $\lambda = 0.37 \text{ eV}$. Electron-electron correlations are parameterized using Slater integrals calculated using Cowan’s code [23, 24], reported in Table S4.

The on-site Coulomb repulsion between 5d electrons is given by the integrals $F_{dd}^{0}, F_{dd}^{2}, F_{dd}^{4}$, and $F_{dd}^{6}$. The Coulomb interaction between the 2p-core hole and 5d electrons is given by $P_{pd}^{0}, P_{pd}^{2}, G_{pd}^{1}$ and $G_{pd}^{3}$.

| $5d^5$ | $5d^4$ |
|------|------|
| $F_{dd}^{0}$ | 0.47 | 0.49 |
| $F_{dd}^{2}$ | 8.83 | 9.20 |
| $F_{dd}^{4}$ | 5.91 | 6.18 |
| $F_{dd}^{6}$ | 0.08 | 0.09 |
| $P_{pd}^{0}$ | 1.03 | 1.07 |
| $P_{pd}^{2}$ | 0.89 | 0.96 |
| $G_{pd}^{1}$ | 0.53 | 0.57 |

TABLE S4. Summary of Slater parameters used in the single site RIXS calculations including all 5d orbitals.

These calculations for both $d^4$ and $d^5$ do not reproduce features $C, F$ and $G$, reaffirming the need for considering Ir-Ir hopping terms. Our RIXS calculations in Fig. S13 for a Ir$^{5+}$ ion show an inelastic feature that coincides in energy with peak $B$, $B = 0.270(37)\text{ eV}$. In Section S6 we ruled out Ir$^{5+}$ impurities concentrations $>1\%$ to be the origin of this feature in Ag$_3$LiIr$_2$O$_6$. Additionally, this model does not properly capture the relative intensities of features $B$ and $C$.

EXACT DIAGONALIZATION INCLUDING HOPPING INTEGRALS

We consider a model for the low energy electronic structure of two Ir sites in the large cubic crystal field limit given by the Hamiltonian $H = H_U + V_{12}$. The Kanamori-type Hamiltonian $H_U$ is given by

$$H_U = U \sum_{\psi} n_{\psi\uparrow} n_{\psi\downarrow} + U' \sum_{\psi \neq \psi'} n_{\psi\uparrow} n_{\psi'\downarrow} + U'' \sum_{\psi < \psi', \sigma} n_{\psi\sigma} n_{\psi'\sigma} - J_H \sum_{\psi \neq \psi', \sigma} c_{\psi\uparrow}^\dagger c_{\psi\downarrow} c_{\psi'\downarrow}^\dagger c_{\psi'\uparrow}^\dagger,$$

(S4)

with on-site Coulomb interaction, $U = 2\text{ eV}$, and Hund’s coupling, $J_H = 0.3\text{ eV}$, [11]. The hopping between Ir sites, $V_{12}$ is given by

$$V_{12} = \begin{pmatrix}
\lambda & \delta & \delta & t_{O} & t_{L} & \delta \\
\delta & \lambda & \delta & t_{O} & t_{L} & \delta \\
\delta & \delta & \lambda & t_{L} & t_{\sigma} & \delta \\
t_{O} & t_{O} & t_{L} & \lambda & \delta & \delta \\
t_{L} & t_{L} & t_{\sigma} & \delta & \lambda & \delta
\end{pmatrix},$$

(S5)

for a complete d-orbital basis ($d_{z^2-r^2}, d_{x^2+y^2}, d_{z^2}, d_{x^2}, d_{y^2}$) following following the labels and nearest-neighbour paths previously considered to model quasi-molecular orbitals [20, 21, 25, 26]. $\delta$ is the non-cubic crystal field strength and we fix the spin orbit coupling constant $\lambda = 0.395 \text{ eV}$.

ROLE OF $J_H$ AND $U$

To efficiently explore the set of energy scales that affect the low energy electronic structure of Ag$_3$LiIr$_2$O$_6$, we fixed the on-site electron-electron correlation, $U = 2\text{ eV}$, and Hund’s coupling $J_H = 0.3\text{ eV}$. These values are well within the range of values used in the literature for other iridates (1.7 < $U < 2.5\text{ eV}$, and 0.2 < $J_H < 0.5\text{ eV}$) [14, 27–29]. In Fig. S14, we show the result of the exact diagonalization calculations as a function of $J_H$ and $U$, with $\lambda = 0.395 \text{ eV}$ and $\delta = -0.075 \text{ eV}$. For $t_{||} = -0.085 \text{ eV}$, $t_O = 0.525 \text{ eV}$, $t_\sigma = -t_{||}$, and $t_{\perp} = -0.05t_{||}$, red markers, we observe minimal variation of the calculated spectrum across a wide range of values of $U$. On the other hand, the splitting between calculated energy levels, in particular below $E_{\text{loss}} < 0.5\text{ eV}$, depends linearly on $J_H/\lambda$. The dashed horizontal lines and shaded boxes indicate the centroids and FWHM of peaks $A - G$. This highlights the dependence of the low energy electronic structure in 4+ iridates on multiple energy scales. When the hopping integrals are not considered, $V_{1,2} = 0$, blue markers, the electronic spectrum cannot account for the observed RIXS dispersion for any physical value of $J_H$ and $U$. 


QUALITY FACTOR

To efficiently explore the phase space defined by the hopping integrals and the non-cubic crystal fields, we define a *quality factor* $QF$ to parameterize the agreement between measured and calculated exciton energies

$$QF = \sum_{p \in \{A, B, C, D, E\}} \frac{1}{N_0} \sum_{i=0}^{N_0} \left( \frac{E_0 - E_p}{\sigma_p} \right)^2.$$  \hfill (S6)

$E_p$ is the measured energy of peak $p \in \{A, B, C, D, E\}$ with FWHM of $\sigma_p$ [see Fig. 1, main text]. $N_0$ is the number of eigenvalues that satisfy $[E_0 - \delta E, E_0 + \delta E] \in [E_p - \sigma/2, E_p + \sigma/2]$, with $\delta E = 0.033$ eV the experimental resolution. Any eigenvalues that lie within range of more than one experimental peak are assigned to the lowest energy peak of the set. We exclude all calculated states at energy transfers less than $\Delta E/2$ from the QF calculation to avoid complications from the elastic line. Experimental features $F$, $G$ and $H$, with $E_{loss} > 1$ eV and proximal to the $e_g$ features, are also excluded from the calculation as their broad energy width artificially enhances their weights and biases the calculation of QF.

We first assume $t_0 = -t_{||}$ and $t_\perp = -0.05 t_{||}$. We then diagonalize the Hamiltonian for different values of $t_{||}$, $t_0$ and $\delta$ in order to find the parameter set that minimizes QF. We perform a brute force minimization in order to explore any correlations between parameters and constrain a global minimum for QF. In Fig. S15 we show the dependence of QF on $t_{||}$, $t_0$ and $\delta$ over a broad range of physically realistic values. Our QF map reveal that $t_{||}$ and $\delta$ are highly correlated: the minimum of QF cannot be reached by varying both parameters independently and for larger $t_{||}$ QF is minimized with smaller $\delta$.

In Fig. S16, we show a comparison of our data with calculated powder averaged RIXS spectra for a range of parameters that fall within 10% of the minimum QF.

POWDER AVERAGED RIXS CROSS-SECTION CALCULATION

We use EDRIXS software package to diagonalize the full Hamiltonian $H = H_U + V_{12}$ and simulate the full momentum and energy dependent RIXS spectra within a dipole approximation [24]. We consider a cluster of four Ir atoms and average the RIXS signal over the three inequivalent Ir-Ir bonds within a Li$_2$IrO$_3$ layer. In our calculation, we set $2\theta = 90^\circ$, fix the incident beam polarization $\epsilon_i$ to lie in the horizontal scattering plane and
average over all outgoing polarization directions $\epsilon_f$ to match the experimental geometry.

The RIXS cross-section is given by

$$I_{\text{RIXS}}(\omega_{\text{in}}, \omega_{\text{loss}}, k_i, k_f, \epsilon_i, \epsilon_f) = \sum_{n} \frac{1}{Z} \exp \left( - \frac{E_i}{k_B T} \right) \times$$

$$\sum_{n} \frac{(f|\hat{D}_f^\dagger|n) \langle n|\hat{D}_i|i \rangle^2}{\omega_{\text{in}} - \hat{H}_n - E_i + i\Gamma_c} \left( \frac{\Gamma}{\pi} \frac{1}{(\omega_{\text{loss}} - E_f + E_i)^2 + \Gamma^2} \right),$$

(S7)

where $k_i$, $k_f$, $\omega_{\text{in}}$, and $\omega_{\text{loss}}$ are the incident and outgoing x-ray wavevectors, incident x-ray energy, and energy transfer respectively. $|i\rangle$ and $|f\rangle$ correspond to the eigenvalue of the initial and final states, with $E_i$ and $E_f$ the corresponding eigenvalues. $Z$ is the partition function and $k_B$ the Boltzmann constant. $|n\rangle$ corresponds to eigenstates of the intermediate state Hamiltonian which includes a 2p core hole and $n + 1$ electrons in the valence shell after absorbing a photon with energy $\omega_{\text{in}}$. $\Gamma_c$ and $\Gamma$ are the lifetime broadening of the intermediate and final state.

$\hat{D}_i$ and $\hat{D}_f^\dagger$ are the transition operators for the x-ray absorption and emission processes. We only include dipolar transitions in our calculation. In this case:

$$\hat{D}_i = \frac{1}{i m \omega_{\text{in}}} \sum_{i=1}^{N} e^{i k_i \cdot R_{\alpha}} \epsilon_i \cdot p_{\alpha},$$  

(S8a)

$$\hat{D}_f^\dagger = \frac{1}{i m \omega_f} \sum_{i=1}^{N} e^{-i k_f \cdot R_{\alpha}} \epsilon_f \cdot p_{\alpha}^\dagger,$$  

(S8b)

where $R_{\alpha}$ is the position of the resonant ion to which electron $\alpha$ is bound and $p_{\alpha}$ is the momentum operator. The term $\hat{D}$ encodes the momentum dependence and depends on the direction between x-ray polarization and the position (momentum) of the bounded electron. For a powder sample, the measured intensity will be a spherical average of this term at fixed momentum transfer.

In order to compare the calculated RIXS intensity with our powder measurement, we perform powder averaging by Monte-Carlo ($N = 1000$) integration of equation S7 over a spherical surface of radius $|Q| = k_z \sin (2\theta/2)$. Although the calculated RIXS excitations from our two site model do not show any dispersion, the powder averaging affects the relative intensities of RIXS features through the transition operators. For our calculations we fixed $\Gamma = 0.005$ eV and we account for experimental resolution through a convolution of the calculated RIXS intensity with a Gaussian profile of FWHM 33 eV. The results of this calculation using a range of optimal parameters set determined by our QF minimization is shown in Fig. S16 and Fig. 4 (d) of the main text.
FIG. S16. Comparison of the calculated RIXS intensity for different values of $t_{||}$, $t_O$ and $\delta$ that are within 10% of the QF minimum. Panel (b), highlighted in orange, shows the parameter set from QF minimization that best matches the RIXS spectrum and is presented in Fig. 4 of the main text.