Resonant inelastic x-ray incarnation of Young’s double-slit experiment


INTRODUCTION

Resonant inelastic x-ray scattering (RIXS) provides a powerful example of particle-wave duality in quantum mechanics. In RIXS, an incident x-ray photon excites an electron out of the core of an atom into an empty valence level. The highly excited atomic state that is produced in this way contains an extremely localized hole in its core, with a size of a few picometers. Subsequently, this intermediate state decays: A valence electron fills the core hole under reemission of a photon with lower photon energy than the incident one. The final excited state may correspond to, e.g., an interband, orbital, or magnetic state. This process occurs because the RIXS intermediate state contains a single core hole that is produced in this way. It is localized over the two atoms. It corresponds to an observer without “which-path” information, i.e., one cannot tell on which atom the core hole was localized in the intermediate state. The emitted x-rays interfere and give rise to a double-slit-type sinusoidal interference pattern as a function of the momentum $q$ that is transferred in the inelastic scattering process.

RESULTS

We have grown single crystals of hexagonal BCIO (space group $P6_3/mmc$) by the melt-solution technique (see Materials and Methods). Each of the Ir$^{4+}$ ions within the structural dimers formally shows a 5$d^8$ configuration, with one hole in the $t_{2g}$ shell. However, the nearest-neighbor Ir–Ir distance of 2.5 Å is even shorter than the 2.7 Å found in Ir metal. Accordingly, the intradimer Ir–Ir hopping is large, driving the formation of quasi-molecular orbitals with large bonding-antibonding splitting. It should be stressed that this situation is very different from the case of a single Ir$^{4+}$ site, where strong spin-orbit coupling ($\lambda \approx 0.4 – 0.5$ eV) splits up the local $t_{2g}$ manifold and yields spin-orbit-entangled $j = 1/2$ moments (see Fig. 2B). Prominent examples showing rich $j = 1/2$ physics are Sr$_3$IrO$_4$ ($7–10$) and Na$_2$IrO$_3$ ($11–13$).

There are two limiting scenarios for an effective description of the electronic structure of BCIO, i.e., for the character of the bonding and antibonding quasi-molecular orbitals. For strong spin-orbit coupling, (anti-)bonding states can be formed from spin-orbit-entangled $j = 1/2$ states (see Fig. 2D). However, a large Ir–Ir hopping may quench the $j = 1/2$ moments, as has been discussed for Na$_2$IrO$_3$ ($14, 15$). In this case, the crystal-field-split $t_{2g}$ orbitals provide a more appropriate basis for the formation of (anti-)bonding states (see Fig. 2C). As will become clear in the following, these substantial differences in the Ir 5$d$ orbitals can be highlighted and quantified by RIXS interferometry, i.e., RIXS measurements of $q$-dependent interference patterns, which reveal the symmetry and character of the excited states.
Figure 3A depicts high-resolution RIXS spectra of BCIO for a fixed incident energy tuned to the Ir L₃ edge (2p → 5d) (see Materials and Methods), which resonantly enhances inelastic scattering from intra-t₂g excitations. With a 5d-t₂g - e²g splitting of about 3 eV, the observed features between 0.5 and 1.5 eV, labeled α, β, and γ, can safely be attributed to intra-t₂g excitations. The absence of dispersion strongly supports a local character (see Supplementary Text). The spectra do not display the characteristic feature of individual j = 1/2 moments, the narrow spin-orbit exciton peaking at about 1.5λ. A textbook example of the latter is found in isostructural Ba₃Ti₂.7Ir0.3O₉, which is in very good agreement with the Ir-Ir distance of 2.5361(7) Å determined at 300 K by x-ray diffraction (see Supplementary Text). Note that Q = 2.914 - 2π/c is incommensurate with the reciprocal lattice vector 2π/c, where c denotes the lattice constant. A clear dichotomy with respect to even/odd Q is also evident from the RIXS spectra in Fig. 3A. Even without further knowledge of the underlying microscopic physics, the observed interference pattern with a period given by the Ir-Ir distance is an unmistakable proof of the double-slit-type RIXS process arising from the quasi-molecular orbital character of the investigated states.

**DISCUSSION**

The most remarkable feature of RIXS interferometry is the ability to determine the symmetry of the low-energy excitations and thus to distinguish between the two limiting scenarios sketched in Fig. 2 (C and D). The symmetry is encoded in the phase of the interference pattern. Young’s canonical elastic double-slit experiment gives a maximum for q = 0, which is equivalent to the cos²(qd/2) dependence observed for peak γ (see Fig. 3C). The cosine denotes the Fourier transform of the double slit, i.e., its structure factor. Strikingly, features α and β show a sin²(qd/2) modulation. In our experiment on structural dimers with a bonding singlet ground state, the sin²(qd/2) or cos²(qd/2) behavior of the observed RIXS features reflects the bonding or antibonding character of the corresponding excited-state wave functions, respectively. This behavior embodies the simple dipole selection rules for both the absorption and reemission processes (see Supplementary Text).

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symmetry of the observed interference patterns agrees with Fig. 2D and suggests that this simplified sketch provides a valid starting point for an intuitive understanding of the three low-energy features $\alpha$, $\beta$, and $\gamma$.

This assignment is corroborated by careful modeling of the Ir$_2$O$_9$ bicatahedral. We take into account spin-orbit coupling $\lambda$, hopping terms within a dimer, the trigonal crystal field $\Delta_{CF}$, and on-site Coulomb correlations described by Hubbard $U$ and Hund exchange $J_H$ (see Materials and Methods). The calculated RIXS spectra and the corresponding $q$-dependent intensities (see Fig. 4) qualitatively agree with our experimental results. In particular, we reproduce the $\sin^2(qd/2)$ behavior of peaks $\alpha$ and $\beta$ and the $\cos^2(qd/2)$ behavior of peak $\gamma$. This implies quasi-molecular orbitals that are governed by a combination of strong spin-orbit coupling $\lambda \approx 0.4-0.5$ eV and strong hopping $\sim 1$ eV. The hopping is about three times larger than between nearest-neighbor $j = 1/2$ moments in Sr$_2$IrO$_4$. The dominant contribution to the ground state is a dimer singlet with $j\text{dim} = 0$ in which the single-site $j = 1/2$ moments occupy a bonding quasi-molecular orbital. As depicted in Fig. 2D, the two lower features $\alpha$ and $\beta$ correspond to excitations to bonding orbitals originating from the $j = 3/2$ spin-orbit exciton, and their splitting is mainly caused by $J_H$ and $\Delta_{CF}$. We find that peak $\gamma$ at $1.2$ to $1.3$ eV corresponds to the antibonding triplet excitation from the $j\text{dim} = 0$ ground state to a $j\text{dim} = 1$ excited state of a dimer. This $j$ flip can be realized by both spin-flip and spin-conserving processes. The former are allowed in $L$-edge RIXS due to the very strong spin-orbit coupling in the 2$p$ shell in the intermediate state. In the calculated spectra, the triplet excitation intensity is somewhat overestimated because of the neglect of the electron-hole continuum above the gap, which provides a possible decay channel for the local excitations considered here with a concomitant increase of the width.

Last, we address the envelope of the sinusoidal interference pattern. The RIXS data cover about 20 Brillouin zones. Still, the amplitude of the intensity modulation does not change strongly, at least for peaks $\alpha$ and $\beta$, allowing us to detect the interference pattern over a broad range of $q$. This is due to the nearly point-like nature of the effective “slits” formed by the core hole in the intermediate states ($I$), i.e., the “slit width” is negligible. The $q$-dependent envelope rather contains valuable information on the dependence of the RIXS matrix elements on the scattering geometry and thereby on the precise wave functions.

CONCLUSION

The comparison of theory and experiment on BCIO shows that the quasi-molecular orbitals, delocalized over the two Ir sites of a dimer, give rise to the RIXS interference effect, which was predicted almost 25 years ago as an inelastic incarnation of Young’s double-slit experiment. Conceptually different interference effects as a function of energy but not of $q$ arise if energetically different intermediate states—located on the same site—contribute coherently (16, 17). In contrast, our experiment realizes the genuine spatial double-slit setup: A photon scatters inelastically on one of two dimer sites. Previously, this was discussed in the context of dimers in VO$_2$ (18), but only a single value of $q$ was analyzed by the limited momentum transfer available in the soft x-ray range. Similarly, studies of magnons in the bilayer compound Sr$_2$Ir$_2$O$_7$ (19) and of stripes in nickelates and cuprates (20) addressed only a few values of $q$. Coverage of a broad range of $q$ fully reveals the interference character and allowed us to unravel the symmetry and character of electronic dimer excitations in BCIO. These results demonstrate the potential of this interference method to probe the electronic structure of materials containing well-defined structural units such as dimers, trimers, or heptamers (21), as well as structures in which the carriers are “localized” only in one direction, e.g., bilayers or ladders. More specifically, our results suggest that RIXS interferometry is ideally suited to explore the role of molecular orbitals in the spin-liquid candidate Ba$_3$InIr$_2$O$_8$ with In$^{3+}$ ions and three holes per dimer (22), as well as to search for Majorana fermions in iridate candidates for

Fig. 3. RIXS data of intra-$_{t_{2g}}$ excitations in BCIO. (A) High-resolution RIXS spectra at $T = 20$ K for different transferred momenta $q = (0.0 mQ)$ with integer $m$ and $Q = 2\pi/d = 2.914 \cdot 2\pi/c$, where $d$ and $c$ denote the intradimer Ir-Ir distance and the lattice constant, respectively. The spectra show a pronounced even/odd behavior with respect to $m$, reflecting the sinusoidal $q$ dependence. Note that the elastic peak is suppressed in $x$ polarization for a scattering angle of $2\theta = 90^\circ$ and that the data for $4Q$ to $7Q$ were measured at $2\theta = 52^\circ$, $67^\circ$, $83^\circ$, and $101^\circ$, respectively. Accordingly, the elastic peak is strongest for $4Q$. (B and C) Interference patterns in the RIXS intensity as a function of $q$. The data cover about 3.5 periods in $Q$, equivalent to more than 20 Brillouin zones (top axis). The intensity was integrated over the energy loss ranges indicated in the figure and normalized by the width $\Delta E$ of the respective energy range. Data in (B) were measured at 10 K with lower energy resolution of 0.36 eV, integrating over features $\alpha$ and $\beta$, to enhance the signal-to-noise ratio. The high-resolution data in (C) discriminate between the three peaks $\alpha$ (dark blue), $\beta$ (light blue), and $\gamma$ (brown). Solid lines depict fits using $a_0 e^{-\eta_1 d} \sin^2(x/2Q + \phi) + b_0 + b_1 l$ with the parameters $Q$, $a_0$, $a_1$, $b_0$, and $b_1$, as well as $\phi = 0$ or $\pi/2$. 

RIXS measurements

RIXS measurements at the Ir $L_3$ edge were performed on the ID20 beamline at ESRF (6). We used an incident energy of 11.2155 keV for $M = \text{Ce}$ and 11.2150 keV for $M = \text{Ti}$ to maximize the resonantly enhanced RIXS intensity of the intra-$t_{2g}$ excitations. An overall energy resolution of 27 meV was obtained by combining a Si(844) backscattering monochromator and $R = 2$ m Si(844) spherical diced crystal analyzers (26). These analyzers make the RIXS setup partially dispersive, i.e., one image on the pixelated detector covers an energy range of approximately 360 meV. Accordingly, the RIXS spectra of Fig. 3A were measured by scanning the energy at constant $q$, while the data in Fig. 3C were collected by scanning $q$ at constant energy. The data in Fig. 3B were measured with a lower resolution of 0.36 eV using a Si(311) channel-cut in place of the Si(844) backscattering monochromator to enhance the signal-to-noise ratio. For both $M = \text{Ce}$ and $M = \text{Ti}$, RIXS measurements were performed on polished (0 0 1) surfaces with the $c$ axis in the horizontal scattering plane and the $a$ axis along the vertical direction. The incident photons were $\pi$ polarized. Samples were cooled using a continuous-flow He cryostat.

Theory

The sketch in Fig. 2D provides a simplified but intuitive picture of the low-energy excitations. For the simulation of the RIXS spectra, we calculated all 66 eigenstates for two $t_{2g}$ holes on two Ir sites of an $\text{Ir}_5\text{O}_9$ biocahedron via exact diagonalization. We started from the Hamiltonian for a single Ir site, taking into account spin-orbit coupling $\lambda \mathbf{S} \cdot \mathbf{L}$ and the trigonal crystal field, $\Delta_{C2}L_z^2$. The on-site Coulomb repulsion between carriers with different spins in the same or in different orbitals is given by $U$ and $U - 2J_{Ir}$, respectively, and the interaction Hamiltonian reads

$$H_C = \sum_{\alpha \neq \beta} n_{\alpha} n_{\beta} + \frac{1}{2} \left( U - 3J_{HF} \right) \sum_{\alpha,\alpha' \neq \beta} n_{\alpha} n_{\alpha'} +$$

$$\left( U - 2J_{HF} \right) \sum_{\alpha,\alpha' \neq \beta} n_{\alpha} n_{\alpha'} +$$

$$\left( U - 2J_{HF} \right) \sum_{\alpha} \left( 15 - 5 \sum_{\alpha' \neq \beta} n_{\alpha} \right)$$

where $n_{\alpha}$ is the number operator for the $t_{2g}$ orbital $\alpha \in \{a_{1g}, e^{x^2-y^2}, e^{z^2}\}$ at site $i$ with $\sigma \in \{\uparrow, \downarrow\}$. In addition, we considered the hopping interactions $t_{a_{1g}}$ and $t_{e^{x^2-y^2}, e^{z^2}}$ between two Ir sites.

The two octahedra forming an $\text{Ir}_5\text{O}_9$ biocahedron are rotated by 180° with respect to each other around the trigonal $z$ axis (see Fig. 2A and fig. S1). This causes a sign change of the $xz$ and $yz$ orbitals in one of the two octahedra, which affects the selection rules of excitations involving the $e^{x^2-y^2}$ orbitals (27). For the calculation of the RIXS spectra, we considered the RIXS matrix elements for single-particle excitations between all 66 states in the dipole approximation for both absorption and reemission. As typical for $t_{2g}$ iridates (28), we neglected multiplet effects between the intermediate-state $2p_{3/2}$ core hole and 5d holes, which considerably simplifies the calculation. It is motivated for the $t_{2g}$ configuration by the full $t_{2g}$ shell in the intermediate state, neglecting the $e^{x^2-y^2}$ holes. Note, however, that spin-orbit coupling mixes $e^{x^2-y^2}$ and $e^{z^2}$ levels. Moreover, this approximation is not fully valid for quasi-molecular orbitals delocalized over two Ir sites, where states with two holes on the same site contribute. For comparison with the experiment, one has to add the RIXS intensities of the two layers of biocahedra present in $\text{Ba}_3\text{CeIr}_2\text{O}_9$ (see Fig. 2A), which, for the present geometry, is equivalent to adding intensities for

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**MATERIALS AND METHODS**

**Crystal growth and characterization**

The $\text{Ba}_3\text{MIn}_2\text{O}_9$ family with the hexagonal (6H)-$\text{BaTiO}_3$ structure is formed for a wide variety of $d_1$, $d_{1-3}$, or tetravalent $M$ ions (5, 23–25). The valence states of $M = \text{Ce}^{4+}$ and $\text{Ti}^{4+}$ yield 5$d^5$ $\text{Ir}^{4+}$ ions. Single crystals of $\text{Ba}_3\text{CeIr}_2\text{O}_9$ and $\text{Ba}_3\text{Ti}_{1.7}\text{Ir}_{0.3}\text{O}_9$ have been grown by the melt-solution technique and spontaneous nucleation. Using stoichiometric amounts of $\text{BaCO}_3$, $\text{CeO}_2$, and $\text{IrO}_2$ for the growth of $\text{Ba}_3\text{CeIr}_2\text{O}_9$ and $\text{BaCO}_3$, $\text{TiO}_2$, and $\text{IrO}_2$ in a ratio of 3:2:1 in the case of $\text{Ba}_3\text{Ti}_{1.7}\text{Ir}_{0.3}\text{O}_9$, and in both cases an addition of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, hexagonal prismatic crystals of about 2-mm size were grown within growth periods of 4 weeks. The crystals were mechanically separated from the flux, washed with cold $\text{H}_2\text{O}$, and characterized by x-ray diffraction, energy-dispersive x-ray analysis, and magnetization measurements.
+q and −q. Last, RIXS spectra were calculated for certain q, values by assuming Gaussian line shape with a fixed width.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/1/eaav4020/DC1

References (30–35)


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