RIXS interferometry and the role of disorder in the quantum magnet Ba$_3$Ti$_3-x$Ir$_x$O$_9$

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Motivated by several claims of spin-orbit driven spin-liquid physics in hexagonal Ba$_3$Ti$_3-x$Ir$_x$O$_9$ hosting Ir$_2$O$_4$ dimers, we report on resonant inelastic x-ray scattering (RIXS) at the Ir $L_3$ edge for different $x$. We demonstrate that magnetism in Ba$_3$Ti$_3-x$Ir$_x$O$_9$ is governed by an unconventional realization of strong disorder, where cation disorder affects the character of the local moments. RIXS interferometry, studying the RIXS intensity over a broad range of transferred momentum $q$, is ideally suited to assign different excitations to different Ir sites. We find pronounced Ir-Ti site mixing. Both ions are distributed over two crystallographically inequivalent sites, giving rise to a coexistence of quasimolecular singlet states on Ir$_2$O$_4$ dimers and spin-orbit entangled $j=1/2$ moments of 5$d^5$ Ir$^{4+}$ ions. RIXS reveals different kinds of strong magnetic couplings for different bonding geometries, highlighting the role of cation disorder for the suppression of long-range magnetic order in this family of compounds.

I. INTRODUCTION

The precise theoretical definition of a quantum spin liquid has been sharpened in recent years \cite{1}, but the elusiveness of experimental realizations has remained \cite{2-4}. Accordingly, the groundbreaking suggestion of Jackeli and Khaliullin \cite{5} to realize Kitaev’s exact spin-liquid solution in, e.g., honeycomb iridates with edge-sharing IrO$_6$ octahedra provoked intense activity \cite{6-15}. Dominant bond-directional Kitaev-type exchange interactions indeed were observed in Na$_2$IrO$_3$ \cite{16}, but long-range magnetic order arises due to the existence of further exchange couplings \cite{17-21}. In contrast, \textit{H$_4$LiIr$_2$O$_6$} was proposed to be a close realization of the Kitaev model, evading magnetic order at least down to 50 mK \cite{22}. However, quantum chemistry calculations and density functional theory find a strong sensitivity of exchange couplings to Ir ion disorder and unintentional deuteration \cite{23-25}, suggesting a more conventional source of magnetic disorder.

Remarkably, several members of the hexagonal iridate family Ba$_3$M$\text{Ir}_2$O$_9$ were claimed to be candidates for spin-liquid behavior \cite{25-27}. The structure hosts triangular layers of Ir$_2$O$_4$ dimers built from face-sharing IrO$_6$ octahedra, see Fig. 1. The versatility of these compounds stems from the valence of the M ions, which extends from +1 to +4 \cite{28-29}. With two holes per dimer such as in Ba$_3$CeIr$_2$O$_9$ with Ce$^{4+}$ and Ir$^{4+}$ ions, the ground state is nonmagnetic \cite{31-30}. RIXS finds quasimolecular orbitals localized on the dimers, i.e., the holes are fully delocalized over a given dimer, and the tightly bound ground-state singlet forms in a bonding orbital built from local $j=1/2$ moments \cite{31}. In Ba$_3$InIr$_2$O$_9$ with three holes per dimer, persistent spin dynamics were reported down to 20 mK in thermodynamic data and with local probes \cite{29}. In RIXS, a quasimolecular $x_{\text{dim}}=3/2$ nature of the local dimer ground state was observed, establishing the compound as a cluster Mott insulator \cite{42}. Such spin-orbit entangled quasimolecular moments with yet to be explored exchange interactions may open up a novel route to quantum magnetism \cite{43}. For four holes per dimer with Ir$^{5+}$ ions, a spin-orbital liquid with weak moments has been claimed in Ba$_3$ZnIr$_2$O$_9$ \cite{30-31}. This contradicts the nonmagnetic behavior expected for interacting Ir$^{4+}$ 5$d^5$ $j=0$ states and again points to a quasimolecular dimer character of the electronic structure.

In Ba$_3$Ti$_3-x$Ir$_x$O$_9$, the comparable ionic radii of Ir$^{4+}$ and Ti$^{4+}$ yield Ti-Ir site disorder \cite{35}, see Fig. 1. However, quantum chemical calculations and density functional theory find a strong sensitivity of exchange couplings to H ion disorder and unintentional deuteration \cite{28-29}, suggesting a more conventional source of magnetic disorder.

In $L$ edge RIXS measurements on Ba$_3$Ti$_3-x$Ir$_x$O$_9$ with...
In the hypothetical absence of Ir-Ti site mixing for \( x = 2 \), Ti (Ir) ions occupy the sites with Wyckoff position \( 2a (4f) \). Hence layers of TiO\(_6\) octahedra (light blue) are sandwiched between layers of Ir\(_2\)O\(_9\) dimers (light green), the latter being built from face-sharing IrO\(_6\) octahedra. The real compound shows Ir-Ti site mixing, i.e., Ir ions also occupy \( 2a \) sites (dark green) and Ti ions also can be found on \( 4f \) sites (dark blue), the latter giving rise to TiIrO\(_3\) units instead of dimers. Right: Local structure around an Ir defect ion on a \( 2a \) site (dark green). It is connected to six neighbors on \( 4f \) sites in corner-sharing geometry with 180° bonds (thick lines). In this example, five of the six neighbors belong to Ir\(_2\)O\(_9\) dimers but there is a single Ir\(^{2+}\)-Ir\(^{3+}\) pair (thick black line) where the Ir ion on the \( 4f \) site is part of an IrTiO\(_3\) unit.

\[ x \in \{0.3, 0.5, 1.5, 1.8\} \], we find a coexistence of quasi-molecular Ir\(_2\) dimer states and single-site \( j = 1/2 \) moments, providing a clear fingerprint of substantial Ir-Ti site mixing. The quasi-molecular dimer character is nailed down via a double-slit-type sinusoidal interference pattern in the RIXS intensity as a function of the transferred momentum \( \mathbf{q} \), in agreement with previous results on Ba\(_3\)CeIr\(_2\)O\(_9\) and Ba\(_3\)InIr\(_2\)O\(_9\) \cite{50}. Additionally, the study of such interference patterns allows us to identify a RIXS peak at 0.15 eV with site-mixing-induced magnetic excitations of Ir moments on \( M \) sites (2a) that are strongly exchange-coupled to neighboring dimer sites (4f) via 180° bonds, see Fig. 1. The 2a – 4f bonding geometry is very similar to the case of Sr\(_2\)IrO\(_4\) \cite{46, 47} which roughly explains the energy scale of 0.15 eV. The ability to disentangle the contributions of different Ir sites in such a strongly disordered system demonstrates the power and versatility of RIXS interferometry.

Our findings on Ba\(_3\)Ti\(_3\)–Ir\(_2\)O\(_9\) highlight the unconventional role that disorder may play in a cluster Mott insulator. Removing a magnetic ion from a cluster such as a dimer does not create a usual vacancy but strongly changes the moment’s character as well as the relevant (exchange) interactions. In our example of dimers, the character changes from quasimolecular \( j_{\text{dim}} = 0 \) to single-site \( j = 1/2 \) moments. For perfect cation order, magnetic interactions for the Ir\(_2\) dimers range from very weak for interdimer exchange couplings up to about 1 eV for intradimer singlet-to-triplet excitations, but cation disorder yields pairs of local moments with exchange coupling of about 0.15 eV. The physics of Ba\(_3\)Ti\(_3\)–Ir\(_2\)O\(_9\) thus is governed by a complex mixture of Ti-Ir site disorder, the statistical coexistence of different magnetic moments, and very different magnetic couplings.

**II. EXPERIMENTAL**

Crystals of Ba\(_3\)Ti\(_3\)–Ir\(_2\)O\(_9\) were grown using BaCO\(_3\), IrO\(_2\), and TiO\(_2\) as educts and BaCl\(_2\) as melt solvent. After the growth process the crystals were mechanically separated from the flux and washed with cold H\(_2\)O. We studied samples with an Ir content \( x \in \{0.3, 0.5, 1.5, 1.8\} \) as determined by energy dispersive x-ray spectroscopy (EDX). The crystals with \( x = 0.3 \) and 0.5 resulted from one growth experiment with a ratio IrO\(_2\):TiO\(_2\) = 1:2, while the crystals with \( x = 1.5 \) and 1.8 were obtained for IrO\(_2\):TiO\(_2\) = 2:1 and otherwise identical growth parameters. This indicates an effective distribution coefficient \( k_{\text{eff}} = c_{\text{Ir}}/c_{\text{melt}} < 1 \) for the concentration of Ir ions in the crystal and the melt, respectively. This causes Ir depletion in the crystals with respect to the melt and thus Ir accumulation in the melt as a function of time. Crystals nucleating later in the course of the unseeded growth experiment grow in a melt that is enriched with Ir, giving rise to a larger Ir content \( x \). From single crystal X-ray diffraction and structure refinements, room-temperature lattice constants of \( a = (5.7103 \pm 0.0011) \) Å and \( c = (14.1516 \pm 0.0029) \) Å were obtained in the hexagonal space group \( P6_3/mmc \) for two samples from the two different batches. The magnetic susceptibility was measured in a commercial SQUID magnetometer (Quantum Design MPMS).
magnetic singlets in the case of two Ir$^{4+}$ ions occupying both 4$f$ sites within a dimer. Therefore, the overall magnetic susceptibility consists of the superposition of different Curie-Weiss and van Vleck contributions based on local moments on 2$a$ or 4$f$ sites and dimers. Because a reliable quantitative separation of the various contributions to $\chi(T)$ is not possible, we restrict ourselves to a strongly simplified effective Curie-Weiss model, which neglects a possible temperature dependence of the effective magnetic moments by setting $\mu_{\text{eff}} = 1.73 \mu_B$ of a spin 1/2. Moreover, we assume temperature-independent van Vleck terms which are included in a constant background susceptibility $\chi_0$.

$$
\chi(T) = n \frac{N_A \mu_{\text{eff}}^2}{3k_B(T - \theta_W)} + \chi_0. 
$$

This yields three adjustable parameters, where $n$ denotes the amount of localized magnetic moments, $\theta_W$ measures their effective interaction strength, and $\chi_0$ is the sum of the overall van Vleck contribution and the core diamagnetism. As shown in Fig. 2 the measured data can be reasonably well described by the simplified model of Eq. (1) with the parameter set $n = 0.16$, $\theta_W = -5.5$ K, and $\chi_0 = 9.5 \cdot 10^{-4}$ emu/mole for $x = 0.5$, while we obtain $n = 0.14$, $\theta_W = -4.7$ K, and $\chi_0 = 6.8 \cdot 10^{-4}$ emu/mole for the sample with $x = 1.5$. Both parameter sets with weakly antiferromagnetic Weiss temperatures and comparable $\chi_0$ values are very similar, as expected due to the very similar $\chi(T)$ data. In view of the very different values of $x$, the very similar results for $n$ are remarkable, but our RIXS data confirm a similar density of local moments in the two samples, see Sec. V A. This indicates that for large $x$ the vast majority of Ir$^{4+}$ ions form singlet dimers.

V. RIXS RESULTS

A low-resolution (0.4 eV) RIXS map of Ba$_3$Ti$_{1-x}$Ir$_x$O$_9$ illustrates the resonance enhancement, see Fig. 3. We find dominant excitations into $e_g^0$ levels above about 3 eV energy loss and charge-transfer excitations at still higher energies. In the following, we focus on the intra-$t_{2g}$ excitations below about 1.2 eV. RIXS spectra of Ba$_3$Ti$_{1-x}$Ir$_x$O$_9$ for $x \in \{0.3, 0.5, 1.5, 1.8\}$ are depicted in Fig. 4 for selected values of $q$. Each panel shows data for different $q$, the component of $q$ parallel to the $c$ axis. To identify dimer features (see below), we express $q$ in terms of $Q_d = \pi/d \approx 5.3 \times \pi/c$. In contrast, Fig. 4 highlights the $h$ dependence for $q_z \approx 6.3Q_d$ and $7.3Q_d$ for $x = 1.8$.

The data in Fig. 4 demonstrate the coexistence of individual $j = 1/2$ sites and dimers with quasimolecular states. The overall line shape changes strongly as a function of $x$ since the contribution of $j = 1/2$ sites dominates for small $x$, see Sec. V A while quasimolecular dimer excitations prevail for large $x$. The dimer excitations set in above about 0.2 eV, see Sec. V B. For $x = 1.5$ and 1.8, we find a further, weak RIXS peak at about 0.15 eV which
is most evident in Fig. [5] as the only feature with a particular $h$ dependence of the intensity. Using RIXS interferometry we demonstrate that this feature corresponds to magnetic excitations related to Ir ions on 2$a$ sites, see Sec. V C.

The elastic line can be suppressed for a scattering angle $2\theta \approx 90^\circ$ for incident $\pi$ polarization. This is illustrated by the data in Fig. 4(d) that were measured with $2\theta \approx 82^\circ$, $87^\circ$, $94^\circ$, and $112^\circ$ for $l = 16.8$, $17.7$, $18.8$, and $21.3$, respectively.

A. Individual $j = 1/2$ moments

For small $x$, the RIXS spectra provide an unmistakable fingerprint of diluted $5d^5$ Ir$^{4+}$ sites. The data predominantly show the well-known two-peak structure of the so-called spin-orbit exciton, i.e., excitations from local $j = 1/2$ moments to $j = 3/2$ excited quartet states which is, however, split by the trigonal crystal field $\Delta_{CF}$ [51]. Features similar to the two narrow peaks at 0.57 and 0.70 eV were observed in many iridates with (weakly) interacting $j = 1/2$ moments [52, 59]. Compared to, e.g., honeycomb Na$_2$IrO$_3$ or square-lattice Sr$_2$IrO$_4$ [46, 47, 52], the small line width of the pronounced peak at 0.57 eV underlines that interactions between individual $j = 1/2$ moments are weak in Ba$_3$Ti$_{3-x}$Ir$_x$O$_9$.

Typical for iridates, Ba$_3$Ti$_{3-x}$Ir$_x$O$_9$ shows a strong cubic crystal-field splitting $10Dq \approx 3$ eV between $t_{2g}$ and $e_g$ states, see Fig. [5]. In this case, the physics of intra-$t_{2g}$ excitations on a single $t_{2g}^2$ site is well described by the Hamiltonian $\Delta_{CF}$  

$$H_{\text{single}} = \lambda \mathbf{S} \cdot \mathbf{L} + \Delta_{CF} L_z^2, \quad (2)$$

where $\lambda$ denotes spin-orbit coupling and $\Delta_{CF}$ the trigonal crystal field. In terms of an IrO$_3$ point-charge model, trigonal elongation or contraction of the oxygen octahedron corresponds to positive or negative $\Delta_{CF}$, but in Ba$_3$Ti$_{3-x}$Ir$_x$O$_9$ with face-sharing octahedra the sign also depends on covalency and interactions with further ions [60]. Based on the crystal structure, $\Delta_{CF} \neq 0$ is already
RIXS intensity (a.u.)

\[ \begin{align*}
10 & \quad 20 & \quad 25 \\
0 & \quad 5 & \quad 10 \\
0 & \quad 5 & \quad 10
\end{align*} \]

modulation. With \( Q \) magnetic excitation that involves an Ir ion on a 2 site, we observe a pronounced energy rise to an intensity modulation along \( h \).

Our solutions of amplitude and offset mainly reflect the change of \( \tilde{\alpha} \) and \( \tilde{\beta} \), see Sec. IV C. For constant \( h \) and \( k \), it shows a period of \( 2Q_{2a} \approx 2.3Q_d \).

In contrast to the dimer features above 0.2 eV, its intensity for \( h = k = 0 \) is enhanced for \( l = 16.8 \) but suppressed for \( l = 19.6 \).

expected for undistorted octahedra. Depending on the sign of \( \Delta_{CF} \), the observed peak energies of 0.57 eV and 0.70 eV yield either \( \lambda = 0.41 \text{ eV} \) and \( \Delta_{CF} = -0.18 \text{ eV} \) or \( \lambda = 0.40 \text{ eV} \) and \( \Delta_{CF} = 0.23 \text{ eV} \). Since the Hamiltonian in Eq. [2] only deals with \( t_{2g} \) electrons, it yields an effective value of \( \lambda \) that slightly depends on \( 10D_q \). Our solutions of \( \lambda = 0.40 \text{ eV} \) or 0.41 eV fall well within the range reported in RIXS on Ir oxides [41] [42] [43] [47] [52] [56] [61] [66].

With Ir\(^{4+}\) ions occupying 4\( f \) and 2a sites, one may expect different values of \( \Delta_{CF} \), and these may cause a further splitting of the peaks at 0.57 eV and 0.70 eV. As stated above, only about 6% of the 2a sites were reported to be occupied by Ir ions for \( x = 1 \) but this value increases to 21% for \( x = 2 \) [26] [28] [35]. For large \( x \), a detailed analysis of the spin-orbit exciton peaks is hindered by the additional presence of dimer features in the spectra. However, the enhanced width of the 0.57 eV peak for \( x = 1.5 \) possibly reflects different values of \( \Delta_{CF} \) on the two sites.

Comparing \( x = 0.3 \) and 0.5, the RIXS intensity of the peak at 0.57 eV increases with \( x \), see Fig. [4] and shows a relative intensity that roughly agrees with the relative Ir concentration. In the same spirit, the integrated intensity of the 0.57 eV peak for \( x = 0.15 \) amounts to about 80% of the value for \( x = 0.5 \), which roughly agrees with the ratio of the \( n \) values determined from \( \chi(T) \), cf. Sec. [IV]. However, the RIXS matrix elements depend on the measurement geometry and the sample orientation, and the intensity is further affected by the surface quality. Therefore, we refrain from a more detailed quantitative comparison of the RIXS intensities obtained on different samples. However, we emphasize that the strong peak at 0.57 eV is observed for all \( x \), demonstrating the presence of individual \( j = 1/2 \) sites even for large \( x \) when the response is dominated by dimers.

B. Quasimolecular dimer excitations

For \( x = 0.5 \), at most 1/4 of the 4\( f \) dimer sites can be occupied by Ir ions, and this number is even smaller if Ir ions also occupy the 2a sites. The pronounced change of the line shape of the RIXS spectra with increasing \( x \), cf. Fig. [4] reflects an increasing density of Ir\(_2\) dimers along with a dramatic difference of the electronic structure of dimers compared to weakly interacting \( j = 1/2 \) moments. For \( x = 1.8 \), the strongest RIXS peak is observed at about 0.35 eV, and the spectra for \( x = 1.5 \) and 0.5 reveal corresponding features at the same energy, i.e., dimers are already formed for \( x = 0.5 \).

In spectroscopy on crystalline materials, studies of the \( \mathbf{q} \)-dependent properties often focus on the dispersion \( \omega(\mathbf{q}) \) of the excitation energy. For excitations localized on a dimer, however, the key feature is the \( \mathbf{q} \) dependence of the RIXS intensity, allowing us to unravel the quasimolecular character of a given excitation [41] [42]. For an individual \( j = 1/2 \) moment on a single site, neglecting interactions, the local excitation to \( j = 3/2 \) states does not show any \( \mathbf{q} \) dependence. The spin-orbit exciton peaks at 0.57 and 0.70 eV support this picture for \( x = 0.5 \) and 0.5 for two different \( \mathbf{q} \) points, see Fig. [4]. Addressing the \( \mathbf{q} \) dependence more explicitly, Fig. [6] shows that the integrated RIXS intensity of the strong 0.57 eV peak is roughly independent of \( q_c \) over many Brillouin zones. This is observed for both \( x = 0.5 \) and 1.5. In contrast, the sinusoidal modulation of the RIXS intensity integrated around 0.35 eV (dark blue symbols in Fig. [6]) shows an ambiguous agreement which is not resolved by the experimental scattering geometry that is necessary to vary \( \mathbf{q} \) over a large range, giving rise to a change of polarization factors. At the same time, the scattering geometry determines self-absorption effects [50] which, however, have been corrected in our data.
For \( x = 1.5 \) and integration from 0.65 to 0.80 eV, we find a modulation with the same period as around 0.35 eV but reduced amplitude (light blue symbols in Fig. 6), suggesting that dimer excitations overlap with the single-site 0.70 eV peak. Remarkably, integration below 0.25 eV (green symbols in Fig. 6) reveals a period that is about 17% larger, pointing towards a different origin of the corresponding excitation. It stems from Ir pairs where one Ir ion is located on a 2\( l \) site, see Sec. V C.

The sinusoidal intensity modulation described by Eq. 3 was also observed in RIXS on magnetic excitations in honeycomb Na\(_2\)IrO\(_3\) where dominant Kitaev interactions yield dynamical spin-spin correlations that are restricted to nearest neighbors on a bond, forming the dynamical magnetic equivalent of a dimer 07. A sinusoidal modulation in \( q \) space reflects the Fourier transform of a dimer. In the case of RIXS, this intensity modulation reveals the dynamical structure factor of a dimer excitation. In other words, it is equivalent to an inelastic realization of a double-slit-type interference pattern 11 18 21. To calculate the corresponding total RIXS amplitude \( A_f(q) \), one has to sum up all scattering processes that lead to a given final excited state \( |f\rangle \). The RIXS process at the Ir \( L_3 \) edge proceeds via an intermediate state with a 2\( p \) core hole that is strongly localized on a given Ir site. In the case of Ir\(_2\)O\(_9\) dimers with quasimolecular orbitals, the scattering process may occur on each of the two Ir sites \( R_i \), over which the holes are delocalized in both the ground state \( |0\rangle \) and the excited state \( |f\rangle \). The summation thus has to run over both sites,

\[
A_f(q) \propto \langle f | \sum_{i \in \{1, 2\}} e^{i q R_i} M_{R_i} | 0 \rangle , \tag{4}
\]

where \( M_{R_i} \) denotes the dipole matrix element for the RIXS process via site \( R_i \) and \( e^{i q R_i} \) is the corresponding phase factor. Assuming a dimer with inversion symmetry, the matrix elements on the two sites share the same modulus but may differ in sign, which yields

\[
A_{\text{inv}}^f(q) \propto e^{i q d/2} \pm e^{-i q d/2} . \tag{5}
\]

Since the RIXS intensity is proportional to the amplitude squared, this yields either \( \sin^2 \) or \( \cos^2 \) behavior, depending on the parity of \( |0\rangle \) and \( |f\rangle \). However, a single Ir\(_2\)O\(_9\) bi-octahedron exhibits mirror symmetry but no inversion symmetry, giving rise to a mixture of \( \sin(q_c d/2) \) and \( \cos(q_c d/2) \) terms in the amplitude. In Ba\(_3\)Ti\(_3\)-Ir\(_2\)O\(_9\), the bi-octahedra in adjacent layers are rotated by \( \pi \) around \( c \) with respect to each other, hence the two different dimer orientations are transformed into each other via inversion, see Fig. 1. Summing the intensities of the two orientations cancels the terms odd in \( q_c \), such that only \( \sin^2(q_c d/2) \) and \( \cos^2(q_c d/2) \) terms survive 11. For the expected RIXS intensity this yields

\[
I_f(q_c) \propto u(q_c) \sin^2(q_c d/2) + v(q_c) \cos^2(q_c d/2) , \tag{6}
\]

where the \( q_c \) dependences of the prefactors again mainly reflect polarization effects. For \( u > v \), this explains the dominant \( \sin^2 \) behavior described by Eq. 3 and observed in Figs. 6 and 7 for the peak at 0.35 eV. The opposite behavior with \( u < v \) resulting in a dominant \( \cos^2 \) term is found for the 0.95 eV peak, see Fig. 7. As discussed below, this indicates a spin-flip character of the 0.95 eV peak. The period \( 2Q_d = 2\pi/d \) provides a measure of the intradimer Ir-Ir distance \( d \). We find \( 2Q_d = (5.34 \pm 0.04) \times 2\pi/c \) which is equivalent to \( d = (2.66 \pm 0.02) \) Å at 20 K, in agreement with the value 2.65 Å determined in elastic x-ray diffraction at 300 K 34.

The two dimer sites are displaced along the \( c \) axis. This explains the intensity modulation as a function of \( l \) and predicts that dimer features are insensitive to \( h \). This is indeed observed above 0.2 eV, see Figs. 5 and 8. In contrast, the RIXS peak at 0.15 eV exhibits a pronounced

![FIG. 6. RIXS interference patterns as a function of \( l \) for \( x = 0.5 \) (a) and 1.5 (b). Measuring on a \((100)\) surface with \( c \) in the scattering plane allows us to cover a large range of \( l \) that includes \( l = 0 \). Data were corrected for self absorption 50 and integrated over the indicated energy ranges. The local, single-site character of the spin-orbit exciton yields roughly constant intensity around 0.57 eV (orange). In contrast, the \( \sin^2(q_c d/2) \) modulation of the 0.35 eV peak (dark blue) with period \( 2Q_d = 2\pi/d \) demonstrate its quasimolecular dimer character. The larger period observed for integration below 0.25 eV for \( x = 1.5 \) (green in (b)) unveils a different microscopic origin related to Ir ions on 2a sites, see Sec. V C. For each point, the integration time was 20 s (orange) and 60 s (blue) in the top panel and 30 s in the bottom panel.](image-url)
The 0.95 eV dimer peak shows a \( \cos^2(q_d/2) \) behavior (red), cf. Fig. 4(c), while a \( \sin^2(q_d/2) \) modulation is observed for integration from 0.275 to 0.45 eV, in agreement with Fig. 6(b). Data were collected on a (100) surface with \( c \) (nearly) perpendicular to the scattering plane, i.e., rotated by 90° with respect to the geometry used in Fig. 6(b). A finite range of \( l \) can be covered by tilting the sample. Solid lines: fits according to \( I(l) = a_0 \sin^2(\pi l/2Q_d) + c_0 \) and equivalently for the \( \cos^2 \) curve, using the period \( 2Q_d = 5.34 \times 2\pi/c \) determined from the data in Fig. 6(b).

A quasimolecular dimer character has been demonstrated in RIXS measurements on the sister compounds \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \) and \( \text{Ba}_3\text{InIr}_2\text{O}_9 \) with two and three holes per dimer, respectively [41, 42]. The short intradimer Ir-Ir distance of about 2.5–2.6 Å [34] gives rise to a very large hopping of the order of 0.5–1 eV [11, 12] and a corresponding large splitting of bonding and antibonding quasimolecular orbitals in which the holes are fully delocalized over a given dimer. As in \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \) with \( \text{Ce}^{4+} \) ions, the \( \text{Ir}_2\text{O}_9 \) dimers in \( \text{Ba}_3\text{Ti}_{3-x}\text{Ir}_x\text{O}_9 \) host two holes that can be placed in the lowest quasimolecular orbital, giving rise to a nonmagnetic ground state [41]. The RIXS data of \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \) show three features peaking at around 0.7, 1.0, and 1.2 eV. Similarly, the dimer features in \( \text{Ba}_3\text{Ti}_{3-x}\text{Ir}_x\text{O}_9 \) for large \( x \) can be roughly described by three peaks at around 0.35, 0.7, and 0.95 eV, suggesting a reduced energy scale for \( M = \text{Ti} \) compared to \( \text{Ce} \). This tentatively can be ascribed to the larger Ir-Ir distance \( d \), which amounts to 2.65 Å [35] in the Ti compounds and 2.54 Å [11] in \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \). In a simple picture, a larger Ir-Ir distance \( d \) reduces hopping and hence a smaller bonding-antibonding splitting. The common character of the dimer states in \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \) and \( \text{Ba}_3\text{Ti}_{3-x}\text{Ir}_x\text{O}_9 \) is supported by the similar \( q \) dependences. In \( \text{Ba}_3\text{CeIr}_2\text{O}_9 \), the two lower-energy dimer features show a pronounced \( \sin^2(q_d/2) \) behavior while the third peak at 1.2 eV exhibits \( \cos^2(q_d/2) \) behavior which is strongly suppressed at large \( l \) [41]. The same can be observed in \( \text{Ba}_3\text{Ti}_{3-x}\text{Ir}_x\text{O}_9 \). The two features at 0.35 and 0.7 eV show a \( \sin^2(q_d/2) \) intensity modulation, see Figs. 4 and 5 while the third peak at 0.95 eV hardly depends on \( l \) for large \( l \), cf. Fig. 4(d), but indeed shows \( \cos^2(q_d/2) \) behavior for small \( l \), see Figs. 6 and 4(c). For \( M = \text{Ce} \), the distinct behavior of the third peak has been shown to arise from the spin-flip character of this excitation [41]. Altogether this suggests that the peak at 0.95 eV for \( x = 1.5 \) and 1.8 corresponds to a singlet-to-triplet dimer excitation.

In contrast to the related compounds \( \text{Ba}_3\text{MIr}_2\text{O}_9 \), the physics of \( \text{Ba}_3\text{Ti}_{3-x}\text{Ir}_x\text{O}_9 \) is governed by strong Ti-Ir site disorder. This is highlighted by the coexistence of Ir\(_2\)O\(_9\) dimers and single Ir sites in TiIr\(_2\)O\(_9\) units for not too small values of \( x \). If dimer formation was energetically unfavorable, it could be avoided for \( x = 0.5 \), and the same argument holds for single sites at large \( x \). The coexistence thus suggests that neither dimers nor single sites are strongly preferred, pointing towards a random distribution of Ir and Ti ions over the dimer sites, in agreement with previous results [20, 28, 32]. Combined with the nonmagnetic character of the dimer ground state, this disorder provides the key to understand the surprising \( x \) dependence of the magnetic susceptibility, see Fig. 2. For small \( x \), the susceptibility reflects the dominant contribution of dilute \( j = 1/2 \) moments located on individual Ir sites. With increasing \( x \), however, the relative contribution of nonmagnetic dimers is enhanced, which may even lead to a suppression of \( \chi(T) \) upon strongly increasing the Ir content.
C. Magnetic excitation on 2a sites

In the following, we address the distinct properties of the 0.15 eV peak, see Figs. 5(b), and 9, and demonstrate how RIXS interferometry allows us to unravel its microscopic origin. For \( x = 1.5 \), integration of the RIXS intensity as a function of \( q_c \) in the energy range 0.125 to 0.25 eV yields a modulation period \( 2Q_{2a} = (0.27 \pm 0.08) \times 2\pi/c \) that is about 17\% larger than the dimer value \( 2Q_d \), see Fig. 6(b). The sinusoidal pattern again points towards the interference of scattering on two sites, but their distance projected onto the \( c \) axis amounts to \( d_{2a} = (2.26 \pm 0.03) \, \text{Å} \). This agrees with the difference of the \( z \) components of \( 2a \) and \( 4f \) sites of 2.22 Å measured in x-ray diffraction at 300 K [35], pointing towards the presence of Ir ions on \( M \) (2a) sites interacting with Ir ions on \( 4f \) sites. These two sites are also displaced perpendicular to \( c \), cf. Fig. 4 giving rise to the \( h \) dependence of the 0.15 eV feature shown in Figs. 2 and 3.

Taking a 2a site as the origin of our coordinate frame, it has six \( 4f \) neighbors at \( \pm r_i \) with \( i \in \{1, 2, 3\} \), see right part of Fig. 1 and sketch in Fig. 9. For simplicity, we consider separate pairs that are built from the Ir ion on the 2a site and by one Ir neighbor on one of the six neighboring \( 4f \) sites. This can be motivated by the fact that the 0.15 eV peak is only observed for large \( x \), in which case most of the neighboring bi-octahedra will be occupied by two Ir ions with two holes forming a stable singlet in a quasimolecular orbital. We neglect the interaction with such singlets, and we may also neglect those bi-octahedra that are occupied by two Ti ions. Relevant to us are the TiIrO\(_6\) bi-octahedra where the Ir \( j = 1/2 \) moment on a \( 4f \) site may interact with one on a 2a site, as indicated by the thick black line on the right side of Fig. 1. For such pairs, we expect a sinusoidal intensity modulation \( \sin^2(q \cdot r_i/2) \), equivalent to Eq. (3). We find

\[
\begin{align*}
\frac{1}{2} q \cdot r_{1,4} &= \pm \left[ (h+2k) \frac{\pi}{3} \pm \frac{\pi}{6.27} \right], \\
\frac{1}{2} q \cdot r_{2,5} &= \pm \left[ (h-k) \frac{\pi}{3} \pm \frac{\pi}{6.27} \right], \\
\frac{1}{2} q \cdot r_{3,6} &= \pm \left[ -(2h+k) \frac{\pi}{3} \pm \frac{\pi}{6.27} \right]
\end{align*}
\]

for \( 2Q_{2a} = 6.27 \times 2\pi/c \). The indices \( i \in \{1, 2, 3\} \) and \( j \in \{4, 5, 6\} \) of the bonds \( \pm r_i \) refer to 2a sites in adjacent layers. The corresponding Ir\(^{2+}\)O\(_6\) octahedra are rotated by \( \pi \) around \( c \), giving rise to the different signs in front of the \( l \) term. The overall sign of \( r_i \) is irrelevant for the \( \sin^2(q \cdot r_i/2) \) term. Note that all possible pairs yield the same \( l \) dependence for \( h = k = 0 \). This agrees with the sinusoidal modulation with a single period \( 2Q_{2a} \) observed for the green symbols in Fig. 6(b), which in turn strongly supports the simple picture of separate pairs. The data in Fig. 6(b) were measured with \( h = 0.1 \), which is nearly equivalent to \( h = 0 \).

Treating each pair separately, we add the intensities for all six kinds of pairs described by Eqs. (7) - (9). This summation over the two different layers of Ir\(^{2+}\)O\(_6\) octa-

![FIG. 9. RIXS interference patterns of Ba\(_5\)Ti\(_{1.5}\)Ir\(_{1.5}\)O\(_9\) as a function of \( h \). The dominant dimer peak at 0.35 eV, integrated from 0.275 eV to 0.45 eV (blue), does not depend on \( h \) since the dimer axis is parallel to \( c \), cf. Eq. (3) and Fig. 4. In contrast, the 0.15 eV peak (dark green) shows a modulation with two different periods along \( h \). The solid line depicts the total fit, cf. Eq. (12), while the light green lines show the two contributions with periods 3 and 3/2 in \( h \). Accordingly, the 0.15 eV peak corresponds to a magnetic excitation for a pair of Ir ions located on neighboring 2a and 4f sites. Sketch: projection of the Ir\(^{2+}\)-O\(_6\) bonds onto the ab plane, illustrating the two values of \( |q \cdot r_i| \) for \( q = (h 0 0) \) r.l.u., cf. Eqs. (7)-(9). The numbers \( i \in \{1, 2, 3\} \) denote the six bonds \( \pm r_i \) for a given 2a site. The Ir\(^{2+}\)O\(_6\) octahedra in the neighboring layers are rotated by \( \pi \) around \( c \), giving rise to the identical projection onto the ab plane.

\[
I[(h k l)] \propto \sum_{i=1}^{6} \sin^2(q \cdot r_i/2)
\]

\[
= 3 + \cos \left( l \frac{2\pi}{6.27} \right) \cdot \left[ 2 \sin^2 \left( \frac{(h+2k)\pi}{3} \right) \right] \\
+ 2 \sin^2 \left( \frac{(h-k)\pi}{3} \right) + 2 \sin^2 \left( \frac{(2h+k)\pi}{3} \right) - 3.
\]

The projection of the different 2a-4f pairs onto the ab plane, sketched in Fig. 9, yields a characteristic dependence on \( h \) and \( k \) for constant \( l \) that allows us to identify corresponding pair excitations. Figure 9 shows the integrated RIXS intensity of the 0.15 eV peak as a function of \( h \) for \( k = 0 \) and \( l = -6.4 \). The latter is nearly equivalent to \( l \approx 0 \) since it is close to a full period \( 2Q_{2a} = 6.27 \times 2\pi/c \). For this \( h \) scan, the model predicts two periods in \( h \), namely 3 and 3/2,

\[
I[(h 0 0)] \propto 2 \sin^2 \left( \frac{h\pi}{3} \right) + \sin^2 \left( \frac{2h\pi}{3} \right),
\]

due to the two different projections of the \( r_i \) on \( (h 0 0) \). The data in Fig. 9 are well described by a fit (dark green line) based on

\[
I_{\text{fit}}(h) = a_0 \left[ 2 \sin^2 \left( \frac{h\pi}{3} \right) + b_0 \sin^2 \left( \frac{2h\pi}{3} \right) \right] + c_0,
\]
where the two contributions are depicted by the light green lines. The observation of the two periods strongly supports our simple model, even though we find a reduced prefactor $b_0 = 0.63$ for the second term compared to Eq. (11). This scenario of separate pairs of Ir ions on $2a$ and $4f$ sites also explains the intriguing $h$ dependence of the 0.15 eV peak revealed in Fig. 5. For $l = 16.8$, the model indeed predicts a maximum of intensity for $h = 0$ and a minimum for $h = 2$, while the opposite is expected for $l = 19.6$, as observed experimentally.

The excitation energy of 0.15 eV roughly can be motivated via the bonding geometry. The IrO$_6$ octahedra around the $2a$ and $4f$ sites share a common corner, giving rise to a 180° Ir-O-Ir bond, see Fig. 1. This bonding geometry is equivalent to the case of square-lattice Sr$_2$IrO$_4$ with strong Heisenberg exchange $J$ and magnon energies extending up to roughly 0.2 eV [46, 47]. For a single bond of two moments coupled by $J$, the excitation energy is of the same order of magnitude as found for zone-boundary magnons on the square lattice, which roughly explains the peak energy of 0.15 eV. This scenario of exchange-coupled local moments in contrast to quasimolecular orbitals is based on the fact that hopping $t$ is significantly smaller in corner-sharing geometry than for face-sharing octahedra. The ratio of the on-site Coulomb repulsion $U$ over $t$ is then large enough to suppress a quasimolecular character and the physics is described by two $j = 1/2$ moments coupled by an exchange interaction $J \propto t^2/U$. Note that a similar RIXS feature was observed at 0.23 eV in Ba$_3$InIr$_2$O$_9$ with three holes per dimer and magnetic $j_{dim} = 3/2$ dimer moments [42]. There, about 7% of Ir ions were observed on the In$_2a$ sites.

Altogether, our results provide strong evidence for the identification of the 0.15 eV peak as a magnetic excitation of a pair of exchange-coupled Ir $j = 1/2$ moments located on neighboring $2a$ and $4f$ sites. This assignment is further supported by the observed symmetry, i.e., the dominant $\sin^2(q \cdot r_{ij}/2)$ character of the interference pattern plotted in Figs. 6(b) and 7 of Eq. (12). The corner-sharing octahedra of a $2a$-$4f$ pair show the same orientation, see Fig. 1. In this case we expect the minus sign in Eq. (5) for a spin-flip excitation, in agreement with the observed $\sin^2(q \cdot r_{ij}/2)$ behavior. In contrast, the two IrO$_6$ octahedra of a face-sharing dimer are rotated by $\pi$ around $c$ with respect to each other. For the intradimer spin-flip at 0.95 eV, this contributes a further minus sign and yields the $\cos^2(q_c.d/2)$ behavior observed in Fig. 2.

VI. CONCLUSIONS

The physics of Ba$_3$Ti$_{13-}Ir_2$O$_9$ is dominated by strong disorder. The similar radii and equal valence of Ir$^{4+}$ and Ti$^{4+}$ ions yield mixed crystals with pronounced Ir-Ti site mixing. For $x \leq 0.5$, our RIXS spectra of samples with $x \in \{0.3, 0.5, 1.5, 1.8\}$ demonstrate the coexistence of single-site $j = 1/2$ moments and Ir$_2$O$_9$ dimers, as expected for a random distribution of Ir and Ti ions. Individually spin-orbit-entangled $j = 1/2$ moments prevail for small Ir content $x$ while the density of Ir$_2$O$_9$ dimers increases with $x$. Due to the large intradimer hopping, the dimers host quasimolecular orbitals in which the holes are fully delocalized over the two dimer sites. Both holes occupy the lowest binding orbital in the dimer ground state, forming a nonmagnetic $j_{dim} = 0$ singlet. The coexistence of nonmagnetic dimers and $j = 1/2$ moments explains the at first sight unconventional behavior of the magnetic susceptibility which is very similar for $x = 0.5$ and 1.5, i.e., for two samples in which the concentration of magnetic Ir ions differs by a factor of three.

These compounds offer a remarkable example for the unusual role that disorder may play in a cluster Mott insulator. Substituting a magnetic ion by a nonmagnetic one typically yields a vacancy in the magnetic system. In a cluster, however, it changes the character of the magnetic moment. In Ba$_3$Ti$_{13-}Ir_2$O$_9$, cation disorder gives rise to different kinds of magnetic moments, and the different moments experience very different coupling strengths. On a dimer, the energy scale for singlet-to-triplet excitations is given by the RIXS peak at 0.95 eV, reflecting the large intradimer hopping. In contrast, the large spatial separation between dimers strongly suppresses interdimer interactions [72]. Considering, e.g., $j = 1/2$ moments on neighboring IrTiO$_2$ bimolecular orbitals, we expect exchange interactions on the order of meV, i.e., three orders of magnitude smaller than the intradimer singlet-to-triplet excitation energy within Ir$_2$O$_9$ units. Additionally, we observe pairs of exchange-coupled $j = 1/2$ moments that arise from Ir ions located on adjacent $2a$ and $4f$ sites. These are connected via a 180° bond that yields a large Heisenberg exchange coupling $J$ similar to the case of square-lattice Sr$_2$IrO$_4$, giving rise to a magnetic excitation at 0.15 eV.

RIXS interferometry enabled us to unravel this complex disorder scenario. The RIXS spectra and in particular the $q$ dependence of the RIXS intensity provide clear fingerprints of the different types of moments. The excitations of local single-site $j = 1/2$ moments are independent of $q$. In contrast, a sinusoidal modulation of the RIXS intensity of orbital excitations is a characteristic hallmark of quasimolecular dimer orbitals, and a predominant $\sin^2(q \cdot r/2)$ or $\cos^2(q \cdot r/2)$ behavior typifies the symmetry and character of the excited states. The RIXS studies of the sister compounds Ba$_3$CeIr$_2$O$_9$ and Ba$_3$InIr$_2$O$_9$ [42] were focused on establishing the distinct quasimolecular character for two or three holes per dimer. In Ba$_3$Ti$_{13-}Ir_2$O$_9$, the periodicity of the modulation allows us to identify which sites contribute to a given excitation. We can distinguish Ir$_2$O$_9$ dimers from $2a$-$4f$ pairs via the distinct modulation period along $l$ as well as via the absence or presence of a characteristic modulation along $h$ or $k$. We expect that our results will trigger many further experimental investigations to exploit the stunning power of RIXS interferometry to study the electronic structure of dimers, trimers, and larger clusters, even in the presence of disorder.
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