High-energy electronic excitations in Sr$_2$IrO$_4$ observed by Raman scattering

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(Dated: November 11, 2014)

Spin-orbit interaction in Sr$_2$IrO$_4$ leads to the realization of the $J_{\text{eff}} = 1/2$ state and also induces an insulating behavior. Using large-shift Raman spectroscopy, we found two high-energy excitations of the d-shell multiplet at 690 meV and 680 meV with $A_{1g}$ and $B_{1g}$ symmetry respectively. As temperature decreases, the $A_{1g}$ and $B_{1g}$ peaks narrow, and the $A_{1g}$ peak shifts to higher energy while the energy of the $B_{1g}$ peak remains the same. When 25% of Ir is substituted with Rh the $A_{1g}$ peak softens by 10% but the $B_{1g}$ peak does not. We show that both pseudospin-flip and non-pseudospin-flip dd electronic transitions are Raman active, but only the latter are observed.

In 5$d$ transition-metal oxides (TMOs), the $d$ electrons are extended in real space and therefore they should have a large bandwidth (W) and a reduced on-site Coulomb correlation (U). As a result, 5$d$ TMOs are expected to be metals instead of insulators as 3$d$ TMOs in which the strong correlation leads to Mott insulating states. However, spin-orbit coupling (SOC) in 5$d$ TMOs is an order of magnitude larger than in 3$d$ TMOs due to the large atomic number. Several iridium oxides including Sr$_2$IrO$_4$ are insulators because of SOC [1–5]. It has been proposed that the interplay between SOC, Coulomb correlation, crystal field splitting, and inter-site hopping can lead to unconventional electronic states for the 5$d$ TMOs [6].

Sr$_2$IrO$_4$ attracted attention as the first realization of a SOC-induced insulator [7, 8]. The spin-orbit interaction (SOI) $\lambda \sim 0.4$ eV in Sr$_2$IrO$_4$ splits the $t_{2g}$ states into bands with $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$. Ir$^{4+}$ (5d$^6$) provides five electrons, and thus the $J_{\text{eff}} = 3/2$ state is fully occupied and the $J_{\text{eff}} = 1/2$ state is half filled. The narrow $J_{\text{eff}} = 1/2$ band then splits into the lower Hubbard band (LHB) and the upper Hubbard band (UHB) due to on-site repulsion, resulting an insulating state [7–11].

Optical conductivity, angle-resolved photoemission spectroscopy, x-ray absorption spectroscopy [7, 12], and resonant inelastic x-ray scattering (RIXS) [13] results are consistent with this scenario, though it has been argued that Sr$_2$IrO$_4$ is a magnetically-ordered Slater insulator [14–16].

Earlier Raman scattering experiments revealed excitations in undoped cuprates around 1.5 eV that were assigned to excitons associated with the gap induced by U (Hubbard gap) in the spectrum of d-d excitations [17–19]. At low temperatures these measurements appeared as closely-spaced broad peaks with the onset just below the gap. Here we report similar excitations in Sr$_2$IrO$_4$ at lower energies ($\sim$0.7 eV). A peak at the same energy has been previously observed by RIXS [20]. Using Raman scattering measurements with polarization analysis and far superior resolution we established that the RIXS feature consists of electronic excitations of $A_{1g}$ and $B_{1g}$ symmetry. Each contribution (especially $A_{1g}$) is surprisingly narrow in energy, and the two contributions have different temperature and Rh-doping dependences. The observed features are consistent with excitons associated with inter-site d-d hopping transitions that do not flip the pseudospin. Our results put strict constraints on any future theory of electronic structure of Sr$_2$IrO$_4$.

High-quality single crystal samples of doped and undoped Sr$_2$IrO$_4$ were synthesized as described elsewhere [2]. Sr$_2$IrO$_4$ has a tetragonal crystal structure, which belongs to the space group $I4_1/acd$ [1]. The IrO$_6$ octahedra are rotated about the c axis by $\sim 11^\circ$.

Different laser lines (457.9-560 nm) from Kr and Ar ion lasers as well as a 532 nm solid state laser were used with a power of 15 mW for the measurements at room temperature and base temperature. Temperature dependence measurements were performed with 2 mW to minimize laser heating. All experiments were performed on a McPherson custom triple spectrometer equipped with a cooled charge-coupled device (CCD) detector. It was configured in a subtractive mode with 50 grooves per mm gratings in the filter stage and 150 g/mm in the spectrometer stage, which gave the resolution of $\sim 8$ meV. The sample was mounted in a top-loading closed-cycle refrigerator. The entrance slit of the spectrometer was opened to 0.5 mm to avoid chromatic aberrations of the collecting optics. The data were corrected for the spectral response of the equipment using a calibrated lamp with a broad spectrum.

The configuration $xx/xy$ denotes that the incident laser polarization is parallel to the primitive cell in-plane crystal axes (a and b), and the scattered light polarization is parallel/perpendicular to the incident laser polarization respectively. The $x'$ and $y'$ directions are rotated 45$^\circ$ in the ab plane with respect to a and b. $xx, xy, x'x'$, and $x'y'$ polarization geometries measure $A_{1g}+B_{1g}$, $A_{2g}+B_{2g}$, $A_{1g}+B_{2g}$, and $A_{2g}+B_{1g}$ respectively in the $D_{4h}$ point group to which the IrO$_6$ octahedra belong. Although the full crystal symmetry is lowered to $C_{4h}$ by the rotation of the octahedra, we will first discuss the results in terms of the representations of the $D_{4h}$ point group and then show that the symmetry lowering does not have a measurable effect.

In addition to the Raman peaks, a broad background
Ref. [21]. We found that it depends strongly on surface preparation and on the part of the sample that is being probed. The lowest background was obtained on samples that were cleaved in high vacuum before being transferred to the cryostat. Based on our investigation, it appears that this background is mostly an artifact of surface degradation although we cannot rule out a component that is intrinsic.

Electronic Raman scattering from Sr$_2$IrO$_4$ is dominated by strong peaks near 5600 cm$^{-1}$ that appear in xx, x’x’, and x’y’ geometries, but not in the xy geometry beyond what is expected from imperfect polarization analysis (Fig. 1) i.e. these peaks exist in the A$_{1g}$ and B$_{1g}$ symmetries but not in B$_{2g}$ or A$_{2g}$ symmetry. The B$_{1g}$ peak appears at 5500 cm$^{-1}$, and the A$_{1g}$ peak is at 5600 cm$^{-1}$.

The A$_{1g}$ and B$_{1g}$ features near 5600/5500 cm$^{-1}$ are enhanced with higher incident laser energy (shorter wavelength), while their positions remain the same, which is consistent with resonant Raman scattering (see Fig. 2).

The A$_{1g}$ peak hardens on cooling from 5600 cm$^{-1}$ to 5700 cm$^{-1}$ saturating for T < 150 K (Fig. 3). Its linewidth narrows on cooling from 1200 to 550 cm$^{-1}$ to below 200 K. The position of the B$_{1g}$ peak, is around 5450 cm$^{-1}$ at all temperatures, and its linewidth narrows from 1200 cm$^{-1}$ to 850 cm$^{-1}$ to below 200 K. At 300 K the B$_{1g}$ feature has a low-energy shoulder that appears as a distinct small peak at 4300 cm$^{-1}$ at low temperature. So the fits to the B$_{1g}$ spectrum include 2 components, a weak one at 4300 cm$^{-1}$ and a strong one at 5450 cm$^{-1}$. Substitution of 25% of Ir with Rh softens the A$_{1g}$ by 80 meV and the B$_{1g}$ peak by 10 meV (Fig. 4) and significantly broadens both peaks.

The peak energies are close to the insulating gap found in several experiments. Optical conductivity spectra exhibit two major peaks assigned to transitions from the occupied $J_{d8} = 1/2$ (LHB) and 3/2 states to the unoccupied $J_{d8} = 1/2$ (UHB) state [7, 22]. We do not expect an exact match to optical conductivity, because optically-active transitions are symmetry forbidden in Raman scattering and vice versa. Scanning tunneling microscopy (STM) studies show the onset of tunneling around 0.5 eV, with the separation between conductance peaks near 0.75 eV, which is near to what we measured [23]. Our Raman features have a similar energy to the recent LDA calculations [9, 24].

Previous work on the insulating compounds of the high $T_c$ cuprates revealed similar peaks as the ones reported here but at much higher energies around 1.5-2 eV [17–19]. They appeared in the A$_{2g}$ symmetry. Peaks at half the energy in the iridates are consistent with a much lower U, which in both cases is responsible for the insulating behavior. The d-d exciton that we observe is much sharper at low temperatures than the exciton peaks in most cuprates with the exception of the ones with the T‘ structure where several sharp peaks appear. Also, the peaks in cuprates are asymmetric and are located at the onset of a broad continuum of electronic scattering above the insulating gap. No such onset is seen in the iridates where the peaks are isolated and there is no broad band of scattering or higher energy peaks up to 1.2 eV.

We now compare our results to a simple calculation of what types of on-site and near neighbor hopping electronic transitions appear in what symmetry. The Raman intensity is proportional to [25]

$$I \propto \frac{1}{Z} \sum_{I,F} |\langle F | \mathbf{R}_{\mu \nu} | I \rangle|^2 e^{-E_I/k_B T} \delta(E_F - E_I - \hbar \omega),$$

(1)

where $I, F$ label energy eigenstates of the electronic system with energies $E_I, E_F$, $\omega$ is the Raman shift, and $Z$ is the partition function. $\mathbf{R}_{\mu \nu}$ is the Raman tensor, with $\mu, \nu = x, y, z$ giving the direction of linear polarization of scattered and incident light in our experiment, respectively. The electronic Raman cross section is typically dominated by the first two terms in perturbation theory. Fig. 2 shows that the intensity of the peaks of interest has a strong laser energy-dependence. Since the first order term does not depend on the laser energy, the second order term must dominate. Thus we focus on this contribution, which is given by:

$$R_{\mu \nu} = p_\mu E_I \frac{1}{E_I + \hbar \omega_I - H_{el} p_\nu},$$

(2)
where $H_{el}$ is the electronic Hamiltonian, $p_{\mu}$ the electron momentum operator, and $\omega_1$ is the frequency of incident light.

In the presence of tetragonal crystal field (CF) and SOC, the $t_{2g}$ manifold splits into three Kramer doublets labeled with $j_1, j_2$ and $j_2$ (Fig. 5(a)) [26–28]. The $j$ ($J_{\text{eff}}^z = \pm 1/2$) and $j$ ($J_{\text{eff}}^z = \pm 3/2$) doublets transform differently under $D_{4h}$ symmetry and time reversal (See supplementary information). Note that $J_{\text{eff}}^z$ is not a good quantum number under $D_{4h}$ CF.

We adopt a tight-binding description of the electronic states, with $c_r^{\dagger}$, creating an electron at the Ir lattice site $r$ in the local spin-orbital state $\alpha$. Here, the spin-orbital state $\alpha \equiv (a, \sigma)$, where $a = j_1, j_2, j_2$ labels the local doublets, and $\sigma = 1, 2$ is the pseudo-spin. We work in real-space. In our description of the Raman process, a photon is absorbed near a lattice site $r$, with the resulting excited intermediate state propagating over some distance before emission of a photon near site $r'$. Far enough away from resonance, the intermediate state will propagate only over a short distance; this leads to the expansion

$$R_{\mu \nu} = \sum_r M_{0,\mu \nu}^{\alpha \beta}(r) c_r^{\dagger} \sigma_{\alpha \beta} f_{r, \beta} + M_{1,\mu \nu}^{\alpha \beta}(r) c_r^{\dagger} f_{r, \beta} + \cdots . \quad (3)$$

Here the first term represents on-site transitions, while the second term describes inter-site processes, in which an electron moves from a site $r$ to a cluster state created by $c_r^{\dagger}$. The cluster state is a linear superposition of spin-orbital states on the four Ir sites nearest to $r$. Sums over repeated indices $\alpha, \beta$ are implied. Longer range terms have been dropped.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Transition & Non-pseudospin-flip & Pseudospin-flip \\
\hline
$j_2 \rightarrow j_1$ & $xx, x'x'$ ($A_{1g}$) & $xy, x'y'$ ($A_{2g}$) \\
\hline
$j_2 \rightarrow j_1$ & $xx, x'y'$ ($B_{1g}$) & $x'x', xy$ ($B_{2g}$) \\
\hline
\end{tabular}
\caption{Polarization and symmetry of on-site Raman transitions with $D_{4h}$ site symmetry. The row indicates the doublets between which the transition occurs, and the column indicates whether a pseudospin flip is involved.}
\end{table}

To interpret the experimental results, we assume significant local antiferromagnetic correlations to temperatures well above the Neel temperature ($T_N = 240$ K), focusing here on $T > T_N$, as the gross features of the Raman spectrum remain largely unchanged as $T$ is lowered through $T_N$. In the low-temperature antiferromagnetic state, the moments lie in the $ab$-plane, with small canting out of the plane that we ignore [8, 29–31].

We first consider an idealized situation, where the Ir-O-Ir bond angle is $180^\circ$ and the symmetry is $D_{4h}$. We focus on on-site transitions within the $t_{2g}$ manifold, so $j_2 \rightarrow j_1$ and $j_2 \rightarrow j_1$ are relevant (the energy of the main peak is likely too large for purely magnetic $j_1 \rightarrow j_1$ transitions)(Fig. 5(a)). The pseudospin structure of each transition is described by the appropriate $2 \times 2$ block of the $6 \times 6$ matrix $M_{0,\mu \nu}(r)$. We always find this $2 \times 2$ matrix to be either proportional to the identity matrix (no pseudospin flip), or to the $\sigma^z$ Pauli matrix (pseudospin flip).

For the on-site transitions, both non-pseudospin-flip and pseudospin-flip processes can occur (See supplementary information). The former should appear in $A_{1g}$ and $B_{1g}$ symmetry and the latter in $A_{2g}$ and $B_{2g}$ symme-
try (Table 1). However any resulting peaks should be exchange-split by about 600 cm\(^{-1}\) [20]. Since the splitting is not observed, we conclude that our peaks are not due to on-site transitions.

For the inter-site transitions, we consider hopping between \(j_1\) doublets on neighboring sites. An electron hops from site \(r\) to a parity-even cluster state, constructed by superposing \(j_1\) doublets on the four neighboring sites (Fig. 5(b)). There are two such Raman-active cluster states, one with \(s\)-wave symmetry and the other with \(d_{x^2−y^2}\) symmetry. The \(s\)-wave/\(d_{x^2−y^2}\) cluster state transforms identically to the on-site \(j/j\) doublet. This means the \(r \rightarrow s/r \rightarrow d_{x^2−y^2}\) inter-site process has the same selection rules as the on-site \(j_2 \rightarrow j_1/j_2 \rightarrow j_1\) transition respectively. Note that pseudospin-flip processes are forbidden by the combination of local antiferromagnetic correlations and the Pauli principle (see Fig. 5(b)), so there should be no exchange-splitting in agreement with experiment. This suggests that the main peaks are due to inter-site transitions.

So far we assumed \(D_{4h}\) site symmetry, but, in reality, the Ir-O-Ir bond angle is away from 180° by 22°, lowering the site symmetry to \(C_{4h}\) (the point group remains \(D_{4h}\)). In this case, both \(j_2 \rightarrow j_1\) and \(j_2 \rightarrow j_1\) transitions (and corresponding inter-site transitions) may produce a non-pseudospin-flip contribution in \(xy\) polarization. That this is not seen suggests the site symmetry is effectively \(D_{4h}\) to a good approximation.

We note that the simple picture above does not explain the differences in temperature and Rh-doping dependence between the \(A_{1g}\) and \(B_{1g}\) peaks, although the broadening may be due to inhomogeneous doping in the sense that the electronic state is different near doped Rh atoms. More work is necessary to elucidate this issue. A more sophisticated calculation that would include band structure is necessary, because the two symmetries probe different k-space regions.

The narrow linewidth at 10 K of the two features is remarkable, especially the 50 meV linewidth of the \(A_{1g}\) feature. In the band picture zone center peaks originate from vertical inter band transitions, i.e their lineshape should reflect the distribution of the separations between valence and conduction bands throughout the Brillouin zone. In order to have very narrow peaks, the valence and conduction bands must be nearly parallel. DFT calculations do show nearly parallel bands [24], but not so as to produce such narrow peaks. Excitonic effects likely play a role in the final state, which may also be responsible for their small linewidth. It is also possible that Raman scattering matrix elements are large only for a small subset of k-space. In any case, we hope that this work will be used as a testing ground for more sophisticated electronic structure calculations.

![Figure 3](image1.png) FIG. 3. The comparison of Raman spectra at 10 K (red) and 300 K (black) in the (a) \(x'x'\) and (b) \(x'y'\) geometries with the laser at 532 nm. The solid lines indicate the peak positions. Temperature dependence of the peak positions and linewidth (FWHM) in the (c) \(x'x'\) and (d) \(x'y'\) geometries.

![Figure 4](image2.png) FIG. 4. The comparison of Raman spectra in \(\text{Sr}_2\text{IrO}_4\) (blue) and \(\text{Sr}_2\text{Ir}_{0.76}\text{Rh}_{0.24}\text{O}_4\) (red) at room temperature with the laser at 457.9 nm.
FIG. 5. Schematic of the on-site and inter-site transitions. (a) Local states and on-site transitions: The SOC and tetragonal CF split the orbital into three doublets labeled with $j_1$, $j_2$, and $j_3$. The non-pseudo-spin-flip electronic transition contributes to the $A_{1g}$ and $B_{1g}$ signal, and the pseudo-spin-flip process contributes the $A_{2g}$ and $B_{2g}$ signal. (b) Inter-site transitions: The ground state configuration is described in the top block. The electron can tunnel from the central site to the s-wave/$d_{x^2-y^2}$ cluster state which transforms identically to the on-site $j_1$ doublet respectively. The gray oval encloses the states on the same site.

neighbor inter-site transitions. More work is necessary to find the energies of intrasite transitions, which should be exchange-split.

We thank A.V. Chubukov and T.P. Devereaux for discussions. Experimental work at the University of Colorado was supported by the National Science Foundation (NSF) under grant No. DMR-1410111. Theoretical work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award No. DE-FG02-10ER46686 (Y.-P. H. and M.H.), and by Simons Foundation grant No. 305008 (M.H. sabbatical support). G.C. acknowledges NSF support via Grant No. DMR-1265162.

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Here, we give details on how symmetry constrains the polarization dependence and pseudospin structure of the electronic Raman transitions considered in the main text. We focus on on-site transitions; as stated in the main text, the inter-site transitions discussed are of the same symmetry as on-site transitions, and do not need to be considered separately here. In addition, we show that the Raman tensor can indeed induce pseudospin-flip processes, even if $R_{\mu\nu}$ is assumed to act only on orbital (and not spin) degrees of freedom.

Beginning with Eq. (3) of the main text, the objective is to use site symmetry and time reversal to constrain the matrix elements for on-site transitions, contained in the $6 \times 6$ matrix $M_{\mu\nu}$. We focus on a single lattice site $r$ and thus drop the site label from our analysis. As discussed in the main text, we consider an idealized case of $D_{4h}$ site symmetry and only later consider breaking down to $D_{2h}$. The analysis proceeds in the high-temperature phase, with no spontaneous symmetry breaking due to long-range magnetic order.

We focus on two $2 \times 2$ blocks of $M_{\mu\nu}$, one describing transitions from a $j$-doublet to another $j$-doublet $M_{j^+\rightarrow j^-}$, and another describing transitions from a $j$-doublet to a $j$-doublet ($M_{j^+\rightarrow j^+}$). The on-site $j_2 \rightarrow j_1$ transition and the inter-site $r \rightarrow s$ transition are both of $j \rightarrow j$ type, while the on-site $j_2 \rightarrow j_1$ and inter-site $r \rightarrow d_{x^2-y^2}$ transitions are of $j \rightarrow j$ type. (The symmetry constraints on $j \rightarrow j$ and $j \rightarrow j$ transitions are the same.)

Ignoring inversion, which acts trivially on the electronic states of interest, $D_{4h}$ is generated by the operations $C_{4z}$ (four-fold rotation about the $z$-axis), $C_{2x}$ (two-fold rotation about the $x$-axis), and $C_{2xy}$ (two-fold rotation about the $(\hat{x} + \hat{y})$-axis). It will also be useful to explicitly consider $C_{2z} = (C_{4z})^2$. We consider the single-ion Hamiltonian obtained by projecting spin-orbit coupling and $D_{4h}$ crystal field to the $t_{2g}$ manifold, which allows us to obtain wave functions for the electronic states of interest. Using these wave functions, we find the following matrices representing the action of $D_{4h}$ symmetry on the $j$-doublets:

$$C_{4z}^j = \begin{pmatrix} e^{-i\pi/4} & 0 \\ 0 & e^{i\pi/4} \end{pmatrix}$$ (1)

$$C_{2z}^j = -i\sigma^z$$ (2)

$$C_{2x}^j = i\sigma^x$$ (3)

$$C_{2xy}^j = \frac{i}{\sqrt{2}}(\sigma^x + \sigma^y).$$ (4)

where $\sigma^x, \sigma^y, \sigma^z$ are the usual $2 \times 2$ Pauli matrices. For $j$-doublets we find:

$$C_{4z}^j = \begin{pmatrix} e^{-i\pi/4} & 0 \\ 0 & e^{i\pi/4} \end{pmatrix}$$ (5)

$$C_{2z}^j = -i\sigma^z$$ (6)

$$C_{2x}^j = i\sigma^x$$ (7)

$$C_{2xy}^j = \frac{i}{\sqrt{2}}(\sigma^x + \sigma^y).$$ (8)

In both cases time reversal is given by

$$T = i\sigma^K,$$ (9)

where $K$ is the complex conjugation operator. We note that these forms only depend on the symmetry properties of the electronic states, which are expected to be captured accurately in our simple treatment.

Now we analyze the constraints on the matrix elements. First, we consider the action of symmetry on $R_{\mu\nu}$, which has to agree with that on the corresponding matrix elements. We only need to consider those operations that take a given component of $R_{\mu\nu}$ into itself (or minus itself):

$$C_{2z} : R_{xx} \rightarrow R_{xx}$$ (10)

$$C_{2z} : R_{xx} \rightarrow R_{xx}$$ (11)

$$C_{2z} : R_{x'y'} \rightarrow -R_{x'y'}$$ (12)

$$C_{2z} : R_{x'y'} \rightarrow -R_{x'y'}$$ (13)

$$C_{2z} : R_{xy} \rightarrow -R_{xy}$$ (14)

$$C_{2z} : R_{xy} \rightarrow -R_{xy}$$ (15)

$$C_{2z} : R_{x' y'} \rightarrow R_{x' y'}$$ (16)

$$C_{2z} : R_{x' y'} \rightarrow -R_{x' y'}$$ (17)

In addition, $R_{\mu\nu}$ is invariant under time reversal.

Now we consider the matrix elements $M_{j^+\rightarrow j^-}$ and $M_{j^+\rightarrow j^+}$. In each case, time reversal allows the matrices $1_{2\times2}$ and $i\sigma^\mu (\mu = x, y, z)$ to appear with arbitrary real coefficients, where $1_{2\times2}$ is the $2 \times 2$ identity matrix. For example, time reversal allows the form $M_{j^+\rightarrow j^-} = a_0 \cdot 1_{2\times2} + a_\mu i\sigma^\mu$, without yet imposing any other symmetries. Using all symmetries gives

$$M_{j^+\rightarrow j^-}, M_{j^+\rightarrow j^+} \propto 1_{2\times2}$$ (18)

$$M_{j^+\rightarrow j^-}, M_{j^+\rightarrow j^+} \propto \sigma^\mu.$$ (19)

The information provided in Table I of the main text follows from these results. We note in particular that only pseudospin-flip transitions contribute in $xy$ polarization.

Supplementary information: High-energy electronic excitations in Sr$_2$IrO$_4$ observed by Raman scattering

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**Effect of $C_{4h}$ site symmetry.** The true Ir site symmetry is $C_{4h}$, which is generated by the operations $C_{4z}$ and inversion. Focusing on effects of this lower symmetry in $xy$ polarization, we find that $M_j^{x\rightarrow j}$ and $M_j^{y\rightarrow j}$ are both allowed to have a non-pseudospin-flip contribution. The fact that a peak is not seen in $xy$ polarization suggests that the breaking of $D_{4h} \rightarrow C_{4h}$ is a weak effect, at least for the electronic states probed by our Raman measurements.

**Below Neel temperature.** Below the Neel temperature, long-range magnetic order lowers the site symmetry. Assuming the moments lie in the $xy$ plane and point along the $x'$ axis, the site symmetry is generated by the operations $C_{2z} T$ and $C_{2xy} \{1-3\}$. All components of $R_{\mu\nu}$ are left invariant by $C_{2z} T$. This operation acts on both doublets as the matrix $C_{2z} T = -i\sigma^x K$, and this allows the matrices (with real coefficients) $1, \sigma^x, \sigma^y, i\sigma^z$ to appear. Focusing again on $xy$ polarization, there are no further constraints on $M_j^{x\rightarrow j}$ and $M_j^{y\rightarrow j}$, so non-pseudospin-flip transitions are allowed to contribute in $xy$ polarization. The absence of a peak indicates that Neel order is not strong enough compared to electronic energy scales to have a significant effect on the Raman transitions probed.

**Raman scattering can flip the pseudospin.** In the absence of spin-orbit coupling, the Raman tensor cannot induce spin-flip processes. This follows from the presence of SU(2) spin rotation symmetry, and the fact that $R_{\mu\nu}$ commutes with SU(2) spin rotations. In the present case, there is substantial spin-orbit coupling, and SU(2) spin symmetry is not present, opening the possibility of pseudospin flips in the Raman process.

To assess whether $R_{\mu\nu}$ indeed contains pseudospin-flip transitions with significant amplitude, we make the conservative assumption that spin-orbit coupling only enters in the initial and final $t_{2g}$ states, ignoring spin-orbit coupling in the intermediate state. As a result $R_{\mu\nu}$ commutes with SU(2) spin rotations, and spin-flip processes are forbidden. However, we find pseudospin-flip processes are nonetheless Raman active. To illustrate this point we focus on a single lattice site for simplicity and assume:

$$R_{\mu\nu} = f_A^\dagger R_{AB} f_B^\sigma.$$  

Here $A, B = yz, xz, xy$ labels the $t_{2g}$ orbital states, $\sigma = \uparrow, \downarrow$ is electron spin, and the $3 \times 3$ matrix $R_{\mu\nu}$ is constrained by site symmetry and time reversal. We are thus assuming that $R_{\mu\nu}$ acts only on the orbital degrees of freedom. Spin-orbit coupling enters via the single-ion Hamiltonian, whose local energy eigenstates (the $j_1$, $j_2$ and $\bar{J}_2$ doublets) have mixed spin and orbital character. We determined the general symmetry-allowed form of $R_{\mu\nu}$. Then transforming the expression for $R_{\mu\nu}$ into the basis of spin-orbital energy eigenstates, we find that pseudospin-flip processes are fully allowed, even though $R_{\mu\nu}$ contains no spin-flip terms. This justifies our analysis of the Raman process including both transitions with and without pseudospin flips.

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