Magnetic Couplings, Optical Spectra, and Spin-Orbit Exciton in 5d Electron Mott Insulator Sr₂IrO₄

Beom Hyun Kim, G. Khaliullin, and B. I. Min

1Department of Physics, PCTP, Pohang University of Science and Technology, Pohang 790-784, Korea
2Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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Based on the microscopic model including spin-orbit coupling, on-site Coulomb and Hund’s interactions, as well as crystal field effects, we investigate the magnetic and optical properties of Sr₂IrO₄. Taking into account all intermediate state multiplets generated by virtual hoppings of electrons, we calculate the isotropic, pseudodipolar, and Dzyaloshinsky-Moriya coupling constants, which describe the experiment quite well. The optical conductivity σ(ω) evaluated by the exact diagonalization method shows two peaks at ~0.5 and ~1.0 eV in agreement with experiment. The two-peak structure of σ(ω) arises from the unusual Fano-type overlap between the electron-hole continuum of the \( J_{\text{eff}} = 1/2 \) band and the intrasite spin-orbit exciton observed recently in Sr₂IrO₄.

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Mott physics is one of the most fundamental phenomena in condensed matter physics giving rise to diverse and fascinating collective behavior of correlated electrons [1]. In Mott insulators, strong on-site Coulomb repulsion (\( U \)) splits the half-filled band into the lower Hubbard band (LHB) accommodating the spin and orbital degrees of freedom of electrons, and the empty upper Hubbard bands (UHBs). The electrons hop into adjacent sites only virtually, overcoming thereby the Mott-Hubbard gaps. Typically, the antiferromagnetic (AFM) ground state is realized due to the kinetic energy gain of the virtual exchange processes. The optical conductivity shows peak structures at the absorption edges corresponding to the transitions between the LHB and UHBs.

Recently, a new class of 5d Mott insulators, such as Sr₂IrO₄ [2–4] and Na₂IrO₃ [5,6], has been discovered, where the strong spin-orbit (SO) coupling is crucial for stabilizing the insulating state. The Coulomb interaction between 5d electrons \( U \sim 2 \) eV is much smaller than that in conventional 3d electron Mott insulators. On the other hand, the SO coupling \( \lambda \approx 0.4 \) eV in iridates is much larger and splits \( ^2T_{1g} \) states of a 5d^5 shell into the half-filled \( J_{\text{eff}} = 1/2 \) and fully-occupied \( J_{\text{eff}} = 3/2 \) states. Then the narrow \( J_{\text{eff}} = 1/2 \) band tends to undergo a Mott transition even at relatively small \( U \) [2,3,7–9].

The issue in iridates is to what extent the physical properties and model descriptions of \( J_{\text{eff}} = 1/2 \) systems are (dis)similar to those of conventional 3d Mott insulators. The best studied member of 5d Mott systems is Sr₂IrO₄ perovskite. Its in-plane canted AFM ground state [4], magnon spectra [10], and finite temperature spin dynamics [11] closely resemble those of parent high-\( T_c \) cuprates, in accord with the theoretical predictions [12] based on the Mott-Hubbard picture. In addition to magnons, resonant inelastic x-ray scattering (RIXS) experiments [10,13] have observed also the higher energy broad peak at ~0.5–0.8 eV. Based on the theoretical expectations [12,14,15] that the SO split \( t_{2g} \) manifold should have a magnetically active mode at ~\( \frac{3}{2} \lambda \), this peak has been attributed to the transition between \( J_{\text{eff}} = 1/2 \) and 3/2 states and termed SO exciton [10].

Concerning the charge excitation spectra, the optical conductivity \( \sigma(\omega) \) of Sr₂IrO₄ shows two peaks at ~0.5 and ~1.0 eV [2] that are preserved up to high temperatures [16]. The first peak was assigned to the transition from occupied \( J_{\text{eff}} = 1/2 \) LHB to \( J_{\text{eff}} = 1/2 \) UHB, while the peak at ~1.0 eV to that from \( J_{\text{eff}} = 3/2 \) to unoccupied \( J_{\text{eff}} = 1/2 \) [2]. This interpretation, however, is based on a picture of single-electron density of states. In fact, there have been no theoretical calculations of \( \sigma(\omega) \) in iridates taking into account the many-electron multiplet structure of excited states, which is known to be essential for the interpretation of optical data. Moreover, there are inherent relations between the optical absorption peaks or intensities and the strength of magnetic couplings (both are determined by the same virtual hoppings and excited multiplets), which enable one to extract the physical parameters, such as \( U \) and Hund’s coupling \( J_H \), from a combined analysis of the magnetic and optical data [17–19]. The aim of the present Letter is to extend this fruitful approach to the 5d electron Mott insulators.

We have calculated the magnetic couplings, optical conductivity, and RIXS spectra in Sr₂IrO₄ by exact diagonalization (ED) of a microscopic model on small clusters, fully incorporating the multiplet structure of Ir ions, SO coupling, tetragonal distortion, and octahedral rotations. The magnetic couplings obtained are consistent with the available data [4,10,11]. Calculated RIXS spectra reproduce the SO exciton mode. More interestingly, we found that, unlike the case of 3d oxides [17–19], the observed peaks in \( \sigma(\omega) \) of Sr₂IrO₄ cannot be directly determined from the multiplet energies and intensities. Instead, the
strong mixing between intersite optical excitations (electron-hole continuum) and intraionic transition between $J_{\text{eff}} = 1/2$ and $3/2$ states (SO exciton) is found to be an essential feature of Sr$_2$IrO$_4$. This implies that neither purely atomic nor a simple band picture is sufficient to describe the small charge-gap iridium oxides.

Model.—To describe the electronic structure of Ir ions, we adopted the following Hamiltonian:

$$
H_{\text{ion}} = \sum_{\sigma \bar{\sigma}} e_{\sigma \bar{\sigma}} n_{\sigma \bar{\sigma}} + \frac{1}{2} \sum_{\sigma \bar{\sigma} \mu \nu} U_{\mu \sigma} c_{\nu \sigma}^\dagger c_{\nu \bar{\sigma}} c_{\mu \sigma} c_{\mu \bar{\sigma}} + \frac{1}{2} \sum_{\mu \nu} J_{\mu \nu} c_{\mu \sigma}^\dagger c_{\mu \bar{\sigma}} c_{\nu \sigma} c_{\nu \bar{\sigma}} + \frac{1}{2} \sum_{\mu \nu} J'_{\mu \nu} c_{\mu \sigma} c_{\mu \bar{\sigma}} c_{\nu \sigma}^\dagger c_{\nu \bar{\sigma}}^\dagger,
$$

where $\tau$ and isospin $\bar{\sigma}$ [12] refer to the lowest three Kramers doublets [the eigenstates in the presence of the tetragonal crystal field splitting $\Delta_{x^2-y^2}$ and SO coupling, see Fig. 1(a)]. The other terms describe the on-site Coulomb and Hund’s interactions, where $\mu$ and $\sigma$ are the orbital and spin indices, respectively. As usual, we parametrize the interaction matrix as $U_{\mu \sigma} = U, U_{\mu \bar{\sigma}} = U = 2J_H$, and $J_{\mu \nu} = J'_{\mu \nu} = J_H [20]$.

Figures 1(b) and 1(c) show all possible multiplets of $d^5$ and $d^4$ electronic configurations. For $d^5$, all three lowest Kramers doublets $\tau_{123}$ are fully occupied. We note that the wave functions of these states are often taken in the limit of $10Dq \rightarrow \infty$, i.e., the admixture of $e_g$ orbitals ($\propto \lambda/10Dq$) in the ground state via SO coupling is ignored. Since the SO coupling in iridates is strong, we fully include the $e_g$ orbital admixture in the lowest Kramers doublets.

FIG. 1 (color online). (a) Energy levels of the $d$ electron in the presence of the cubic crystal field $10Dq$, the tetragonal crystal field $\Delta_{x^2-y^2}$, and the SO interaction $\lambda$ [29]. The lowest multiplet levels of (b) $d^5$ and (c) $d^4$ configurations including SO $\lambda$ and the Hund’s coupling $J_H$. (d) Two-site and (e) four-site clusters in the $xy$ plane, which were employed in the evaluation of the magnetic couplings and conductivity $\sigma(\omega)$.

Because an electron hops between nearest-neighbor (NN) Ir sites via an oxygen [see Fig. 1(d)], and the charge transfer energy $\Delta$ between Ir-$5d$ and O-$2p$ is large ($\Delta \sim 3.3$ eV [21]), we assumed the following effective NN hopping Hamiltonian:

$$
H_{ij} = \sum_{\tau \bar{\tau} \sigma' \bar{\sigma}'} (t_{ij,\tau \bar{\tau} \sigma' \bar{\sigma}'} c_{\tau \sigma'}^\dagger c_{\bar{\tau} \bar{\sigma}'} + \text{H.c.}),
$$

where the effective hopping integral between $\tau \bar{\tau}$ and $\tau' \bar{\tau}'$ states is $t_{ij,\tau \bar{\tau} \sigma' \bar{\sigma}'} = \sum_{\sigma} \sqrt{(1+\epsilon_j)(1+\epsilon_i)}$. We calculated the $pd$-hopping matrix $t_{ij,\tau \bar{\tau} \sigma' \bar{\sigma}'}$ between 5d Ir and 2p O orbitals in terms of two parameters $t_{p\bar{d}}$ and $t_{p\bar{d} \bar{p}}$ [22].

Magnetic interactions.—We considered the Ir$_1$-Ir$_2$ pair described by the following Hamiltonian:

$$
H = H_1 + H_2 + H_{12}.
$$

Here $H_1$ and $H_2$ are the ionic Hamiltonians given by Eq. (1), and $H_{12}$ is the hopping term of Eq. (2). Using the ED method, we solved this Hamiltonian numerically, taking into account all possible multiplets allowed for the $d^5$-$d^5$ and $d^4$-$d^4$ configurations, and obtained eigen values $E_n$ and eigenstates $|\psi_n\rangle$ of the Ir-Ir cluster. The Hamiltonian can be then expressed as $H = \sum_n E_n |\psi_n\rangle\langle\psi_n|$. Without the hopping term $H_{12}$, the Ir-Ir pair would have four degenerate states denoted by $|\psi^0_n\rangle$ ($i = 1 \text{ to } 4$). The magnetic interactions are generated by virtual hoppings among them. The resulting effective magnetic Hamiltonian can be obtained by applying the projection operator $P_{1/2} = \sum_{i=-1}^1 |\psi^0_i\rangle\langle\psi^0_i|$ onto $H$ [23]:

$$
\mathcal{P}_{1/2}H\mathcal{P}_{1/2} - \frac{1}{4} \text{Tr}(\mathcal{P}_{1/2}HP_{1/2}) = \hat{S}_1 \cdot \mathcal{J} \cdot \hat{S}_2,
$$

where $\hat{S}$ is isospin one-half, and $\mathcal{J}$ is a $3 \times 3$ tensor.

Consistent with symmetry considerations as well as with Ref. [12], we found that Eq. (4) comprises four distinct nonvanishing terms,

$$
\mathcal{J}\hat{S}_1 \cdot \hat{S}_2 + \delta J_\parallel \hat{S}_{1z} \hat{S}_{2z} + \delta J_{xy}(\hat{S}_1 \cdot \hat{r}_{12})(\hat{S}_2 \cdot \hat{r}_{12}) + \mathbf{D} \cdot \hat{S}_1 \times \hat{S}_2,
$$

corresponding to isotropic Heisenberg ($J$), symmetric ($\delta J_\parallel$, $\delta J_{xy}$) and antisymmetric ($\mathbf{D}$) anisotropy uncouplings between NN Ir moments. We note that only the $z$-component Dzyaloshinsky-Moriya (DM) vector $\mathbf{D}$ survives because of the mirror symmetry with respect to the $xy$ plane, i.e., $\mathbf{D} = (0, 0, D)$.

Figure 2 presents the magnetic coupling constants, calculated by using the parameters provided in Table I, as a function of Ir-O-Ir bonding angle $\phi$. The $10Dq$ and $\Delta$ values are adopted from Refs. [13,21,24] and $\lambda$ from Refs. [24,25]. We have determined the optimal values of $U, J_H, t_{pd}$ such that they describe both the magnetic and optical data properly [26]. We set tetragonal splitting $\Delta_{xy} = 0.15$ eV; at this value, $|D/J|$ ratio becomes $\approx 0.34$.
and yields the spin canting angle of \( \approx 9.3^\circ \) at \( \phi = 158^\circ \) (as in \( \text{Sr}_2\text{IrO}_4 \)). As shown in the inset of Fig. 2, when \( \Delta_{xy} \) is too small, \(|D/J|\) ratio becomes too large to describe the observed spin canting. Approximately, we find that \( D \propto \sin(2\phi) \). The spin canting angle of \( \approx 9.3^\circ \) is close to those found in previous studies [12,27]. Noteworthy is the Ising coupling \( \delta J_z = J_z - J_{xy} \) in Eq. (5) is enhanced when decreasing bonding angle \( \phi \). We also calculated a pseudodipolar coupling \( \delta J_{xy} \) for different \( J_H \) values and found that \( \delta J_{xy} \) becomes zero at \( J_H = 0 \). Both of these observations agree with the analytical results [12].

Summarizing our results for magnetic interactions in \( \text{Sr}_2\text{IrO}_4 \), we obtained the following values at \( \phi = 158^\circ \): \( J \approx 76.8 \), \( D \approx -26.2 \), \( \delta J_z \approx 5.9 \), and \( \delta J_{xy} \approx 8.6 \) meV. With these coupling constants, the interactions of Eq. (5) lead to the canted AFM state with Ir moments lying in the \( xy \) plane, as observed in \( \text{Sr}_2\text{IrO}_4 \) [4]. The calculated isotropic coupling \( J \) is in close agreement with the experimental value of \( J \approx 60 \) meV [10]. Unusually large anisotropic couplings \( D, \delta J_z, \delta J_{xy} \) found here are the direct fingerprints of strong SO interaction.

**Optical conductivity and RIXS spectra.**—In 3d Mott insulators, the hopping between NN sites plays a dominant role in \( \sigma(\omega) \) that shows peak structures near the ionic multiplet states \( d_p^{\mu+1} - d_p^{\mu+1} \) [17–19], and the 2-site cluster may capture essential features of \( \sigma(\omega) \). In contrast, 5d Mott insulators have weaker Coulomb repulsion and thus a duality of atomic and band nature of correlated electrons is more pronounced [10]. In order to capture the delocalization of optically excited electron-hole (e-h) pairs, we consider here a \( 2 \times 2 \) cluster shown in Fig. 1(e).

We considered all possible multiplets within the \( d^5-d^5-d^3-d^5 \) and \( d^3-d^6-d^3-d^5 \) charge configurations. In order to clarify the origin of optical peaks, it is useful to classify the Hilbert space into 6 subspaces [see Fig. 3(a)]: \( H_1 \) of four \( d^5 \) doublets (\( D \)), \( H_2 \) of one or more quartets (\( Q \)) among four \( d^5 \) configurations, \( H_3 \) of two \( D \)’s of \( d^3 \) and NN e-h pairs \( d'(S)-d'(A) \), \( H_4 \) of two \( D \)’s of \( d^3 \) and next-nearest-neighbor (NNN) e-h pairs \( d'(S)-d'(A) \), \( H_5 \) of two \( D \)’s of \( d^3 \) and (NN and NNN) e-h pairs \( d'(T, P, P', S')-d'(A) \), and the remaining states (\( H_6 \), . . .) that involve, e.g., simultaneous intersite e-h transitions and local SO exciton \( Q \). All the above configurations couple to each other via the hopping Hamiltonian of Eq. (2).

We have solved the Hamiltonian matrix with the ED method, and obtained \( \sigma(\omega) \) from the following relation:

\[
\sigma(\omega) = \frac{\pi e^2}{\hbar}\sum_{n<\omega} p_n |\langle \psi_n | \hat{J} | \psi_n \rangle|^2 \delta(\omega + E_n - E_m),
\]

where \( v \) is volume per Ir site, \( p_n \) is the probability density of eigenstate \( | \psi_n \rangle \), and \( \hat{J} \) is the current operator. We set \( \beta^{-1} = k_B T = 30 \) meV to avoid the finite size effect. A function \( \delta(\omega) \) is treated with broadening of 0.05 eV.

Figure 4(a) shows the result for \( \sigma(\omega) \) calculated by using the parameters from Table I. Two peaks are revealed clearly at \( \sim 0.5 \) and \( \sim 1.0 \) eV, in good agreement with experiment. The estimated value of \( \sigma(\omega) \) at \( \sim 0.5 \) eV is also consistent with the experimental data. For \( \omega > 0.6 \) eV, calculated \( \sigma(\omega) \) is smaller than that observed.

**TABLE I.** Physical parameters in units of eV.

<table>
<thead>
<tr>
<th>( D )</th>
<th>( \Delta )</th>
<th>( \Delta_{xy} )</th>
<th>( U )</th>
<th>( J_H )</th>
<th>( \lambda )</th>
<th>( t_{pdr} )</th>
<th>( t_{pdx} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>3.3</td>
<td>0.15</td>
<td>1.86</td>
<td>0.5</td>
<td>0.4</td>
<td>-1.8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

![FIG. 2 (color online). Magnetic coupling constants between NN Ir ions (\( \hat{t}_{12} \parallel \hat{x} \)) with respect to the bonding angle (\( \phi \)). \( J_{xx}, J_{yy}, \) and \( J_{zz} \) represent diagonal parts of the superexchange tensor \( J \). \( J_{xy} = J + \delta J_{xy} \), and \( J_z = J + \delta J_z \), are deduced from Eq. (5). \( D \) is a \( z \) component of the DM vector \( \hat{D} \).

![FIG. 3 (color online). (a) Schematic diagrams of possible multiplets included in subsets (\( H_1 \)) of the Hilbert space. \( D \), \( Q \), \( S \), and \( T \) refer to multiplets of \( d^5 \) and \( d^3 \), as labeled in Figs. 1(b) and 1(c), and \( A \) denotes a nondegenerate \( d^5 \) state. \( H_1 \) includes also diagrams (not shown) with \( P \), \( P' \), \( S' \) multiplets of the \( d^3 \) state [Fig. 1(c)] instead of \( T \). (b) Two examples of optically active transitions that contribute to \( \sigma(\omega) \) at low energies. The final states \( H_1 \) and \( H_3 \) have an overlap with the on-site local SO exciton \( Q \) (i.e., \( H_5 \) sector), due to intersite hoppings between \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) states, resulting in the two-peak structure of \( \sigma(\omega) \).]
shows that the first peak shown in inset of Fig. 4(a), however, is incomplete in iridates. Indeed, as higher energy transitions involving $T/C_{24}$ contrast to the observation that the spectral weight of $j$ states more SO excitons, excitations in purely local ionic multiplets. (b) Calculated $L_3$ edge (solid line) and $10 \times L_2$ edge (dotted line) RIXS spectra at $q = (\pi, \pi)$. Dashed line: experimental data [10]. (c) Projected excitation spectra: $\Lambda_1$ represents the magnon band, $\Lambda_2$ contains one or more SO excitons, $\Lambda_3$ and $\Lambda_4$ represent NN and more distantly separated $e$-$h$ excitations derived from the $J_{\text{eff}} = 1/2$ states, respectively, and $\Lambda_5$ shows the $e$-$h$ continuum of $J_{\text{eff}} = 3/2$ states. $\Lambda_2$ refers to other excitations, e.g., simultaneous transitions in $e$-$h$ and SO exciton channels.

The possible reasons for this discrepancy are the contributions from the $pd$-charge transfer peak at $\sim 3$ eV and from two or more $e$-$h$ pair excitations not included here.

Shown in Figure 4(b) is the RIXS spectra, calculated by employing the inelastic x-ray scattering operator of Ref. [15] instead of $J_\sigma$ in Eq. (6). At the $L_3$ edge, intense magnon (below 0.25 eV) and SO exciton (0.5–1.0 eV) bands are obtained, while the intensity at the $L_2$ edge is nearly vanishing, in agreement with experiments [10,13].

Of particular interest is the origin of two peaks in $\sigma(\omega)$ and their relation to the SO exciton. In 3$d$ Mott insulators, each peak would correspond to the specific multiplet of $d^{n-1} - d^{n+1}$ with the spectral weight proportional to $|\langle d^{n-1} d^{n+1} | J_\sigma | d^n d^n \rangle|^2$ [17–19]. Such a simple ionic multiplet picture, however, is incomplete in iridates. Indeed, as shown in inset of Fig. 4(a), $\sigma(\omega)$ based on this picture shows that the first peak $|DDDD\rangle \rightarrow |ASDD\rangle$ transition in Fig. 3(b) is much stronger than those corresponding to higher energy transitions involving $T$, $P$ multiplets [28], in contrast to the observation that the spectral weight of $\sim 1.0$ eV peak is even larger than that of $\sim 0.5$ eV peak [Fig. 4(a)].

To understand how the $e$-$h$ delocalization effects lead to strong deviations from a simple ionic picture, it is instructive to analyze the underlying excitation spectra in more detail. To this end, we evaluated the projected excitation spectrum (PES) of the $2 \times 2$ cluster into the subspaces $H_i$ introduced above:

$$\Lambda_i(\omega) = \sum_n \sum_{m \in H_i} |\langle \psi_n | m \rangle|^2 \delta(\omega - E_n),$$  

where $|m\rangle$ represents the orthonormal basis of the subspace $H_i$. We can identify the PES in Fig. 4(c) as follows: $\Lambda_1$ represents magnon sector, $\Lambda_2$ is related to one or more intrasite $D$-$Q$ transitions (SO excitons), $\Lambda_3$ and $\Lambda_4$ are the $e$-$h$ continuum of $J_{\text{eff}} = 1/2$ states, and $\Lambda_5$ describes the $e$-$h$ continuum of $J_{\text{eff}} = 3/2$ bands.

We notice intriguing features in Fig. 4(c): (i) $\Lambda_1$ and $\Lambda_2$ show the peaks in the range of 0–0.25 and 0.5–1.0 eV, respectively. These peaks are manifested in the RIXS spectra as the magnon and SO exciton bands. $\Lambda_2$ shows also the high energy peak at $\sim 1.5$ eV, which however does not directly couple to the RIXS process since it contains two SO excitons residing on different sites. (ii) $\Lambda_3$ and $\Lambda_4$ ($J_{\text{eff}} = 1/2$ $e$-$h$ continuum) are located in the wide range of 0.5–1.5 eV. This fact reveals that not only the lower but also the higher peak of $\sigma(\omega)$ is attributed to the $e$-$h$ continuum of $J_{\text{eff}} = 1/2$ states, contrary to a previous interpretation based on a simple band picture [2]. (iii) $\Lambda_3$ (NN $e$-$h$ contribution) is depleted in the vicinity of the SO exciton $\Lambda_2$. The mixing of these modes is natural in view of the nonzero overlap between quasidegenerate $[ASDD] \in H_3$ and $[DQDD] \in H_2$ states [see Figs. 3(a) and 3(b)] by virtue of intersite hoppings.

The PES thus shows that the optically active $e$-$h$ continuum of $J_{\text{eff}} = 1/2$ band and the optically forbidden SO exciton [10] are located in the same energy range of 0.5–1.5 eV, and there is considerable mutual interaction between these excitations due to the interband hopping between $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ states. The two-peak structure in $\sigma(\omega)$ results from this unusual mixing among different excitations, which is reminiscent of the characteristic behavior of the Fano resonance.

To conclude, we presented a unified description of magnetic couplings, optical conductivity, and RIXS spectra in Sr$_2$IrO$_4$ within the model including strong SO coupling and ionic multiplet effects. The results obtained are consistent with the available experimental data. Since the SO splitting and the Mott-Hubbard charge gap are of similar scale, an unusual coupling between two different types of excitations—the optically inactive SO exciton and the optically active $e$-$h$ continuum—is induced due to the interband mixing of $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ states. Although this effect is not very essential for NN magnetic interactions, it plays a crucial role in determining the shape of optical spectra: the $e$-$h$ continuum is suppressed in the vicinity of the SO exciton inherent to iridates. The unusual
Fano-type coupling between the rich ionic multiplet excitations and electronic continuum seems to be a characteristic feature of $J_{\text{eff}} = 1/2$ Mott insulators. This phenomenon is rooted in the atomic-band duality of 5$d$ electrons and should therefore be generic to iridates with an unusual hierarchy of energy scales.

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*binmin@postech.ac.kr

[28] This is because an average value of dipole matrix element \[ \langle |\langle A^{\text{DD}}|J_{\text{SDD}}\rangle |^{2}\rangle \] is about ten times larger than, e.g., \[ \langle |\langle A^{\text{DD}}|J_{\text{SDD}}\rangle |^{2}\rangle \].
[29] In the limit of $10Dq \to \infty$, the energy splitting between $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ is $1.5\lambda$ [12,15]. At finite $10Dq$ values, however, this splitting increases: for $10Dq = 3.0$ eV, it is about $1.7\lambda$. 

*binmin@postech.ac.kr