Mixing between $J_{\text{eff}} = \frac{1}{2}$ and $\frac{3}{2}$ orbitals in Na$_2$IrO$_3$: A spectroscopic and density functional calculation study

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We investigated the electronic structure of Na$_2$IrO$_3$ using optical spectroscopy, first-principles calculation, and x-ray absorption spectroscopy. We found that the electronic structure of Na$_2$IrO$_3$ is mainly determined by anisotropic hopping interactions and spin-orbit coupling. Due to the hopping interaction, the orbital character of the bands near the Fermi level deviates from the spin-orbit coupling-induced $J_{\text{eff}} = 1/2$ states. Polarization-dependent O 1s x-ray absorption spectroscopy showed that the $J_{\text{eff}} = 1/2$ state of an Ir atom can be mixed with the $J_{\text{eff}} = 3/2$ state of the neighboring Ir atom. This result implies that mixing between the $J_{\text{eff}} = 1/2$ and $3/2$ states in the valence spin state should be carefully considered in proposed exotic states of Na$_2$IrO$_3$, such as topological insulator and quantum spin liquid states.

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Recently, iridates have received much attention as emergent materials for novel quantum phenomena, including spin-orbit coupling (SOC)–driven Mott transition or topological effects. Most iridates have the Ir$^{4+}$ valence state with $t_{2g}^5$ electrons near the Fermi level, $E_F$, and the strong SOC transforms the $t_{2g}^5$ states into the $J = (L + S)$ states. The spin-orbital admixture can be represented with effective total angular momentum $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$, as observed in layered perovskite Sr$_2$IrO$_4$. The $J_{\text{eff}}$ quantum states of valence electrons will provide a new basis for understandings of 5d transition metal oxides, in which SOC is much stronger than in 3d transition metal oxides.

Na$_2$IrO$_3$ is a particularly intriguing material whose $J_{\text{eff}}$ states may lead to novel ground states. Na$_2$IrO$_3$ has edge-sharing IrO$_6$ octahedra that form a honeycomb lattice, where the exchange interaction between two Ir atoms can be highly anisotropic. Within the $J_{\text{eff}}$ quantum state, it has been proposed that the magnetic ground state of Na$_2$IrO$_3$ could be explained in terms of the Kitaev–Heisenberg model. Many researchers have tried to identify quantum spin liquid, one of the ground states of the Kitaev–Heisenberg model. In addition, the transfer integral between the next nearest neighboring Ir orbital via the oxygen orbitals is complex and spin dependent. This could induce a nonzero Berry phase, leading to a topologically nontrivial band structure in Na$_2$IrO$_3$. It should be noted that the central presumption for the nontrivial ground states in Na$_2$IrO$_3$ is the full occupation of four $J_{\text{eff}} = 3/2$ states and single electron occupation in the $J_{\text{eff}} = 1/2$ state.

However, the orbital characters of the valence bands of Na$_2$IrO$_3$ have not been elucidated. Earlier theoretical work assumed the ideal $J_{\text{eff}} = 1/2$ orbital in a cubic octahedron and suggested the nontrivial electric and magnetic ground states in Na$_2$IrO$_3$. Later, detailed structural studies showed that Ir-O octahedra have a rather significant trigonal distortion, which makes the larger O-Ir-O bond angle about $94.5^\circ$. Bhattacharjee et al. pointed out that the crystal field due to the large trigonal distortion could destabilize the $J_{\text{eff}} = 1/2$ states. However, a recent resonant inelastic x-ray scattering experiment revealed that the trigonal crystal field is minimal; thus, the SOC-induced $J_{\text{eff}} = 1/2$ orbital scenario is still valid in Na$_2$IrO$_3$. On the other hand, Mazin et al. theorized that the pure $J_{\text{eff}} = 1/2$ atomic-orbital scenario might not be valid in Na$_2$IrO$_3$ due to the extended nature of the 5d orbitals and the honeycomb structure. They suggested that the highly anisotropic hopping interaction in the Ir-O-Ir network causes electrons to move only within a honeycomb composed of six Ir ions. This interaction results in quasimolecular orbitals, which are distinct from the pure $J_{\text{eff}} = 1/2$ and $3/2$ states. In these respects, it is important to identify the orbital character of the bands near $E_F$ before we attempt to identify theoretically suggested nontrivial ground states in Na$_2$IrO$_3$.

In this paper, we investigate the effects of anisotropic hopping interactions and SOC on the electronic structure of Na$_2$IrO$_3$ using optical spectroscopy, first-principles calculations, and x-ray absorption spectroscopy (XAS). We observed five clear $d$-$d$ transitions in optical conductivity, $\sigma(\omega)$, which can be understood in terms of the Ir $t_{2g}$ state splitting due to the anisotropic hopping interaction and SOC. Our polarization-dependent O 1s XAS data provide experimental evidence that the orbital character of the valence bands of Na$_2$IrO$_3$ is a mixture of $J_{\text{eff}} = 1/2$ and $3/2$ states.

High-quality single-crystal Na$_2$IrO$_3$ was grown using a self-flux method from off-stoichiometric quantities of IrO$_2$ and Na$_2$CO$_3$. We measured the near-normal incident $ab$-plane reflectance spectrum, $R(\omega)$, in the energy region between 10 meV and 1 eV at room temperature, and determined the optical constants between 0.74 and 5 eV using spectroscopic ellipsometry. We obtained $\sigma(\omega)$ using Kramers–Kronig analysis. We also measured transmission spectra, $T(\omega)$, of thin crystals in the energy region between 10 meV and 1 eV to see minute spectral features. We performed the O 1s XAS experiment at the 2A beamline of the Pohang Light Source in...
In the inset of Fig. 1(a), the absorption spectra obtained from features can be seen more easily in (b) GGA, (c) GGA data below 1 eV. Results from DFT calculations: band structures of Lorentz oscillator model fit. The inset of panel (a) shows absorption Black circles represent the experimental data, and the solid line is the of Na2IrO3 using a density functional theoretical (DFT)
total electron yield mode. We calculated the band structure
of Na2IrO3, which is based on the linear combination
projected characters of thepseudoatomic orbital formalism.25 We used the Perdew–
Burke–Ernzerhof generalized gradient approximation (GGA)
hopping, resulting in three separate energy regions of bands.

The band dispersions from the GGA calculation are shown in Fig. 1(b). All of the calculated bands near Ef are very flat and located in three separate energy regions between −2 and +0.5 eV. These band dispersion features result from the formation of the quasimolecular orbital states, as pointed out by Mazin et al.22 Namely, in the honeycomb lattice of Na2IrO3, the spatial orientations of the Ir 5d5/2 and O 2p orbitals suppress the hopping in one particular direction at each Ir site. The direction of the highly anisotropic Ir-O-Ir hopping varies from one Ir site to another, which effectively causes electrons to move only in one hexagon, similar to the case of benzene. Such electron motion results in quasimolecular orbital states. Note that benzene has well-separated, flat energy levels with singlet, doublet, doublet, and singlet degeneracies.26 According to Mazin et al., the highly lying singlet and doublet states in Na2IrO3 become degenerate due to the O-assisted next nearest neighbor hopping, resulting in three separate energy regions of bands.

The effects of the SOC on the electronic structure of Na2IrO3 are illustrated in the result of the GGA + SOC calculation in Fig. 1(c). The SOC splits the energy levels from three to six well-separated energy regions. Note that in this band structure five d-d transitions between the t_{2g} orbitals are expected, as indicated by the arrows in Fig. 1(c). This is consistent with the experimentally observed five-peak structure in σ(ω). The quantitative agreement between the d-d transition energies of experiment and calculation can be achieved when the on-site Coulomb interaction U = 1.0 eV is included [Fig. 1(d)]. As shown in Table I, the GGA + SOC + U calculation produced d-d transition energies that matched well with the experimental values. These calculation results demonstrate that the five distinct d-d transitions in our σ(ω) data can be understood in terms of the combined effect of the formation of the quasimolecular orbital states and SOC in the honeycomb lattice of Na2IrO3.

The colors in Fig. 1(d) indicate the projection of the GGA + SOC + U calculation results to $J_{\text{eff}} = 1/2$ (yellow color) and 3/2 (black color) orbitals. One can see that the states near the $E_F$ have orbital characters close to the

<table>
<thead>
<tr>
<th>Band gap</th>
<th>Experiment</th>
<th>GGA + SOC</th>
<th>GGA + SOC + U</th>
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<tbody>
<tr>
<td>A</td>
<td>0.52</td>
<td>0.30</td>
<td>0.53</td>
</tr>
<tr>
<td>B</td>
<td>0.72</td>
<td>0.67</td>
<td>0.86</td>
</tr>
<tr>
<td>C</td>
<td>1.32</td>
<td>1.05</td>
<td>1.22</td>
</tr>
<tr>
<td>D</td>
<td>1.66</td>
<td>1.24</td>
<td>1.39</td>
</tr>
<tr>
<td>E</td>
<td>1.98</td>
<td>1.65</td>
<td>1.88</td>
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where $S_n$, $\omega_n$, and $\gamma_n$ represent the strength, resonant frequency, and scattering rate of the nth oscillator, respectively. The results of the conductivity fitting are summarized in Table I.
$J_{\text{eff}} = 1/2$ state, and the others exhibit characters close to the $J_{\text{eff}} = 3/2$ state. However, our calculation shows that there should be considerable mixing between $J_{\text{eff}} = 1/2$ and $3/2$ orbitals in every band. For example, unoccupied states and topmost-occupied states near $E_F$ have $J_{\text{eff}} = 3/2$ projections of about 14% and 30%, respectively. Such orbital mixings could be important for investigations of numerous proposed novel ground states of Na$_2$IrO$_3$.

To better understand the orbital characters of the bands near the $E_F$, we performed O 1s XAS. The O 1s XAS reflects the transition from the O 1s core level to the unoccupied O 2$p$ states that are hybridized with the Ir 5$d$ orbitals. Because the Ir 5$d$ orbitals can hybridize with the surrounding 2$p$ waves of six oxygen ions only when their point symmetries coincide, we can obtain information on the Ir 5$d$ orbital characters using polarization-dependent XAS.29 Figure 2(a) shows the six oxygen ions only when their point symmetries coincide, Ir $5^d$ at 70$^\circ$ experimental geometry. We fixed the incident angle of light to the Ir honeycomb plane, and the photon direction and along the undistorted Ir-O direction, as displayed in Fig. 2(a).

Figure 2(b) shows the polarization-dependent O 1s orbital characters and their polarization dependence cannot be explained based on local interactions. The SOC cannot result in energy splitting and polarization dependences of the $e_g$ orbital states, because the $e_g$ orbital states are insensitive to SOC. The local trigonal distortion cannot explain the energy splitting of the $e_g$ states, either, because $e_g$ states provide a good basis for trigonal symmetry. Thus, the energy splitting and polarization dependence of these two peaks implies that a nonlocal interaction affects the orbital character of Na$_2$IrO$_3$ significantly.

Now we consider peak $\alpha$, which exhibits little polarization dependence. The intensity ratio of peak $\alpha$ in $\pi$ and $\sigma$ polarizations is estimated to be 0.88 $\pm$ 0.07. For comparison, we evaluated the intensity ratio in $\pi$ and $\sigma$ polarizations for the pure $J_{\text{eff}} = 1/2$ orbitals. We calculated the hybridization between pure atomic $J_{\text{eff}} = 1/2$ orbitals and O 2$p$ orbitals with the inclusion of the reported value of the trigonal structural distortion in Na$_2$IrO$_3$.31 We found that the intensity ratio $\pi/\sigma$ should be 1.6 for the highly distorted IrO$_6$ cluster.31 This value is higher than the experimental value of 0.88 $\pm$ 0.07. Therefore, the negligible polarization dependence of peak $\alpha$ indicates that the real orbital character of the unoccupied $t_{2g}$ state should differ from that of the pure atomic $J_{\text{eff}} = 1/2$ orbital.

To explain the deviation of the orbital character of the $t_{2g}$ states from the $J_{\text{eff}} = 1/2$ orbital, we considered the anisotropic hopping interaction.22 The left side of Fig. 3(a) shows the Ir honeycomb net structure of Na$_2$IrO$_3$. The arrows on the right side of Fig. 3(a) indicate the dominant hopping processes in the Ir 5$d$ in honeycomb structure between two nearest neighboring Ir atoms via O 2$p$ orbitals. Electrons in the $d_{xz}$ ($d_{xy}$) orbital at one Ir site can hop to the $d_{xz}$ ($d_{xy}$) orbital of another Ir site via O 2$p_{x}$, while electrons in the $d_{xy}$ orbital at one Ir site cannot hop to any orbital at another Ir site via O 2$p_{x}$. Due to this anisotropic intersite hopping process, the $J_{\text{eff}} = 1/2$ state ($\mp \sqrt{2/3} [d_{xy}, \pm 1/2] + i[d_{x^2\text{-}y^2}, \mp 1/2]$) can be mixed with the $J_{\text{eff}} = 3/2$ orbital ($\mp \sqrt{2/3} [d_{xy}, \mp 1/2] + i[d_{x^2\text{-}y^2}, \mp 1/2]$). In the same way, the $J_{\text{eff}} = 1/2$ state can be mixed with other $J_{\text{eff}} = 3/2$ states, $\mp \sqrt{2/3} [d_{xy}, \mp 1/2] + i[d_{x^2\text{-}y^2}, \mp 1/2]$ and $\mp \sqrt{2/3} [d_{xy}, \pm 1/2] + i[d_{x^2\text{-}y^2}, \pm 1/2]$, via O 2$p_{x}$, and 2$p_{y}$, respectively.

The mixed $J_{\text{eff}} = 1/2$ and 3/2 states explain the small polarization dependence of peak $\alpha$ in our XAS data. Due to the hybridization discussed above, the waveform of electrons of Ir ions can be written as $\Psi = \sqrt{1 - |A|^2} |J_{\text{eff}} = 1/2\rangle - A |J_{\text{eff}} = 3/2\rangle$, where $A$ is a complex mixing coefficient. Using this waveform, we calculated the $\pi/\sigma$ intensity ratio with $\psi_{\alpha}$ located at 528.7, 530.8, and 531.5 eV, respectively. Because the features are broad, possible chemical shifts in the O 1s core hole energy can be neglected. Peak $\alpha$ can be attributed to the unoccupied $t_{2g}$ orbital states, and peaks $\beta$ and $\gamma$ are due to the unoccupied $e_g$ states. It is interesting to note that whereas the peaks related to $e_g$ states ($\beta$ and $\gamma$) show polarization dependence as well as sizable splitting, the peak associated with $t_{2g}$ states ($\alpha$) exhibits negligible polarization dependence.

To obtain insight into the orbital character of the $t_{2g}$ state, we first considered the polarization dependence of peaks $\beta$ and $\gamma$, coming from $e_g$ states. As shown in Fig. 2(b), peak $\beta$ ($\gamma$) is stronger in out-of-plane (in-plane) polarization. The energy splitting of $e_g$ orbitals and their polarization dependence cannot be explained based on local interactions. The SOC cannot result in energy splitting and polarization dependences of the $e_g$ orbital states, because the $e_g$ orbital states are insensitive to SOC. The local trigonal distortion cannot explain the energy splitting of the $e_g$ states, either, because $e_g$ states provide a good basis for trigonal symmetry. Thus, the energy splitting and polarization dependence of these two peaks implies that a nonlocal interaction affects the orbital character of Na$_2$IrO$_3$ significantly.

FIG. 2. (Color online) (a) Experimental geometry of polarization-dependent O 1s XAS. The primed coordinate $z'$ ($x'$ and $y'$) is perpendicular (parallel) to the Ir honeycomb plane, and $x$, $y$, and $z$ are along the undistorted Ir-O direction. $\sigma$ polarization is parallel to the Ir honeycomb plane, and $\pi$ polarization is perpendicular to both incident photon direction and $\sigma$ polarization. (b) Polarization-dependent O 1s XAS data. Red triangles and blue circles represent $\pi$ polarization and $\sigma$ polarization data, respectively. The inset of panel (b) shows O 1s XAS raw data in broad energy region.
For the pure white. The experimental lines in Fig. 3(b) are contour plots for given values of \( J \) as a function of the portion of the minimum and maximum value of \( \Psi \). The left side of panel (a) shows the Ir honeycomb net structure in \( \text{Na}_2\text{IrO}_3 \). For simplicity, we only show the hopping process in rectangular Ir-O-Ir chains. (b) Calculated peak intensity process in the region surrounded by the black circle, which contains the variation in the \( \Psi \) XAS data for distorted IrO\(_6\) octahedra as a function of the portion of the \( J_{\text{eff}} = 3/2 \) in the ground state of \( \Psi = \sqrt{1-|A|^2} \left| J_{\text{eff}} = 1/2 \right| - A \left| J_{\text{eff}} = 3/2 \right| \), where \( A = \text{Re}[A] + i\text{Im}[A] \) is the complex mixing coefficient. The black lines are contour plots for given values of \( \pi/\sigma \), and corresponding values are shown in white. The experimental \( \pi/\sigma \) ratio of 0.88 is shown with the red line.

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FIG. 3. (Color online) (a) Schematic diagram of the hopping process in \( \text{Na}_2\text{IrO}_3 \). The left side of panel (a) shows the Ir honeycomb net structure in \( \text{Na}_2\text{IrO}_3 \). For simplicity, we only show the hopping process in the region surrounded by the black circle, which contains two Ir atoms. Blue and red arrows indicate the dominant hopping process in rectangular Ir-O-Ir chains. (b) Calculated peak intensity process in rectangular Ir-O-Ir chains. (b) Calculated peak intensity process in the region surrounded by the black circle, which contains the variation in the XAS data for distorted IrO\(_6\) octahedra as a function of the portion of the \( J_{\text{eff}} = 3/2 \) in the ground state of \( \Psi = \sqrt{1-|A|^2} \left| J_{\text{eff}} = 1/2 \right| - A \left| J_{\text{eff}} = 3/2 \right| \), where \( A = \text{Re}[A] + i\text{Im}[A] \) is the complex mixing coefficient. The black lines are contour plots for given values of \( \pi/\sigma \), and corresponding values are shown in white. The experimental \( \pi/\sigma \) ratio of 0.88 is shown with the red line.

The observation of sizable mixing between \( J_{\text{eff}} = 1/2 \) and 3/2 orbitals implies that localized \( S = 1/2 \) (pseudospin, in that case) Hamiltonian might not be appropriate to account for the ground states of \( \text{Na}_2\text{IrO}_3 \). Most of proposed theoretical models that predict exotic ground states of \( \text{Na}_2\text{IrO}_3 \) assumed the full-fledged \( J_{\text{eff}} = 3/2 \) orbital and half-filled \( J_{\text{eff}} = 1/2 \) orbital.\(^{4,5}\) Under this circumstance, we can construct \( S = 1/2 \) Hamiltonian, similar to the 3d transition metal oxides system. However, our experimental results clearly showed that the orbital character of \( \text{Na}_2\text{IrO}_3 \) deviates from the localized \( J_{\text{eff}} = 1/2 \) orbital. Instead, as Mazin \textit{et al.} pointed out,\(^{22}\) our XAS data indicated the delocalized nature of electrons in \( \text{Na}_2\text{IrO}_3 \). Therefore, we insist that \( S = 1/2 \) Hamiltonian needs to be modified to understand the orbital and magnetic ground state of \( \text{Na}_2\text{IrO}_3 \).

In conclusion, we found that the anisotropic hopping interaction in the honeycomb Ir lattice contributes to \( J \)-state mixing in \( \text{Na}_2\text{IrO}_3 \). Along with the strong SOC effect, \( J \)-state mixing explains the experimental observations of the five \( d-d \) transitions in optical conductivity and the negligible polarization dependence of the \( 2s \) peak in the XAS spectra. These findings suggest that the mixed nature of the \( J_{\text{eff}} = 1/2 \) and 3/2 states should be taken into account in future studies of novel ground states of \( \text{Na}_2\text{IrO}_3 \).

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MIXING BETWEEN $J_{\text{eff}} = \frac{1}{2}$ AND $\frac{1}{2} \ldots$

24The DFT code, OpenMX, is available at the web site (http://www.openmx-square.org) released under the GNU General Public License.
28M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, Group Theory: Application to the Physics of Condensed Matter (Springer, Berlin, Heidelberg, Germany, 2008), Sec. 7.5.3.
31We only considered trigonal distortion itself and ignored the effects of the trigonal crystal field because there is theoretical and experimental evidence of a small trigonal crystal field in Na$_2$IrO$_3$.
32The optical $d$-$d$ transition can be understood as an electron hopping from one Ir site to another Ir site via O 2$p$ orbitals. Because the Ir-O-Ir angle is close to 90$^\circ$ in Na$_2$IrO$_3$, hopping between the $J_{\text{eff}} = 1/2$ orbital states of the nearest neighbors is strongly suppressed. Therefore, the weak strength of peaks A and B in optical conductivity [Fig. 1(a)] implies that the contribution of the $J_{\text{eff}} = 1/2$ orbital to states near the $E_F$ is much stronger than that of the $J_{\text{eff}} = 3/2$ orbital.