Almost pure $J_{\text{eff}} = \frac{1}{2}$ Mott state of $\text{In}_2\text{Ir}_2\text{O}_7$ in the limit of reduced intersite hopping

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The pyrochlore iridate $\text{In}_2\text{Ir}_2\text{O}_7$ is a $J_{\text{eff}} = \frac{1}{2}$ Mott insulator with frustrated magnetism. Despite the large trigonal distortion, only a small admixture of $J_{\text{eff}} = \frac{3}{2}$ component in the $J_{\text{eff}} = \frac{1}{2}$ bands is observed as compared with other pyrochlore iridates $\text{A}_2\text{Ir}_2\text{O}_7$ (A = trivalent cation). We argue that the reduced intersite hopping between the $J_{\text{eff}} = \frac{1}{2}$ and the $J_{\text{eff}} = \frac{3}{2}$ manifold, due to the large trigonal distortion and the covalent character of In-O bonds, plays a predominant role in the distinct behavior of $\text{In}_2\text{Ir}_2\text{O}_7$. Such effect of the intersite hopping should not be dismissed in the local physics of $J_{\text{eff}} = \frac{1}{2}$ Mott insulators.

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Transition-metal oxides containing $5d$ elements have been receiving attention in the search for novel electronic states generated by the interplay between moderate on-site Coulomb repulsion, $U \sim 2$ eV, and strong spin-orbit coupling, $\lambda_{\text{SOC}} \sim 0.5$ eV [1]. Complex iridium oxides have been studied as a platform in this pursuit [2]. The common building block in those iridates is an IrO_6 octahedron, where five d electrons occupy the t_{2g} manifold. Strong spin-orbit coupling splits the t_{2g} manifold into the completely filled lower $J_{\text{eff}} = \frac{3}{2}$ quartet and the half-occupied upper $J_{\text{eff}} = \frac{1}{2}$ doublet. $J_{\text{eff}} = \frac{1}{2}$ states, consisting of the superposition of d_{xy} , d_{yz} , and d_{xz} orbitals including complex components [3], dominate the transport and magnetic properties.

Pyrochlore iridates, $\text{A}_2\text{Ir}_2\text{O}_7$ (A = trivalent ion), where the interplay of U and λ_{SOC} takes place on a frustrated lattice, are expected to host novel electronic phases, including those with nontrivial topological character [4–6]. $\text{A}_2\text{Ir}_2\text{O}_7$ crystallizes in a cubic structure with space group $Fd\bar{3}m$ consisting of two interpenetrating pyrochlore networks of A and Ir cations [Fig. 1(a)]. Their electronic ground states evolve with the ionic radius of the A cation [7,8]. The ionic size of A cations in $\text{A}_2\text{Ir}_2\text{O}_7$ is too small to maintain the regular IrO_6 octahedron and therefore the lattice distorts. The IrO_6 octahedron is trigonally compressed, which decreases the Ir-O-Ir angle in the neighboring IrO_6 octahedra [Fig. 1(b)]. The bond bending reduces the intersite hopping between the neighboring Ir sites and thus controls the t_{2g} bandwidth. The smaller the ionic radius, the smaller the bandwidth. With the largest A cation reported, $\text{Pr}_2\text{Ir}_2\text{O}_7$ is a semimetal with a quadratic band

dispersion and remains metallic down to the lowest temperature [9,10]. With decreasing A size, namely, reducing the bandwidth, the system undergoes a metal-insulator transition [8] accompanied by a magnetic transition. There has been accumulating evidence that an all-in-all-out (AIAO) magnetic order is formed [11,12]. The AIAO ordered phase around the metal-insulator transition is discussed to be a Weyl semimetal [13,14]. With decreasing the size of A cations further to Y^{3+} , the system becomes a Mott insulator. While the resistivity shows an insulating behavior up to room temperature, the magnetic transition occurs only at low temperatures.

The trigonal compression of IrO_6 octahedra has a pronounced impact also on the local orbital states. The trigonal distortion for an isolated regular IrO_6 octahedron splits the $J_{\text{eff}} = \frac{3}{2}$ quartet into two Kramers doublets [15,16]. In addition to the trigonal compression of IrO_6 , the long-range crystal field, namely, that originating from neighboring A and Ir cations, is discussed to be as large as ~ 0.3 eV and thus comparable to or even greater than that from oxygen anions [17]. The $(J_{\text{eff}} = \frac{1}{2})$ -derived state under such trigonal crystal fields should have an admixture of the $J_{\text{eff}} = \frac{3}{2}$ component and cannot be described by the pure $J_{\text{eff}} = \frac{1}{2}$ wave function [18,19]. In $\text{A}_2\text{Ir}_2\text{O}_7$ the intersite hopping between J_{eff} manifolds may come into play and further modify the $(J_{\text{eff}} = \frac{1}{2})$ -derived states [20,21]. For the elucidation of $J_{\text{eff}} = \frac{1}{2}$ physics in real materials, consideration of the noncubic crystal field and the $J_{\text{eff}} = \frac{3}{2}$ mixing is necessary.

To identify how the $J_{\text{eff}} = \frac{1}{2}$ state of $\text{A}_2\text{Ir}_2\text{O}_7$ is modified by the combined crystal-field effect from the distortion of IrO_6 octahedra and surrounding cations and also by the intersite hopping, we attempted to synthesize new pyrochlore iridates with a small A cation hosting an even larger trigonal distortion. We discovered a new pyrochlore iridate $\text{In}_2\text{Ir}_2\text{O}_7$ with a nonmagnetic In^{3+} ion occupying the A site. The In^{3+} ion has the smallest A -site ionic radius (0.92 Å) among the reported $\text{A}_2\text{Ir}_2\text{O}_7$ pyrochlores and renders the most distorted IrO_6 octahedra. $\text{In}_2\text{Ir}_2\text{O}_7$ is an insulator and shows

FIG. 1. (a) Crystal structure of $\text{In}_2\text{Ir}_2\text{O}_7$. (b) Local structure of two corner-sharing IrO_6 octahedra. The blue arrows indicate the direction of trigonal compression. (c) Ir L_3 edge RIXS spectrum of the $\text{In}_2\text{Ir}_2\text{O}_7$ polycrystalline sample at $T = 7$ K with incident energy $E_i = 11\,215$ eV. The Gaussian fits of the peaks are represented by a dashed blue line. The excitations labeled as E_1 and E_2 correspond to the ones depicted in (d). (d) Splittings of $J_{\text{eff}} = \frac{1}{2}$ and $\frac{3}{2}$ states into three Kramers doublets (ϕ_0 , ϕ_1 , and ϕ_2) under a trigonal crystal field in a single-ion description. (e) The energy split $\Delta E = E_2 - E_1$ against Δx for $A_2\text{Ir}_2\text{O}_7$, where $A = \text{Pr}$ [28], Y [17], and In .

antiferromagnetic ordering at $T_m = 55$ K. In the resonant inelastic x-ray scattering (RIXS) spectrum, the presence of a sizable splitting of $J_{\text{eff}} = \frac{3}{2}$ states was identified. Despite the expected enhancement of trigonal crystal field, the magnitude of splitting of $J_{\text{eff}} = \frac{3}{2}$ states was found to be smaller than those of other $A_2\text{Ir}_2\text{O}_7$ with reduced trigonal distortion. Our electronic structure calculations demonstrate that the ($J_{\text{eff}} = \frac{1}{2}$)-derived bands of $\text{In}_2\text{Ir}_2\text{O}_7$ consist predominantly of $J_{\text{eff}} = \frac{1}{2}$ wave function in contrast to other pyrochlore iridates with comparable or even reduced trigonal distortion. We argue that the long-range trigonal crystal field is responsible for unusual material dependence of the splitting of the $J_{\text{eff}} = \frac{3}{2}$ band and that the intersite hopping plays a dominant role in bringing $J_{\text{eff}} = \frac{3}{2}$ character in the ($J_{\text{eff}} = \frac{1}{2}$)-derived band.

The polycrystalline sample of $\text{In}_2\text{Ir}_2\text{O}_7$ was synthesized by a high-pressure synthesis technique [22]. The x-ray powder diffraction pattern of the product indicates a high purity phase of pyrochlore $\text{In}_2\text{Ir}_2\text{O}_7$ with small amounts of impurities (~ 3 wt %) [22]. The Rietveld analysis gives a cubic pyrochlore structure with space group $Fd\bar{3}m$. $\text{In}_2\text{Ir}_2\text{O}_7$ has the smallest cubic lattice parameter $a = 9.9884(4)$ Å among the reported pyrochlore iridates. The degree of trigonal distortion in cubic pyrochlores can be parametrized by the x fractional coordinate of the O1 atom. $x_c = 0.3125$ corresponds to the case of a regular IrO_6 octahedron. $x \neq x_c$ indicates

FIG. 2. Temperature-dependent (a) resistivity $\rho(T)$, (b) magnetic susceptibility $M/H(T)$, and (c) specific heat $C(T)$ of the $\text{In}_2\text{Ir}_2\text{O}_7$ polycrystalline sample. The inset of (a) shows the Arrhenius plot of $\rho(T)$ and the black line indicates the fit at high temperatures. In (b), the black arrows denote the zero-field-cooling ($\rightarrow$) and field-cooling ($\leftarrow$) curves. The inset shows the temperature dependence of inverse magnetic susceptibility, and the black line indicates the Curie-Weiss fit. The inset of (c) shows specific heat divided by temperature around the anomaly at 55 K.

that the IrO_6 octahedron is trigonally distorted, where $x > x_c$ gives trigonal compression with an Ir-O-Ir angle reduced from the ideal $\sim 141^\circ$, commonly found in pyrochlore iridates [Fig. 1(b)]. $x = 0.3405(5)$ for $\text{In}_2\text{Ir}_2\text{O}_7$ [22] yields the largest trigonal compression and the smallest Ir-O-Ir angle of $125.8(3)^\circ$ among pyrochlore iridates.

The resistivity measurement [Fig. 2(a)] shows that $\text{In}_2\text{Ir}_2\text{O}_7$ is an insulator. From the Arrhenius fit the activation energy around room temperature is estimated to be ~ 100 meV [inset of Fig. 2(a)], which is comparable to those of strongly insulating Ir oxides [29,30]. Magnetic susceptibility $M/H(T)$ in Fig. 2(b) shows a Curie-Weiss behavior on cooling from room temperature [31]. Since In^{3+} is nonmagnetic, the magnetic response originates from the $5d$ electrons of Ir^{4+} . The Curie-Weiss fit between 350 and 600 K yields an antiferromagnetic interaction of $\theta_{\text{CW}} = -443(7)$ K and an effective magnetic moment μ_{eff} of $1.72(1) \mu_B$. The effective moment is close to that of the $J_{\text{eff}} = \frac{1}{2}$ state with $g = 2$, which suggests that the admixture of $J_{\text{eff}} = \frac{3}{2}$ and other states is not appreciable. At $T_m = 55$ K, an anomaly accompanying a hysteresis between the field-cooling and zero-field-cooling measurements is observed. The history-dependent contribution originates from a weak ferromagnetic moment of $10^{-4} \mu_B$. In the specific heat $C(T)$ [Fig. 2(c)], a clear jump at the onset temperature of the weak ferromagnetic transition is observed evidencing a bulk magnetic transition. Analogous behavior was observed in other pyrochlore iridates such as $\text{Y}_2\text{Ir}_2\text{O}_7$, where an AIAO magnetic ordering of iridium moments takes

place at T_m [32]. The small magnetic moment below T_m is discussed to originate from the AIAO domain boundaries [33]. It is reasonable to ascribe the magnetic transition in $\text{In}_2\text{Ir}_2\text{O}_7$ to AIAO ordering. The large ratio $f = |\theta_{\text{CW}}|/T_m \sim 8$, together with the small magnetic entropy change at T_m ($\sim 5\%$ of $R \ln 2$), implies the presence of strong frustration, as expected from the frustrated pyrochlore lattice.

The Curie-Weiss temperature of $|\theta_{\text{CW}}| \sim 450$ K may represent the strength of exchange coupling, which is smaller than those of other insulating pyrochlore iridates such as $\text{Y}_2\text{Ir}_2\text{O}_7$ (~ 1180 K) and $\text{Lu}_2\text{Ir}_2\text{O}_7$ (~ 725 K) [22]. This likely reflects the smaller intersite hopping t expected in the strongly distorted Ir-O network, since the exchange coupling J_{ex} is scaled by t^2 as $J_{\text{ex}} \sim t^2/U$.

In order to study the orbital states of $\text{In}_2\text{Ir}_2\text{O}_7$, we performed RIXS measurement at the Ir L_3 edge [Fig. 1(c)]. In addition to the elastic peak, we observe three clear features at 0.48(1), 0.86(1), and 4.14 eV. The two sharp peaks located below 1 eV correspond to excitations within the t_{2g} manifold, while the one at 4.14 eV corresponds to excitations from the t_{2g} to e_g manifold. The split between the t_{2g} and e_g manifold is larger than those of other pyrochlore iridates [22]. In the absence of distortion in an isolated IrO_6 octahedron, only one excitation peak from $J_{\text{eff}} = \frac{3}{2}$ to $J_{\text{eff}} = \frac{1}{2}$ would be observed within the t_{2g} manifold. The presence of two sharp excitations implies the splitting of the $J_{\text{eff}} = \frac{3}{2}$ quartet into two Kramers doublets [ϕ_1 and ϕ_2 in Fig. 1(d)], as observed in other pyrochlore iridates [16,17,28]. The widths of two low-energy peaks in the RIXS spectrum of $\text{In}_2\text{Ir}_2\text{O}_7$ (~ 200 meV) are significantly smaller than those of other reported pyrochlore iridates (~ 300 meV), likely reflecting the smaller bandwidth as identified in the band calculation shown below.

The energy difference of the two low-lying peaks, $\Delta E = E_2 - E_1$, represents the splitting of the $J_{\text{eff}} = \frac{3}{2}$ manifold. We may ascribe the splitting to the trigonal crystal field originating from the compression of IrO_6 . As the strength of this trigonal field can be parametrized by the deviation of the x coordinate of the O1 atom from the ideal value ($\Delta x = x - x_c = x - 0.3125$), the magnitude of splitting is expected to scale with Δx . In Fig. 1(e), ΔE for $\text{In}_2\text{Ir}_2\text{O}_7$ is compared with those for $\text{Y}_2\text{Ir}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ with smaller Δx . We find that ΔE does not depend on Δx appreciably and even decreases with increasing Δx . Factors other than the trigonal distortion of the IrO_6 octahedron, such as long-range crystal field from other cations and/or intersite hopping, should play an important role in the splitting of the $J_{\text{eff}} = \frac{3}{2}$ band.

In order to clarify the combined effect of these factors on Ir $5d$ t_{2g} states, band structure calculations were performed for $A_2\text{Ir}_2\text{O}_7$ for $A = \text{In}$, Lu , and Y . $\text{Y}_2\text{Ir}_2\text{O}_7$ has the least trigonally compressed IrO_6 , while $\text{Lu}_2\text{Ir}_2\text{O}_7$ and $\text{In}_2\text{Ir}_2\text{O}_7$ host nearly identical trigonal distortion. Neither Y^{3+} nor Lu^{3+} carries magnetic moments. The density of the Ir t_{2g} states (DOS) projected onto $J = \frac{5}{2}$ ($J_{5/2}$) and $J = \frac{3}{2}$ ($J_{3/2}$) states are shown in Fig. 3. Since the on-site Coulomb repulsion U is not incorporated, the calculations produce a metallic ground state for all three materials.

The pure $J_{\text{eff}} = \frac{1}{2}$ wave function comprises only the $J_{5/2}$ states while the $J_{\text{eff}} = \frac{3}{2}$ wave function consists of both $J_{5/2}$

FIG. 3. $J_{3/2}$ and $J_{5/2}$ resolved DOS for Ir t_{2g} bands in $A_2\text{Ir}_2\text{O}_7$ for $A = \text{Y}$, Lu , and In . The area beneath the curve of $J_{3/2}$ -derived DOS is filled for clarity. The Fermi level E_F is indicated by dashed black lines. The ratio of the area under the $J_{5/2}$ - and $J_{3/2}$ -derived DOS curves within ± 0.5 eV of E_F (± 0.4 eV for $A = \text{In}$) is shown.

and $J_{3/2}$. Figure 3 shows that the states within ± 0.4 eV near E_F have $J_{\text{eff}} = \frac{1}{2}$ character, while those below -0.4 eV are $J_{\text{eff}} = \frac{3}{2}$ ones. Nonetheless, a sizable $J_{3/2}$ weight near E_F is present, indicative of an admixture of the $J_{\text{eff}} = \frac{3}{2}$ component to the $J_{\text{eff}} = \frac{1}{2}$ states. Since the trigonal crystal field mixes $J_{\text{eff}} = \frac{1}{2}$ and $\frac{3}{2}$ states, one would expect more $J_{\text{eff}} = \frac{3}{2}$, and consequently $J_{3/2}$, weight near E_F in $\text{In}_2\text{Ir}_2\text{O}_7$ and $\text{Lu}_2\text{Ir}_2\text{O}_7$ as compared to $\text{Y}_2\text{Ir}_2\text{O}_7$. In contrast to this assumption, a comparable contribution of $J_{3/2}$ states appears in $\text{Lu}_2\text{Ir}_2\text{O}_7$ and $\text{Y}_2\text{Ir}_2\text{O}_7$, despite the larger distortion in the former. This is evidenced by the ratio of the areas under $J_{5/2}$ and $J_{3/2}$ DOS shown in Fig. 3. The $J_{\text{eff}} = \frac{3}{2}$ weight around E_F is appreciably smaller in $\text{In}_2\text{Ir}_2\text{O}_7$ than not only that of $\text{Y}_2\text{Ir}_2\text{O}_7$, but also of $\text{Lu}_2\text{Ir}_2\text{O}_7$ with a comparable trigonal distortion, distinctly pointing to the formation of an almost pure $J_{\text{eff}} = \frac{1}{2}$ state in $\text{In}_2\text{Ir}_2\text{O}_7$. The t_{2g} bands of $\text{In}_2\text{Ir}_2\text{O}_7$ are narrower (~ 1.7 eV) than those of $\text{Lu}_2\text{Ir}_2\text{O}_7$ (~ 2.0 eV) despite a comparable magnitude of trigonal distortion.

Properties of pyrochlore iridates are expected to vary as a function of the A cation radius, and $\text{In}_2\text{Ir}_2\text{O}_7$ seemingly adheres to this assumption. Its smallest A cation in the series produces the largest trigonal distortion and the smallest bandwidth, as observed in the band calculation (Fig. 3), and manifested in the peak widths of E_1 and E_2 excitations in RIXS [Fig. 1(c)]. While the lack of scaling of ΔE with Δx might be explained by the contribution of the long-range crystal field, the origin of the contrast of the bandwidth and the orbital character between $\text{In}_2\text{Ir}_2\text{O}_7$ and $\text{Lu}_2\text{Ir}_2\text{O}_7$, despite nearly the same degree of trigonal distortion, has yet to be addressed. The intersite hopping and the covalency of the A-O bonds likely play an important role in fostering the ground state of pyrochlore iridates.

To verify our hypothesis, we performed band calculations for model pyrochlore iridates with Ir d - d hopping suppressed up to the third neighbors, which is achieved by substitution of 15 out of 16 Ir ions in a cubic unit cell with Hf, giving a chemical formula of $A_2(\text{Ir}_{1/16}\text{Hf}_{15/16})_2\text{O}_7$ [22]. By suppressing hopping and varying the degree of the trigonal compression of the IrO_6 octahedron, we attempt to separate the impact of intersite hopping from that of trigonal crystal fields.

We find that the model compounds with suppressed intersite hopping (Fig. 4) show strongly reduced $J_{\text{eff}} = \frac{3}{2}$ character near E_F as compared to $A_2\text{Ir}_2\text{O}_7$ (Fig. 3) even with the same

FIG. 4. $J_{3/2}$ and $J_{5/2}$ resolved DOS for Ir t_{2g} bands for model $A_2(\text{Ir}_{1/16}\text{Hf}_{15/16})_2\text{O}_7$ for $A = \text{In}$ and Y for undistorted ($\Delta x = 0$) IrO_6 and the experimentally observed distortion of IrO_6 . The area beneath the curve of $J_{3/2}$ -derived DOS is filled for clarity. The ratio of the area under the $J_{5/2}$ - and $J_{3/2}$ -derived DOS curves within ± 0.3 eV of E_F is shown.

degree of trigonal distortion of IrO_6 octahedra. It is clear from these results that the intersite hopping, rather than the crystal field, plays a predominant role in the mixing of $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ states. In Fig. 4(b), a clear splitting of $J_{\text{eff}} = \frac{3}{2}$ bands of about 0.1 eV is observed even for the undistorted Y model compound, which evidences that the effect of the crystal field originating from neighboring cations is not negligible [17]. The splitting is enhanced by introducing the trigonal distortion observed experimentally, implying that the crystal field from both oxygen atoms and neighboring cations plays a significant role in the splitting of the $J_{\text{eff}} = \frac{3}{2}$ bands. Both In and Y model compounds with the experimentally observed trigonal distortion show a splitting of the $J_{\text{eff}} = \frac{3}{2}$ states of ~ 0.15 eV, which is smaller than that observed in the experiment ($\Delta E = 0.4$ eV). This may point to the involvement of other mechanisms, such as the molecular orbital formation due to the Ir-Ir and Ir-O hybridization, in the splitting of the $J_{\text{eff}} = \frac{3}{2}$ manifold.

The distinct electronic state of $\text{In}_2\text{Ir}_2\text{O}_7$ can be rationalized by the fact that the t_{2g} bands for $\text{In}_2(\text{Ir}_{1/16}\text{Hf}_{15/16})_2\text{O}_7$, as shown in Fig. 4(a), acquire dispersion in contrast to $\text{Y}_2(\text{Ir}_{1/16}\text{Hf}_{15/16})_2\text{O}_7$ (Fig. S7 in [22]). The hybridization of $\text{In } 5s$ and $5p$ states with $\text{O } 2p$ states is not small due to the covalent character of the In-O bond, which provide an extra hopping path between the remote Ir atoms in the model

supercell lattice. In $\text{In}_2\text{Ir}_2\text{O}_7$, the Ir-O-Ir bonds, rather than those via the In-O bonds, dominate the intersite hopping. We argue that the effect of In-O hybridization manifests itself differently: the presence of covalent In-O bonds reduces the Ir-O hybridization and the intersite hopping via Ir-O-Ir bonds. This explains the smallest bandwidth and the pronounced $J_{\text{eff}} = \frac{1}{2}$ character found in $\text{In}_2\text{Ir}_2\text{O}_7$ (Fig. 3). The covalent In-O bond may also mask the effect of the crystal field of the In^{3+} ion acting on Ir atom.

In summary, $\text{In}_2\text{Ir}_2\text{O}_7$ is a Mott insulator with nearly pure $J_{\text{eff}} = \frac{1}{2}$ character. The orbital states in pyrochlore iridates can be described as the interplay of three effects: trigonal crystal field, intersite hopping, and A-site covalency. The crystal field comprises the contributions from the distortion of IrO_6 octahedra as well as Ir and A cations, and splits the ($J_{\text{eff}} = \frac{3}{2}$)-derived states. This crystal field does not introduce substantial $J_{\text{eff}} = \frac{3}{2}$ character into the $J_{\text{eff}} = \frac{1}{2}$ band. The intersite hopping instead plays a central role in mixing of the J_{eff} states. The covalent In-O bonds reduce the Ir-O hybridization and suppress the intersite hopping of Ir d electrons and thus the orbital mixing, resulting in the nearly pure $J_{\text{eff}} = \frac{1}{2}$ state. The sizable intersite hopping in the other $A_2\text{Ir}_2\text{O}_7$ in contrast gives stronger mixing of the $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ states than $\text{In}_2\text{Ir}_2\text{O}_7$. Therefore, the effects of intersite orbital mixing and bond covalency, in addition to local structural distortion, need to be properly incorporated in order to understand their electronic structure. The importance of these factors would not be limited to pyrochlore iridates, and should be common in a wide variety of $5d$ and $4d$ transition-metal compounds with spatially extended d orbitals. Those effects should be taken into account in designing materials hosting novel spin-orbit-entangled phases such as topological semimetal or quantum magnet.

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