\( J_{\text{eff}} = 1/2 \) Mott-Insulating State in Rh and Ir Fluorides

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Discovery of new transition metal compounds with large spin orbit coupling coexisting with strong electron-electron correlation among the \( d \) electrons is essential for understanding the physics that emerges from the interplay of these two effects. In this study, we predict a novel class of \( J_{\text{eff}} = 1/2 \) Mott insulators in a family of fluoride compounds that are previously synthesized, but not characterized extensively. First principles calculations in the level of all electron density functional theory + dynamical mean field theory indicate that these compounds have large Mott gaps and some of them exhibit unprecedented proximity to the ideal, \( SU(2) \) symmetric \( J_{\text{eff}} = 1/2 \) limit.

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Interest in 5\( d \) compounds has been blossoming in recent years in response to the scientific advances and applications in the areas of topological insulators, multiferroics, and thermoelectrics. At the forefront of this activity are the \( Ir \) compounds, because of the interesting interplay between itinerancy, the electronic correlations, and strong spin-orbit coupling (SOC) [1]. This strong coupling between the spin and orbital degrees of freedom gives rise to various interesting phases, such as the exotic spin-liquid phase predicted in honeycomb iridates, or the recently observed Fermi arcs and the spin-orbit induced Mott insulating phase in the perovskite-related \( Ir \) oxides [1–4]. In these latter systems, the SOC splits the sixfold degenerate \( Ir \) \( t_{2g} \) states into four occupied \( J_{\text{eff}} = 3/2 \) and two half-occupied \( J_{\text{eff}} = 1/2 \) states. The bands formed by the \( J_{\text{eff}} = 1/2 \) states are much narrower than the width of the whole \( t_{2g} \) manifold in the absence of SOC, and as a result, the system can be easily drawn to a Mott-insulating phase with even a modest amount of correlations on the \( 5d \) \( Ir \) atom [5–8].

The most widely studied SOC induced correlated insulator is \( \text{Sr}_2\text{IrO}_4 \), which is an antiferromagnetic insulator below 240 K [3,9]. There are numerous studies that involve strain and pressure on this material, and various related compounds are also extensively studied [10–16]. However, despite being the prototypical system, \( \text{Sr}_2\text{IrO}_4 \) is far from being the ideal \( J_{\text{eff}} = 1/2 \) Mott insulator: the existence of the insulating state above the Néel temperature is due to short range order, which is around 100 lattice constants even 20 K above the Néel temperature [17], hence \( \text{Sr}_2\text{IrO}_4 \) was termed a “marginal Mott insulator.” This marginal nature of the insulating state was confirmed theoretically, as the first-principles calculations, which neglect short range order, predict a bad metallic state in the paramagnetic phase [18]. Also, the crystal structure of \( \text{Sr}_2\text{IrO}_4 \) is far from cubic: It has the tetragonal space group \( I4_1/\text{acd} \). The tetragonal symmetry breaks the degeneracy of the \( t_{2g} \) orbitals, and thus the \( J_{\text{eff}} = 1/2 \) orbitals mix, moving the system away from the ideal limit where the moments are \( SU(2) \) invariant. Since \( SU(2) \) symmetric \( J_{\text{eff}} = 1/2 \) insulators are proposed to exhibit superconductivity when doped [19], it is important to identify new compounds that are true \( J_{\text{eff}} = 1/2 \) Mott insulators with sizable gaps.

In this study, we predict a novel class of \( J_{\text{eff}} = 1/2 \) Mott insulator compounds that are both very close to the \( SU(2) \) limit and have large charge gaps in the paramagnetic state. We achieve this by considering crystal structures that are not commonly studied in the context of correlated electron physics. We focus on a group of already synthesized iridium and rhodium fluoride compounds and use first-principles calculations at the level of fully charge self-consistent density functional theory + dynamical mean field theory (DFT + DMFT) to show the presence of the \( J_{\text{eff}} = 1/2 \) insulating state in these compounds. We thus expand the search for new \( J_{\text{eff}} = 1/2 \) insulators to the family of fluorides, and for the first time show that the \( J_{\text{eff}} = 1/2 \) state can exist in a rhodium compound.

We begin our search for new \( J_{\text{eff}} = 1/2 \) insulators by the well-known observation that lower bandwidth favors the Mott insulating phase. The \( \text{Sr}_{n+1}\text{V}_{n}\text{O}_3n+1 \) Ruddlesden-Popper (RP) series nicely demonstrates this point [20]:

The \( n = \infty \text{SrVO}_3 \) is a correlated metal. In this compound, the oxygen octahedra are corner sharing, and the number of nearest neighbor transition metal ions is \( z = 6 \). With decreasing \( n \), \( z \) decreases monotonically from \( z = 6 \) to \( z = 4 \) for \( \text{Sr}_2\text{VO}_4 \) (\( n = 1 \)). This leads to a decrease of the bandwidth as \( n \) decreases, and as a result there is a metal-insulator transition as a function of \( n \), and \( \text{Sr}_2\text{VO}_4 \) is a Mott insulator [20]. The \( \text{Sr}_{n+1}\text{Ir}_{n}\text{O}_{3n+1} \) compounds also behave similarly: The perovskite \( \text{SrIrO}_3 \) (\( z = 6 \)) is a correlated metal, the \( n = 2\text{Sr}_3\text{Ir}_2\text{O}_{7} \) (\( z = 5 \)) is barely an insulator, and the \( n = 1 \text{Sr}_2\text{IrO}_4 \) (\( z = 4 \)) is the well-known \( J_{\text{eff}} = 1/2 \) insulator [3,9].

A strategy to obtain a small bandwidth and hence a possible \( J_{\text{eff}} = 1/2 \) Mott insulator in an iridate compound is to look for crystal structures where the connectivity of anion octahedra is low. The extreme case is a structure that
consists of isolated IrO$_6$ octahedra that are not corner, edge, or face sharing with any other octahedra. But, to the best of our knowledge, there exists no structure with isolated MO$_6$ units in transition metal oxides. However, isolated hexafluoro-transition metal complexes (MF$_6$) are known to exist and are very common in fluoride compounds [21]. The Ir ion in many of these compounds has the $d^9$ electronic configuration, and hence can lead to the $J_{\text{eff}} = 1/2$ Mott insulating phase.

As an example of this group of compounds, we consider the alkali metal hexafluoro iridates and rhodates with the chemical formula $A_2$MF$_6$ and the so-called K$_2$GeF$_6$ (KGF) crystal structure [22,23] shown in Fig. 1. Here, $A$ is the alkali metal ion and $M$ is the transition metal ion. Each $M$ ion (in our case either Ir or Rh) is in the center of an F$_6$ octahedron. The space group is trigonal P3m1. While there is no symmetry element that imposes the octahedra to be regular, all six $M$-$F$ bond lengths are equal and the $F$-$M$-$F$ angles are close to 90°. The site symmetry of the $M$ ion is 3m, and the threefold degenerate $t_{2g}$ states are split into $2 + 1$. However, unlike in the RP compound Sr$_2$IrO$_4$, all ligands are symmetry equivalent [Figs. 1(c)–1(d)], and as a result an equally distorted octahedron is expected to cause a smaller splitting of the $t_{2g}$ states in the $A_2$MF$_6$ compounds than in the RP compounds.

The $M$ ions form regular triangular layers [Fig. 1(b)]. The octahedra and the local coordinate axes of all $M$ ions are aligned in a parallel fashion. The out-of-plane lattice constant $c$ is smaller than the in-plane lattice constant $a$, and as a result, the band structure is of three-dimensional character. The Ir and Rh cations we consider have 4+ formal valence and 5 electrons in their $t_{2g}$ orbitals in this structure. Since the MF$_6$ octahedra are isolated in the sense that there are no $F$ ligands that are coordinated to two different $M$ ions, the effective hopping between the $M$ ions is small and hence the $d$ bands at the Fermi level are expected to be extremely narrow, rendering the system a strong Mott insulator.

In Fig. 2, we show the densities of states (DOS) of Rb$_2$IrF$_6$ and Rb$_2$RhF$_6$, obtained from density functional theory in the generalized gradient approximation (GGA) [24] using the full-potential linear augmented wave formalism as implemented in WIEN2k [25], and using the experimental crystal structures [26,27]. When the SOC is not taken into account, both compounds have very similar DOS [Figs. 2(a)–2(b)]: There is a narrow (~400 meV) band that consists of the transition metal $t_{2g}$ states, which is partially occupied. The $t_{2g}$-$e_g$ splitting is ~3 eV, and the $e_g$ states are well above the Fermi level. There is no other state than the $t_{2g}$ states around the Fermi level for a 4–5 eV interval.

The strong spin orbit coupling due to the heavy Ir ion in Rb$_2$IrF$_6$ dramatically alters the band structure of this compound [Fig. 2(c)]. The partially filled $t_{2g}$ band near the Fermi level is split into two bands, a lower lying $J_{\text{eff}} = 3/2$ band with four electrons, and a half-filled $J_{\text{eff}} = 1/2$ band that crosses the Fermi level. The latter is extremely narrow (~100 meV) but since the Mott physics is beyond DFT, this theory predicts metallic state. The Rh ion in Rb$_2$RhF$_6$, which is above Ir in the periodic table, introduces a much weaker SOC than Ir. As a result, even when SOC is taken into account, the $J_{\text{eff}} = 3/2$ states are not energetically separated from the $J_{\text{eff}} = 1/2$ ones. However, it is still possible to identify the two overlapping peaks corresponding to these two groups of states in the DOS.

Both of these compounds have narrow, half-filled $J_{\text{eff}} = 1/2$ bands near the Fermi level, indicating that a small amount of on-site correlations can drive them into a

![FIG. 1 (color online).](image-url) (a) The K$_2$GeF$_6$ (KGF) crystal structure. (b) The MF$_6$ octahedra are aligned parallel and form triangular layers. The alkali metals are both above and below these layers, shown by green and red. (c) Coordination environment of the transition metals in the KGF and (d) the $n = 1$ RP structure. Chemically inequivalent F ions in the RP structure are shown by blue and red.

![FIG. 2 (color online).](image-url) DOS of Rb$_2$IrF$_6$ and Rb$_2$RhF$_6$ within density functional theory, with and without spin-orbit coupling.
Mott-insulating state. While this state is beyond DFT at the GGA level, it is possible to capture the Mott insulating phase using DMFT [28]. DFT + DMFT has been successfully applied to reproduce the properties of various Mott insulators and it has been recently used to study the $J_{\text{eff}} = 1/2$ insulating phase in Sr$_2$IrO$_4$ [5]. As a result, it is the natural method of choice to study the possibly Mott insulating electronic structure of the hexafluoro iridates and rhodates. We chose the same on-site Coulomb repulsion in these compounds as estimated for iridates and rhodates. We have chosen the upper and lower Hubbard bands are clearly separated (a) Rb$_2$IrF$_6$ and (b) Rb$_2$RhF$_6$ from DFT + DMFT [31]. Both compounds are Mott insulators, with wide gaps close to ~2 eV. In Rb$_2$IrF$_6$, the upper and lower Hubbard bands are clearly separated and have $J_{\text{eff}} = 1/2$ character, indicating that Rb$_2$IrF$_6$ is a $J_{\text{eff}} = 1/2$ Mott insulator. In Rb$_2$RhF$_6$, the lower Hubbard band overlaps with the fully occupied, uncorrelated $J_{\text{eff}} = 3/2$ bands and so cannot be clearly seen in the $A(k, \omega)$ plot. However, the upper Hubbard band has a clear $J_{\text{eff}} = 1/2$ character and therefore this compound is a $J_{\text{eff}} = 1/2$ insulator as well. To the best of our knowledge, this is the first report of a $J_{\text{eff}} = 1/2$ insulator in a compound that does not contain iridium, after the recently discovered RuCl$_3$ [32]. Furthermore, both of these compounds have the largest gaps ever reported for a $J_{\text{eff}} = 1/2$ insulator. Both the large gaps, and the possibility of the $J_{\text{eff}} = 1/2$ state in a rhodate compound are thanks to the nonconnectivity of the MF$_6$ octahedra in the KGF structure, and the resulting very narrow $J_{\text{eff}} = 1/2$ bands.

In passing, we note that replacing Ir with Rh in Sr$_2$IrO$_4$ leads to a metallic phase both because of the much weaker SOC [33] but also possibly because of the slightly larger electronegativity of the Rh ion. In the KGF fluorides, the charge gap is large, which makes the electronegativity difference negligible, and also the SOC is not necessary for the Mott insulating phase (it is essential only for the $J_{\text{eff}} = 1/2$ character). As a result, even the rhodates in this structure are $J_{\text{eff}} = 1/2$ Mott insulators. (See the Supplemental Material [34].)

Encouraged by the success of our strategy to look for $J_{\text{eff}} = 1/2$ Mott insulators in this class of compounds, we also performed DFT + DMFT calculations in three other compounds with the same crystal structure, Cs$_2$IrF$_6$, K$_2$IrF$_6$, and K$_2$RhF$_6$. While these compounds have significantly different lattice constants due to the different alkali metals they contain, we find all of them to be $J_{\text{eff}} = 1/2$ insulators with large gaps as well. All of these compounds were synthesized and their crystal structures were studied before [22,23,26,27,35–37], but there is very little information on their magnetic properties or conductivities. Our predictions call for more experiments to characterize these materials better. We predict a fluctuating magnetic moment of 1.6 $\mu_B$ in both Rb$_2$IrF$_6$ and Rb$_2$RhF$_6$, which is smaller than the value expected for an ideal spin-1/2 Mott insulator (1.73 $\mu_B$) because of the charge fluctuations (there is a > 10% probability that there are six electrons in the $t_{2g}$ orbitals). These values are ~12% larger than what is measured in Cs$_2$IrF$_6$ in Ref. [35], but ~8% smaller than the value measured in the Rh compounds in Ref. [26] at room temperature.

The ideal $J_{\text{eff}} = 1/2$ state is $SU(2)$ invariant, and so it has no magnetic anisotropy. However, systems such as Sr$_2$IrO$_4$ are observed not to be exactly at this limit due to deviations of the wave function from the ideal $J_{\text{eff}} = 1/2$ [10]. The reason is that Sr$_2$IrO$_4$ lacks cubic symmetry: It has the space group $I4_1/acd$, which is tetragonal, and hence the three $t_{2g}$ orbitals of the Ir ion are split into a degenerate doublet and a singlet. The deviation from ideal $J_{\text{eff}} = 1/2$ state is small but not negligible, and it depends strongly on biaxial strain and pressure [5,12,38]. In the KGF structure, the space group is trigonal, and the $t_{2g}$ irreducible representation is split into two, a singlet $A_1g$ and a doublet $E_g$, similar to Sr$_2$IrO$_4$. This also introduces a deviation from the $J_{\text{eff}} = 1/2$ state and a resultant magnetic anisotropy.

In order to see how much the wave function is different from the ideal $J_{\text{eff}} = 1/2$ state, we study the hybridization function $\Delta(\omega)$ used in the DMFT calculation [39]. It is given by

\[
\Delta(\omega) = \sum_{\mathbf{k}, \sigma} \rho_{\mathbf{k}, \sigma}(\omega) - \rho_{\mathbf{k}, \sigma}(\omega + \Delta(\omega))
\]
\[
\frac{1}{\omega - \Delta(\omega) - \Sigma(\omega)} = \sum_k \hat{P}_k \frac{1}{\omega - e_k - \hat{P}^{-1}_k \Sigma(\omega)},
\]

where \(\Sigma(\omega)\) is the DMFT self-energy, \(e_k\) are the DFT Kohn-Sham eigenvalues, and \(P\) and \(\hat{P}^{-1}\) are the projector and the embedder on the transition metal site. In the high frequency limit \(\omega \to \infty\), the eigenvalues of the \(\Delta\) matrix give the atomic energy levels (including both the crystal field and the spin-orbit coupling) and it is related to the single ion anisotropy. In the \(\omega \to 0\) limit, it is related to low energy electronic excitations. The two eigenvectors of \(\Delta\) with the largest eigenvalues are the \(J_{\text{eff}} = 1/2\) like states \(|\psi_{+1/2}\rangle\) and \(|\psi_{-1/2}\rangle\). The inner products of these with the ideal \(J_{\text{eff}} = 1/2\) states \(|J_{1/2, \pi/2}\rangle\) can be used as a measure of how close the system to the \(SU(2)\) limit is. However, this product is second order in the mixing, and a better measure is the coefficients in the expansions of \(|\psi_{\pm 1/2}\rangle\). This measure is used in Ref. [5] to study the effect of tetragonal symmetry breaking in \(\text{Sr}_2\text{IrO}_4\). Under a trigonal perturbation, the \(t_{2g}\) orbitals are split into a singlet and a doublet as \(|\psi_{\pm 1/2}\rangle = (1/\sqrt{3})(|d_{x^2-y^2}\rangle \pm |d_{z^2}\rangle + |d_{xy}\rangle)\) for \(|\psi_{+1/2}\rangle\), and \(|\psi_{-1/2}\rangle = (1/\sqrt{3})(|d_{xy}\rangle \pm \alpha|d_{z^2}\rangle + \alpha^2|d_{x^2-y^2}\rangle)\), where \(\alpha = e^{i\pi/3}\). A generalization of the \(J_{\text{eff}} = 1/2\) states that takes into account this splitting is

\[
|\psi_{+1/2}\rangle = \frac{\sqrt{3} - 2\alpha^2}{3} (-|a_1\downarrow\rangle + (1-i)|a_1\uparrow\rangle) + \frac{\gamma}{3} (-|e_+\downarrow\rangle + (\alpha^2 - ia\alpha)|e_+\uparrow\rangle) + |e_+\downarrow\rangle + (\alpha - ia^2)|e_+\uparrow\rangle),
\]

\[
|\psi_{-1/2}\rangle = \frac{\sqrt{3} - 2\alpha^2}{3} (-|a_1\uparrow\rangle + (1+i)|a_1\downarrow\rangle) + \frac{\gamma}{3} (|e_+\uparrow\rangle + (\alpha^2 + ia\alpha)|e_+\downarrow\rangle) + |e_+\uparrow\rangle + (\alpha + ia^2)|e_+\downarrow\rangle).
\]

Here, \(\gamma\) quantifies the deviation from the ideal limit, and \(\gamma = 1\) gives \(|\psi_{\pm 1/2}\rangle = |J_{1/2, \pi/2}\rangle\). A large \(|1 - \gamma|\) indicates strong deviation from the Heisenberg regime, and leads to large magnon gaps, even larger than the spin wave bandwidth in \(\text{Sr}_2\text{IrO}_4\). Since hybridization is frequency dependent, so is \(\gamma\). In \(\text{Rb}_2\text{IrF}_6\), the low frequency \(\gamma_0 = 0.987\) and the high frequency \(\gamma_\infty = 0.992\). Compared to \(\text{Sr}_2\text{IrO}_4\) which has \(\gamma_0 = 1.03\) and \(\gamma_\infty = 1.02\), the electronic state in \(\text{Rb}_2\text{IrF}_6\) is much more isotropic, and closer to the ideal \(SU(2)\) limit. The rhodate compound \(\text{Rb}_2\text{RhF}_6\), which has weaker SOC, shows a more significant deviation from the ideal limit: It has \(\gamma_0 = 1.020\) and \(\gamma_\infty = 0.935\).

This very isotropic behavior despite the noncubic space group of \(\text{Rb}_2\text{IrF}_6\) can be better understood considering the local coordination geometry of the transition metal ion. The site symmetry of Ir is \(\bar{3}m\). The elements of the point group include various rotations, such as a threefold rotation around [001] and a twofold rotation around [100] [Fig. 1(c)]. As a result, all six F ligands around a M ion are symmetry equivalent: They are chemically identical, and their F-M bond lengths are the same. The deviation from the ideal cubic symmetry on the M site is only due to the presence of further neighbors that reduce the symmetry, and the deviation of the F octahedra from a regular octahedron. This latter effect is quite small (the largest F-M-F bond angle variance in the compounds we consider is less than 6°), and as a result, the Ir ion is in an almost cubic environment. In the RP family of iridate compounds, the site symmetry of the Ir ion can be as high as \(4/mmm\). However, despite a fourfold rotation and various twofold rotation axes that pass through the Ir ion [Fig. 1(d)], there is no threefold rotation in the point group, and there are two chemically distinct ligands around each Ir ion. The apical oxygens, shown by red in Fig. 1(d), are bonded to only one Ir ion, whereas the other oxygens are bonded to two Ir each. This necessarily results in very a noncubic local environment of the Ir ion, which leads to deviations from the ideal \(J_{\text{eff}} = 1/2\) state even when the Ir-O bond lengths are artificially set to be equal.

In conclusion, we identified a new class of \(J_{\text{eff}} = 1/2\) Mott insulators, which includes the first two examples of such compounds without iridium after the recently discovered RuCl₃ [32]. These materials are wide gap Mott insulators, with no visible tendency towards magnetic ordering, and some of them are also closer to the isotropic \(SU(2)\) limit than the well-studied \(\text{Sr}_2\text{IrO}_4\). This work extends the search for new materials which display an interplay of correlations with spin-orbit coupling to fluoride compounds. We posit that the \(J_{\text{eff}} = 1/2\) Mott insulating phase is very common in transition metal fluorides with isolated Ir⁺⁺F₆ and Rh⁺⁺F₆ complexes. Studying other structure types that satisfy this property would lead not only to the discovery of new \(J_{\text{eff}} = 1/2\) Mott insulators but also to many other strongly correlated complex fluorides with interesting physical properties.

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[28] In the DFT + DMFT implementation that we used [39], a self-energy $\Sigma$ which contains all Feynman diagrams local to the Ir ion is added to the Kohn-Sham Hamiltonian. The self-energy is obtained by solving the local impurity problem using continuous time quantum Monte Carlo [29,30] and full charge self-consistency is obtained by repeating DFT and DMFT steps.


[31] In our DMFT calculations, the temperature is taken to be 0.01 eV. While in the beginning of the calculations the symmetry of the self-energy is broken and magnetic ordering is allowed, it became spin-symmetric after a few iterations, indicating that the compounds do not have any strong tendency towards magnetic ordering at this temperature.


