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Breakdown of $J = 0$ nonmagnetic state in d^4 iridate double perovskites: A first-principles study

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Through first-principles calculations, we study the electronic structure of double-perovskite iridates with Ir in the d^4 valence state. Contrary to the expected strong spin-orbit driven $J = 0$ nonmagnetic state, we find finite moment at the Ir site, exhibiting breakdown of the $J = 0$ state. We further find the band structure effect rather than the crystal field effect to be responsible for this breakdown. The antiferromagnetic superexchange interaction between Ir moments, in general, makes these compounds insulating.

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In recent times, the thrust in oxide research has been extended to 5*d* transition metal oxides, especially iridates, with spin-orbit coupling (SOC) playing an important role. The most spectacular manifestation of this is the observation of the $j_{\mathrm{eff}} = 1/2$ Mott insulating state in layered iridates with the Ir^{4+} (d^5) valence state [1]. The counterintuitive, insulating nature of these compounds with extended 5*d* wave functions can only be explained by invoking strong SOC. SOC splits the octahedral crystal field split Ir t_{2g} states into lower energy $j_{\mathrm{eff}} = 3/2$ and higher energy $j_{\mathrm{eff}} = 1/2$ states. The half-filled $j_{\mathrm{eff}} = 1/2$ state for the d^5 configuration of Ir^{4+} becomes insulating upon switching on the correlation effect [2]. While most study focuses on d^5 iridates [3], it is interesting to ask what happens for other fillings, e.g., d^4. According to the split $j_{\mathrm{eff}} = 3/2$ and $j_{\mathrm{eff}} = 1/2$ scenario within single-particle theories, the d^4 configuration should result in a nonmagnetic insulating solution.

Following this idea, the double-perovskite iridate like $\mathrm{Sr_2YIrO_6}$ (SYIO) was synthesized [4], where Ir is in the nominal 5+ or d^4 state. Surprisingly, the compound was found to be magnetic with well formed magnetic moments at Ir sites, ordering at low temperature. This curious observation was argued to be due to a noncubic crystal field effect of the the monoclinic symmetry of $\mathrm{Sr_2YIrO_6}$ [4]. The noncubic distortion, however, appeared to be small, the maximum deviation of the Ir-O bond length from the average in $\mathrm{IrO_6}$ octahedra being only ≈ 0.03 Å. This is expected to give rise to a small effect, especially in the scale of atomic spin-orbit coupling of Ir. The same study also reported another compound $\mathrm{Sr_2GdIrO_6}$ (SGIO) which forms in a cubic structure [5]. The *Pn*-3 symmetry of this cubic structure however allows for the tilt/rotation of the $\mathrm{IrO_6}$ octahedra as well as the trigonal distortion of the $\mathrm{IrO_6}$ octahedra with ∠O-Ir-O deviating from 90°. The authors proposed [4] that the cubic symmetry of SGIO would lead to a nonmagnetic state of Ir, although the confirmation of this through bulk measurement is difficult due to the presence of a strong magnetic ion like Gd^{3+} with $4f^7$ configuration. This situation becomes even more puzzling with the recent report on a Ba analog of SYIO, $\mathrm{Ba_2YIrO_6}$ (BYIO), which forms in a cubic *Fm*-3*m* structure. As opposed to the *Pn*-3 symmetry of SGIO, the *Fm*-3*m* neither allows for trigonal distortion nor allows for the rotation or tilt of octahedra. In spite of this perfect cubic situation, a preliminary investigation [6] involving fitting susceptibility data gave an effective magnetic moment of 0.57 μ_B/Ir and a Curie-Weiss constant of −135 K. NMR measurement shows the presence of spin fluctuations [6]. Independent measurements also seem to support the presence of magnetism [7].

To the best of our knowledge, no rigorous theoretical study exists to probe this interesting situation. The theoretical study presented in Ref. [4] is an exact diagonalization study of an atomic-like model Hamiltonian in parameter space without any consideration of the hopping or band structure effect. The inclusion of hopping is expected to change the scenario significantly as discussed in Ref. [8]. The d^5 iridates [9], namely the two-dimensional compound $\mathrm{Sr_2IrO_4}$ with an effective half-filled one-band $j_{\mathrm{eff}} = 1/2$ description, in contrast with the metastable three-dimensional perovskite structured [10] $\mathrm{SrIrO_3}$ with large mixing between $j_{\mathrm{eff}} = 1/2$ and $j_{\mathrm{eff}} = 3/2$, also seems to point towards this. In the present Rapid Communication, we carry out a detailed study of the electronic structure of the three double-perovskite compounds SGIO, SYIO, and BYIO in terms of first-principles density functional theory (DFT) and tight-binding model calculations. Our study provides insight into this curious, unexpected situation, thereby shedding light on the important role of band structure effect in the iridate problem.

The DFT calculations have been carried out in the plane wave basis [11] using the projector augmented wave potentials [12,13]. The results have been further checked in terms of calculations in the full potential linear augmented plane wave (FLAPW) basis [14]. The exchange-correlation functional was chosen to be that of the generalized gradient approximation (GGA) [15] and that with the supplemented +U correction (GGA+U) [16]. The SOC was dealt through the second variational method. The tight-binding Ir-only Hamiltonian was obtained through a downfolding calculation implemented within the *N*th-order muffin tin orbital (NMTO) method [17]. The technical details of the methods can be found in the Supplemental Material (SM) [18].

The top two panels of Fig. 1 show the experimentally determined crystal structures of SGIO [4], SYIO [4], and BYIO [19]. We note that while the Ir-O bond lengths are all the same in SGIO, ∠O-Ir-O deviates from 90° by 0.1°. The $\mathrm{IrO_6}$

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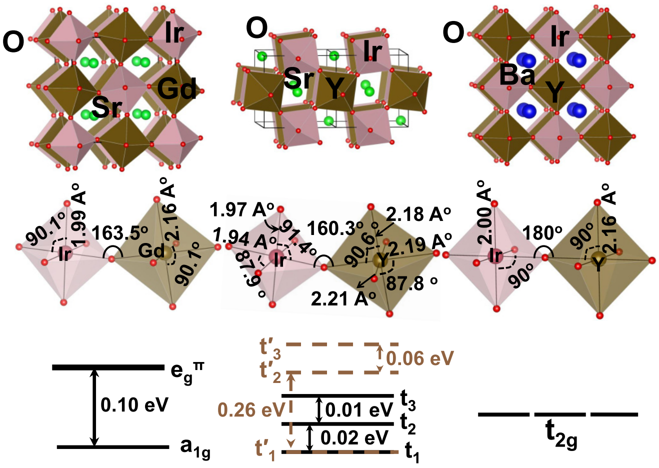

FIG. 1. (Color online) Structural details and crystal field splitting for SGIO, SYIO, and BYIO (from left to right). Upper panel: Crystal structures projected onto *ab* plane. Middle panel: The corner-shared IrO_6 and BO_6 ($B = $ Gd/Y) octahedra. Marked are various bond lengths and bond angles. Bottom panel: The crystal field splitting within t_{2g} block of Ir. The levels marked in dashed lines show the results for SY(G)IO. See text for details.

octahedra are rotated and tilted, making an angle of $\approx 164^\circ$ to the GdO_6 octahedra. Moving to SYIO, we find Ir-O bond lengths become unequal with a difference of ≈ 0.03 Å, while ∠O-Ir-O deviates from 90° by 1.4°, and IrO_6 octahedra are rotated/tilted with ∠Ir-O-Y of 160°. For BYIO, IrO_6 octahedra are completely regular with equal Ir-O bond lengths, ∠O-Ir-O $= 90^\circ$ and ∠Ir-O-Y $= 180^\circ$. The bottom panel shows the crystal field splitting of Ir t_{2g} states for SGIO, SYIO, and BYIO, obtained from NMTO-downfolding [17] calculations. BYIO in perfect cubic symmetry gives rise to degenerate Ir t_{2g} levels. The monoclinic symmetry of SYIO lifts the degeneracy of Ir t_{2g} levels completely with three nondegenerate levels. However the splitting between the levels is found to be small, $\approx 0.01-0.02$ eV. The trigonal distortion in SGIO breaks the degeneracy of Ir t_{2g} levels into singly degenerate a_{1g} and doubly degenerate e_g^π levels. We find this splitting to be 0.1 eV, an order of magnitude larger than that found for SYIO. Thus contrary to the assumption in Ref. [4] the crystal field splitting in SGIO is even larger than that in SYIO. We find this relatively large crystal field splitting is assisted by the hybridization of Gd-*f* states with Ir-*d* states. To check this, we calculated the crystal field splitting of the hypothetical compound, SY(G)IO having the same monoclinic crystal structure as SYIO, with Y ions replaced by Gd. The crystal field splitting for this compound, as shown in dashed lines in the bottom and middle panels of Fig. 2, is found to be an order of magnitude larger than that of the real SYIO compound, stressing the role of hybridization from Gd-*f*.

The electronic structure and magnetic moments for the three compounds, as given in plane wave basis calculations, are shown in Fig. 2 and Table I, respectively. Examining the spin-polarized GGA density of states assuming the parallel alignment of Ir spins, as shown in Fig. 2, we find the states close to Fermi level are dominated by Ir t_{2g} states. Without consideration of spin-orbit coupling, the magnetic moment at the Ir site is found to be about 1.1 μ_B, with the missing moment located at O sites due to large Ir-O hybridization. The net moment/f.u. for SYIO and BYIO is found to be 2.0 μ_B in accordance with the low-spin $S = 1$ state of Ir^{5+}. This leads to a half-metallic situation with filled Ir t_{2g} bands in the majority spin channel, and minority spin Ir t_{2g} states crossing the Fermi level. In the case of SGIO the moment/f.u. turns out to be 5.0 μ_B due to the magnetic moment of Gd which points antiparallel to the magnetic moment of Ir. Upon

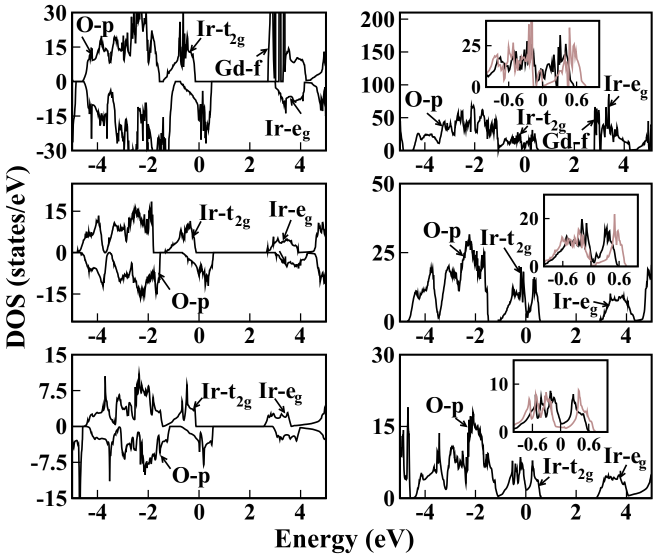

FIG. 2. (Color online) Total density of states of SGIO (top panels), SYIO (middle panels), and BYIO (bottom panels) calculated within spin-polarized GGA (left) and GGA+SOC (right). The dominant orbital characters have been marked. The zero of the energy is set at Fermi level. The insets in the right panels show the comparison of the GGA+SOC (black) and GGA+SOC+U (brown/gray) density of states, in the energy range of −1 eV to +1 eV around the Fermi energy.

TABLE I. Magnetic moments (μ_B) of SGIO, SYIO, and BYIO calculated within spin-polarized GGA, GGA+SOC, and GGA+SOC+U. The tiny moments at Sr/Ba sites are not shown. Orbital moments are given in parentheses.

	GGA				GGA+SOC GGA+SOC+U			
	Gd (Y)	Ir	O	Total /f.u.	Gd (Y)	Ir	O	Total /f.u.
SGIO	−6.82	1.07	0.11	−5.00	−6.78	0.69	0.07	−5.64
					(−0.03)	(0.14)	(0.01)	
					−6.76	0.72	0.06	−5.69
					(−0.04)	(0.25)	(0.02)	
SYIO	0.01	1.13	0.12	2.00	0.0	0.46	0.05	0.81
					(0.0)	(0.09)	(0.01)	
					0.00	0.51	0.05	0.86
					(0.00)	(0.15)	(0.01)	
BYIO	0.02	1.11	0.11	2.00	0.01	0.59	0.06	1.07
					(0.00)	(0.10)	(0.01)	
					0.00	0.62	0.06	1.07
					(0.00)	(0.19)	(0.01)	

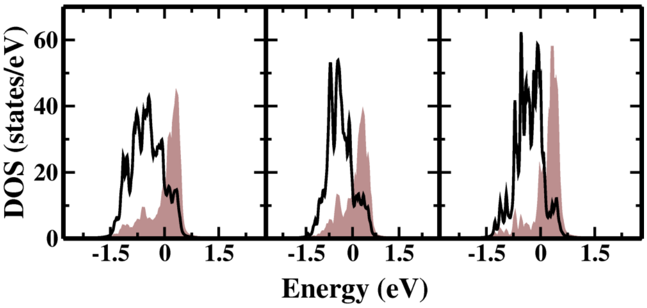

FIG. 3. (Color online) t_{2g} DOS projected onto $j_{\text{eff}} = 1/2$ (shaded area) and $j_{\text{eff}} = 3/2$ (solid line) for SGIO (left panel), SYIO (middle panel), and BYIO (right panel). The zero of the energy is set at Fermi level.

switching on the SOC, with spin quantization axis pointed along [001], the magnetic moment at the Ir site is found to survive for all three compounds, irrespective of the absence or presence of noncubic crystal field and its strength. Our result on BYIO is in very good agreement with calculation carried out in the full potential local orbital (FPLO) basis set with fully relativistic GGA functional [20]. This puts the explanation for the breakdown of the $J = 0$ state, given in Ref. [4] in terms of noncubic crystal field, in question. The spin moment at the Ir site as calculated in GGA+SOC turned out to be about 0.5–0.7 μ_B with orbital moment of ≈ 0.1 μ_B. Inclusion of the correlation effect beyond GGA, in terms of GGA+SOC+U calculation with U value chosen as 2 eV, is found to increase the moment at the Ir site, with enhanced orbital moment of ≈ 0.2 μ_B. This follows the expectation that correlation enhances the spin-orbit effect, as has been discussed earlier in the literature [21]. We find the m_l/m_s ratio to be 0.2–0.3, much less than 1. This is to be contrasted with $BaIrO_3$ for which the ratio is found to be as high as 4 [22]. This points towards only moderately strong spin-orbit effect in these compounds.

To probe this, we show in Fig. 3 a plot of Ir t_{2g} DOS projected onto $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ states. We find the mixing to be significantly large, $\approx 30\% - 35\%$, thereby j being not a good quantum number any more. This drifts the Ir d states away from the ideal $J = 0$ state. The partial mixing, however, leads to opening of a pseudogap in the spectrum in GGA+SOC calculation, which becomes more pronounced on application of missing correlation effect in GGA+SOC+U calculation (cf. insets in Fig. 2).

In the next step, we proceed to investigate the possible magnetic structure. To the best of our knowledge, no neutron scattering data exist for any of the discussed double perovskites. Thus our theoretical predictions can be validated in future experiments.

We first consider the case of SYIO and BYIO which have nonmagnetic Y ion at the B site. We note that the Ir sublattice forms an fcc lattice. Considering this structure, there are two major magnetic superexchange paths, that between nearest-neighbor (NN) Ir^{5+} ions, separated by a distance of $\sqrt{2}a_p$ (a_p is the cubic lattice parameter), and that between next-nearest-neighbor (NNN) Ir^{5+} ions separated by a distance of $2a_p$, involving Ir-O-Y-O-Ir. Our total energy calculation shows NNN Ir-Ir magnetic interaction to be an order of magnitude smaller than NN Ir-Ir magnetic interaction. As discussed in Refs. [23,24] if the strength of NNN interaction is negligible, then the Ir ions are expected to show type-I antiferromagnetic (AFM) spin ordering (see SM [18] for illustrations of the spin configurations) driven by the single-ion anisotropy. However, if the strength of the NNN AFM superexchange interaction is significant, but still less than the NN coupling, then a type-III spin ordering is stabilized. For the case in which the NNN interaction becomes larger than the NN interaction, a type-II spin ordering is favored, which is neglected in our analysis. We carried out GGA+SOC+U total energy calculations of the nonmagnetic, ferromagnetic (FM), as well as AFM type-I and type-III ordering of Ir spins for SYIO and BYIO. For both SYIO and BYIO we found type-I spin ordering to be the lowest energy configuration with Ir spins oriented in-plane (*ac* plane for SYIO [25]). See SM [18] for details on energetics. The anisotropy thus turned out to be of easy plane, with value 1.4 meV for SYIO and 0.5 meV for BYIO. The electronic structure of the lowest energy type-I AFM state with Ir spins oriented in-plane turned out to be insulating for both SYIO and BYIO with a gap of 135 meV and 85 meV, respectively. Our GGA+SOC+U calculations for the lowest energy magnetic configurations not only provide insulating solutions but also tend to stabilize magnetism further. The spin (orbital) moment at the Ir site for the type-I antiferromagnetic spin ordering calculated in the plane wave basis of VASP is found to be 0.72 (0.28) μ_B and 0.66 (0.26) μ_B for SYIO and BYIO, respectively. The slightly larger values of the moments in comparison to the magnetic configuration of parallel Ir spins presented in Table I further point to the stability of the type-I magnetic configuration.

The situation gets dramatically changed in the case of SGIO, in which the B site is occupied by the strong magnetic ion like Gd^{3+}. The strong AFM coupling between Gd and Ir spins drives FM alignment of spins within Ir and Gd sublattices. The finite magnetocrystalline anisotropy induced by SOC, estimated to be 1.7 meV, makes the spins oriented in-plane. The resultant electronic structure shows an insulating gap of 34 meV. The spin (orbital) moment at the Ir site for SGIO with spins oriented in-plane is found to be 0.75 (0.27) μ_B, similar to values quoted in Table I. The theoretically estimated band gap values of SYIO and SGIO are underestimated compared to experimental estimates, but the trend remains the same with SYIO showing larger band gap than SGIO. Note that the disordering effect due to antisite disorder [26] is not considered in the calculations.

The above theoretical analysis finds that the $J = 0$ nonmagnetic state gets destabilized in the studied case of double-perovskite iridates, including the case of BYIO with perfect cubic symmetry. The essential idea of synthesizing d^4 iridates in the double-perovskite structure was to increase the Ir-Ir separation, thereby bringing the situation closer to the atomic limit. As shown in our study, the extended nature of Ir-5*d* wave functions together with 3-dimensional connectivity in double-perovskite structure makes the band structure effect important, preventing realization of the $J = 0$ limit. The dominant contribution to bandwidth turns out to be from NN Ir-Ir hopping across the face with 12 such neighbors, as found also in the case of $Sr(Ca)_2CrSbO_6$ [27]. The other possible route to achieve the $J = 0$ state may be by reducing the connectivity to 2 dimensions. In this context, we touch upon the case of $NaIrO_3$, a novel post-perovskite compound with pentavalent iridium Ir^{5+} ions synthesized recently [28]. The susceptibility measurements as well as DFT calculations [28] confirm the nonmagnetic state of Ir in this compound. This was thus considered to be an illustrative example of realization of the $J = 0$ nonmagnetic state, in marked contrast with the series of compounds studied here. The IrO_6 octahedra in $NaIrO_3$, however, is found to be highly distorted, and our calculation of crystal field splitting of the t_{2g} manifold shows all t_{2g} levels to be split completely with a large separation of ≈ 0.6 eV within themselves (see SM [18] for details). This level splitting is comparable with Hund's exchange in 5d Iridates which is estimated to be about 0.4–0.5 eV [29]. This in turn stabilizes the configuration $(\uparrow\downarrow)(\uparrow\downarrow)(0)$, resulting in a nonmagnetic solution and complete quenching of the spin-orbit effect. Our calculation considering the experimental crystal structure gave rise to a nonmagnetic, metallic solution with little difference found between calculated GGA, GGA+SOC, and GGA+SOC+U electronic structures. We further found that theoretical optimization of the structure results in a nearly insulating solution, in conformity with the experimentally observed semiconducting behavior with variable range hopping [28], without the necessity of invoking a strong correlation effect [30]. We thus conclude that the nonmagnetic semiconducting ground state of $NaIrO_3$ is a strong crystal field driven $S = 0$ state rather than a spin-orbit driven $J = 0$ state.

In summary, we theoretically investigated the proposal of stabilization of the nonmagnetic $J = 0$ state driven by strong spin-orbit effect in a series of d^4 iridates in the double-perovskite structure. We showed that the band structure effect, rather than the noncubic crystal field effect, causes breakdown of the $J = 0$ state in these compounds. The situation in iridate double perovskites considered in the present study is thus an intermediate situation, where the spin-orbit coupling λ quenches the spin considerably and unquenches the orbital moment, but the bandwidth (W) effect prevents realizing the atomic-like $J = 0$ nonmagnetic state, as shown schematically in Fig. 4. We further found that the finite moments at Ir sites couple antiferromagnetically, except for the case of Sr_2GdIrO_6, for which the strong AFM coupling between large Gd spin and Ir spin forces the Ir spins to align ferromagnetically within themselves. While our DFT results support the two-site exact diagonalization result of Ref. [8], which showed the instability of the $J = 0$ state in d^4 filling upon reduction in λ/t (t being the two-site hopping interaction), our conclusion of AFM interaction between Ir-d^4 spins is in disagreement with the FM exchange, inferred in Ref. [8]. The AFM exchange between Ir spins turned out to be crucial to drive these double-perovskite compounds insulating. Considering the case of post-perovskite $NaIrO_3$ with 2-dimensional connectivity, we found that strong crystal field effect leads to quenching of spin-orbit effect and stabilization of $S = 0$ nonmagnetic state, rather than $J = 0$ nonmagnetic state. We note that by considering 2-dimensional connectivity in $NaIrO_3$, the dispersive bandwidth is reduced by $\approx 45\%$ compared to the studied double-perovskite compounds. However this gain is counterbalanced by the large distortion driven crystal field effect. Moving to lower dimensionality might be helpful, if the distortion can be prevented.

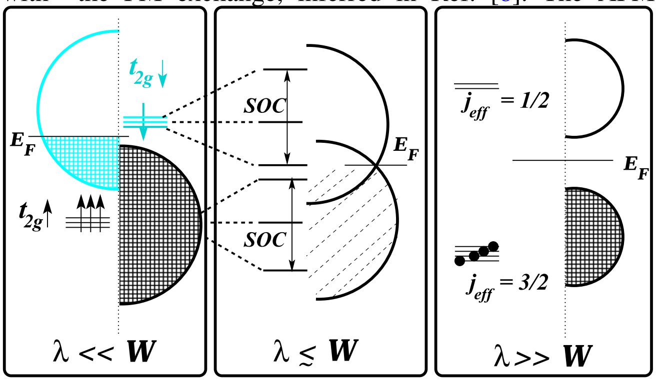

FIG. 4. (Color online) The evolution of the t_{2g} electronic states of Ir^{5+} upon increasing λ/W. The scenario including the finite-bandwidth effect starting from the atomic energy levels at different strengths of λ is shown. For $\lambda \ll W$, an $S = 1$ state with magnetic moment of 2 μ_B is realized, while at the opposite limit of $\lambda \gg W$ a $J = 0$ state is realized. As discussed in the text, double-perovskite compounds lie in an intermediate situation.

Finally, the present analysis has been carried out within the framework of single-particle theory and the relevance of many-body effects, if they are at all relevant, needs to be explored. The importance of the structure-property relationship and the band structure effect as has emerged from the present analysis should be useful in understanding the properties of iridates in general. We hope that our detailed study will motivate further experimental investigation.

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