Antiferromagnetic Slater Insulator Phase of Na$_2$IrO$_3$

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Using a hybrid density-functional theory (DFT) calculation including spin-orbit coupling (SOC), we predict that the zigzag antiferromagnetic (AFM) ground state of the honeycomb layered compound Na$_2$IrO$_3$ opens the observed insulating gap through a long-range magnetic order. We show that the effect of SOC and the correction of self-interaction error inherent in previous local or semilocal DFT calculations play crucial roles in predicting the band gap formation in Na$_2$IrO$_3$. It is revealed that the itinerant AFM order with a strong suppression of the Ir magnetic moment is attributed to a considerable hybridization of the Ir 5d orbitals with the O 2p orbitals. Thus, our results suggest that the insulating phase of Na$_2$IrO$_3$ can be represented as a Slater insulator driven by itinerant magnetism.

Recently, there have been intensive studies concerning the interplay between the spin-orbit coupling (SOC), the on-site Coulomb repulsion ($U$), and the bandwidth ($W$) in 5d transition metal oxides (TMO). Compared to 3d orbitals in 3d TMO, 5d orbitals in 5d TMO are spatially more extended to yield a relatively smaller (larger) value of $U$ ($W$). On the other hand, the strength of the SOC in 5d TMO is enhanced due to the higher atomic numbers of transition metals. The resulting energy scales arising from SOC, $U$, and $W$ in 5d TMO may become comparable to each other, leading to a broad spectrum of exotic quantum phases such as topological insulator, spin liquid, and Mott insulator. In particular, the nature of the insulating phase in iridium (Ir) oxides has been under intense debate whether it is a Mott-type insulator or a Slater-type insulator. Here, the gap formation in the Mott-type insulator is driven by electron correlation while that in the Slater-type insulator is associated with magnetic ordering.

As a prototypical example of 5d TMO, we here focus on Na$_2$IrO$_3$, where Ir atoms form a honeycomb lattice and each Ir atom is surrounded by an octahedron of six O atoms [see Fig. 1(a) and 1(b)]. It was experimentally observed that Na$_2$IrO$_3$ has the antiferromagnetic (AFM) insulating ground state with a zigzag spin alignment [Fig. 1(c)] below the Néel temperature $T_N \approx 15$ K. However, the insulating gap is preserved even at room temperature. This separation between the insulating behavior and the onset of AFM ordering may imply that Na$_2$IrO$_3$ can be regarded as a Mott insulator driven by electron correlations. To address the nature of the insulating phase in Na$_2$IrO$_3$, it was suggested that the Ir$_{5g}$ bands locating around the Fermi energy would be treated in terms of relativistic atomic orbitals with the effective angular momentum $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$. Here, the upper $j_{\text{eff}} = 1/2$ band decoupled from the lower $j_{\text{eff}} = 3/2$ bands was presumed to be half-filled, and therefore Ir atoms can have localized magnetic moments corresponding to an effective spin one-half Ir$^{5+}$ ion. This $j_{\text{eff}}$ scenario caused by strong SOC leads not only to a novel magnetic structure suggested from the Kitaev-Heisenberg model but also to a spin-orbit Mott insulator where the half-filled $j_{\text{eff}} = 1/2$ band splits into two Hubbard bands by taking into account on-site Hubbard $U$.

However, contrasting with such highly localized $j_{\text{eff}} = 1/2$ orbitals at Ir atoms, a recent $ab$ initio density functional theory (DFT) calculation together with the tight-binding model analysis showed that the $t_{2g}$ bands can be described by quasimolecular orbitals (QMOs) which are fully delocalized over six Ir atoms forming a honeycomb lattice. Despite this rather itinerant character of QMOs, the explicit treatment of $U$ was required to obtain the observed insulating gap of $\sim 0.34$ eV. It is thus likely that the effect of electron correlations plays an indispensable role in describing the insulating phase of Na$_2$IrO$_3$, thereby being represented as a Mott insulator.

By contrast, we here propose a different mechanism for the observed insulating phase of Na$_2$IrO$_3$ based on a long-range magnetic order. This magnetically driven insulating phase through an itinerant single-particle approach can be represented as a Slater insulator. It is noticeable that a rather delocalized character of the Ir $t_{2g}$ states, as described by QMOs, may be associated with the self-interaction error (SIE) inherent to the conventional DFT calculations with the local density approximation (LDA) or the generalized gradient approxi-
Note that the SIE causes the electron density to artificially spread out because delocalization reduces the spurious self-repulsion of electron. This so-called delocalization error tends to give an inaccurate estimation of the ionization energy and the electron affinity, resulting in the underestimation of band gap. In this regard, previous LDA and GGA calculations may not adequately describe the insulating phase of Na$_2$IrO$_3$. Therefore, it is very challenging to examine how the electronic properties of Na$_2$IrO$_3$ can be changed by the correction of SIE with an exchange-correlation functional beyond the LDA or GGA.}

** Results and discussion**

We begin to study the experimentally observed zigzag AFM ground state of Na$_2$IrO$_3$ using the PBE calculation. The optimized structural parameters such as the Ir-Ir bond lengths $d_{12}$ and $d_{23}$ in Fig. 1(b) and the Ir-O-Ir bond angles $\theta_{12}$ and $\theta_{23}$ in Fig. 1(b) are given in Table I. The calculated values of $\theta_{12} = 99.84^\circ$ and $\theta_{23} = 98.51^\circ$ (greater than the ideal 90$^\circ$ Ir-O-Ir bond angle) show a sizable trigonal distortion of the IrO$_6$ octahedra, consistent with an XRD analysis. Figure 2(a) shows the calculated band structure and density of states (DOS) of the zigzag AFM structure, which exhibit the presence of partially occupied Ir $t_{2g}$ states at the Fermi level ($E_F$), indicating a metallic feature. Note that there are twelve $t_{2g}$ bands which originate from four different Ir atoms within the unit cell of the zigzag AFM structure. It is noticeable that, for the $t_{2g}$ states locating near $E_F$, the partial DOS projected onto the O 2$p$ orbitals amounts to ~50% of that projected onto the Ir 5$d$ orbitals [see Fig. 2(a)], indicating a considerable hybridization between the two orbitals. Indeed, the spin characters of the $t_{2g}$ state at $E_F$, as shown in Fig. 2(a), reveal the electron delocalization over IrO$_6$ octahedra on each zigzag chain side. These aspects of the $t_{2g}$ states lead not only to a smaller magnetic moment of $\sim 0.53 \mu_B$ for an Ir atom compared to the effective spin $S = 1/2$ moment assumed in the Kitaev-Heisenberg model but also a slightly induced magnetic moment of $\sim 0.10 \mu_B$ for the O$_1$ atom [see Fig. 2(b) and Table II]. It is noteworthy that the PBE calculation may involve the over-delocalization of the $t_{2g}$ states due to the SIE, therefore incorrectly predicting the zigzag AFM structure to be metallic rather than insulating.

In order to correct the SIE, we use the HSE functional to optimize the zigzag AFM structure. We find that the structural parameters slightly depend on the magnitude of $\alpha$ in the HSE functional (see Table I): i.e., $d_{12}$ and $d_{23}$ change little by less than 0.01 Å in the range of 0 $< \alpha \lesssim 0.08$, but, as $\alpha$ increases to 0.1, $d_{12}$ ($d_{23}$) decreases (increases) by $\sim 0.02$ (0.04) Å. We also find a drastic variation of the band structure and DOS as a function of $\alpha$. Especially, the DOS at $E_F$ is found to decrease as $\alpha$ increases up to 0.08, giving rise to the creation of a pseudogap. For $\alpha > 0.08$, the pseudogap is turned into an insulating gap whose magnitude increases with increasing $\alpha$ (see Fig. 3). Figure 4(a) shows the band structure and DOS of the zigzag AFM structure, obtained using the HSE calculation with $\alpha = 0.05$. It is seen that, compared with the PBE result [Fig. 2(a)], (i) the DOS for the occupied $t_{2g}$ states is shifted to a lower energy and (ii) the DOS at $E_F$ is much reduced. We note that, as $\alpha$ increases, the Ir magnetic moment increases compared to that obtained using the PBE calculation (see Table II), reflecting that the HSE functional corrects the over-delocalization of Ir 5$d$ electrons due to the SIE of the PBE functional.

According to the $j_{\text{eff}}$ scenario, the SOC splits the $t_{2g}$ states into the $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ states, and the experimental 0.34 eV-gap

![Figure 1](image)

** Figure 1 | Crystal structure of Na$_2$IrO$_3$. (a) projection on the xy plane and (b) projection on the xz plane. a$_1$, a$_2$, and a$_3$ denote unit vectors of the unit cell. The large, medium, and small circles represent Na, Ir, and O atoms, respectively. Three different AFM structures with the zigzag, stripy, and Néel spin orders are schematically shown in (c), where the solid and open circles indicate up and down spins.**

| Table I | Ir-Ir bond lengths $d_{12}$ and $d_{23}$ (Å) in Fig. 1(b) and Ir-O-Ir bond angles $\theta_{12}$ and $\theta_{23}$ (°) obtained using the PBE and HSE calculations, in comparison with the experimental data |
|----------|----------------|-----------------|-----------------|-----------------|-----------------|
| PBE      | 3.129          | 3.139           | 99.84           | 98.51           |
| HSE$_{\alpha=0.05}$ | 3.130          | 3.138           | 100.23          | 98.86           |
| HSE$_{\alpha=0.1}$  | 3.109          | 3.180           | 99.51           | 99.73           |
| Experiment [Ref. 19] | 3.130          | 3.138           | 99.45           | 97.97           |
bands, consistent with the experimental observation of the five $d$-$d$ interband transitions in optical conductivity \(^{14}\). Since the HSE + SOC calculation with $\alpha = 0.05$ adequately predicts the insulating electronic structure of the zigzag AFM ground state, we can say that the insulating phase of Na$_2$IrO$_3$ can be represented as a spin-orbit Slater insulator through itinerant magnetism. We note that the optimal HSE + SOC value of $\alpha = 0.05$ reproducing the experimental 0.34 eV-gap \(^{14}\) is smaller than that ($\alpha = 0.15$) obtained from the HSE

![Figure 3](image-url)  
**Figure 3** Calculated band gap of the zigzag AFM structure as function of the mixing factor $\alpha$ in the HSE functional.

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**Figure 2**  
(a) Band structure and DOS of the zigzag AFM structure, obtained using the PBE functional. The band dispersions are plotted along the symmetry lines shown in the Brillouin zone of the unit cell (see the inset). The total DOS, Ir 5$d$ partial DOS, and O 2$p$ partial DOS are displayed with solid, dot-dashed, and dotted lines, respectively. The energy zero represents the Fermi level. The charge characters of the spin-up and spin-down $t_{2g}$ states near the Fermi level are shown with an isosurface of 0.004 e/Å$^3$. (b) In (b), the spin-up (spin-down) density is displayed in bright (dark) color with an isosurface of 0.004. (~ 0.004) e/Å$^3$, and the two different species of O atoms are denoted as O$_1$ (for O atoms on the same zigzag chain side) and O$_2$ (for O atoms between two zigzag chains).

was opened by taking into account an on-site interaction $U$ of 1–3 eV, leading to a conclusion that the insulating phase of Na$_2$IrO$_3$ can be represented as a spin-orbit Mott insulator \(^{12–14}\). In this study, we examine the effect of SOC on the electronic structure of the zigzag AFM structure using the HSE + SOC calculation. Here, we employ the optimized HSE structure because the effect of SOC changes little the Ir–Ir bond lengths and the Ir–O–Ir bond angles by less that 0.01 Å and $^\circ$, respectively. As shown in Fig. 3, the inclusion of SOC opens the band gap $E_g$, which monotonically increases with increasing $\alpha$. For $\alpha = 0.05$ (equivalent to the PBE + SOC calculation), we obtain $E_g = 0.05$ eV, in good agreement with a previous PBE + SOC calculation \(^{14}\). On the other hand, as $\alpha$ increases to 0.05, $E_g$ becomes 0.33 eV, close to the experimental value of 0.34 eV \(^{14}\). The HSE + SOC band structure and DOS computed with $\alpha = 0.05$ are displayed in Fig. 4(b). It is seen that (i) the $t_{2g}$ bands just below and above $E_f$ become almost dispersionless, thereby possibly correcting the over-delocalization of the $t_{2g}$ states, and (ii) there are six separated energy regions for the $t_{2g}$

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**Table II** Magnitude of the magnetic moments (in units of $\mu_B$) of Ir, O$_1$, and O$_2$ atoms obtained using the PBE, HSE, PBE + SOC, and HSE + SOC calculations.

|        | Ir  | O$_1$ | O$_2$ |
|--------|-----|-------|-------|
| PBE    | 0.53| 0.10  | 0.00  |
| HSE$_{\alpha=0.05}$ | 0.56| 0.11  | 0.00  |
| HSE$_{\alpha=0.1}$  | 0.62| 0.11  | 0.00  |
| PBE + SOC          | 0.33| 0.06  | 0.05  |
| HSE + SOC$_{\alpha=0.05}$ | 0.37| 0.06  | 0.05  |
| HSE + SOC$_{\alpha=0.1}$ | 0.41| 0.06  | 0.05  |

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![Figure 4](image-url)  
**Figure 4** Band structure and DOS of the zigzag AFM structure, obtained using (a) the HSE and (b) HSE + SOC calculations with $\alpha = 0.05$. The magnetic moment ($M_x$, $M_y$, $M_z$), obtained using the HSE + SOC calculation with $\alpha = 0.05$, is drawn in (c). Here, $M_i$ is calculated by integrating the corresponding component of magnetic moment inside the PAW sphere with a radius of 1.4 (0.8) Å for Ir (O). In (c), the circles represent Ir atoms.
Neél AFM structures are very small, not only is structure. Since the energy differences among the zigzag, stripy, and instance, the HSE calculation for the Cs 3C60 crystal predicted 33 not neutron and XRD experiment 18. These theoretical and experimental

Thus, our results indicate a significant Slater-type character of gap

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oxides. We note that other 5

We performed the HSE

Conclusion

We performed the HSE + SOC calculation to investigate the zigzag AFM ground state of Na2IrO3. We found that the observed insulating gap of ~0.34 eV 11 is well predicted by not only taking into account the SOC but also correcting the SIE inherent in the LDA or the GGA.

1. Okada, Y. et al. Imaging the evolution of metallic states in a correlated iridate. Nat. Mater. 12, 707–713 (2013).
2. Shitade, A. et al. Quantum spin Hall effect in a transition metal oxide Na2IrO3. Phys. Rev. Lett. 102, 256403 (2009).
3. Pesin, D. & Balents, L. Mott physics and band topology in materials with strong spin-orbit interaction. Nat. Phys. 6, 376–381 (2010).
4. Okamoto, Y., Nohara, M., Aruga-Katori, H. & Takagi, H. Spin–liquid state in the S = 1/2 hyperkagome antiferromagnet Na4Ir3O8. Phys. Rev. Lett. 99, 137207 (2007).
5. Machida, Y., Nakatsuji, S., Onoda, S., Tayama, T. & Sakakibara, T. Time-reversal symmetry breaking and spontaneous Hall effect without magnetic dipole order. Nature 463, 210–213 (2010).
6. Chaloupka, J., Jackeli, G. & Khaliullin, G. Kitaev-Heisenberg model on a honeycomb lattice: possible exotic phases in iridium oxides. Phys. Rev. Lett. 105, 027204 (2010).
7. Kim, B. J. et al. Novel Ia3 = 1/2 Mott state induced by relativistic spin-orbit coupling in Sr2IrO4. Phys. Rev. Lett. 101, 076402 (2008).
8. Kim, B. J. et al. Phase-sensitive observation of a spin-orbital Mott state in Sr2IrO4. Science 323, 1329–1332 (2009).
9. Jackeli, G. & Khaliullin, G. Mott insulators in the strong spin-orbit coupling limit: From Heisenberg to a quantum compass and Kitaev models. Phys. Rev. Lett. 102, 017205 (2009).
10. Ogushi, K. et al. Resonant X-ray diffraction study of the strongly spin-orbit-coupled Mott insulator Ca3Ni2Ge2O7. Phys. Rev. Lett. 110, 217202 (2013).
11. Singh, Y. et al. Relevance of the Heisenberg-Kitaev model for the honeycomb lattice iridates A2IrO3. Phys. Rev. Lett. 108, 127203 (2012).
12. Singh, Y. & Gegenwart, P. Antiferromagnetic Mott insulating state in single crystals of the honeycomb lattice material Na4Ir3O8. Phys. Rev. B 82, 064412 (2010).
13. Grestarsson, H. et al. Crystal-field splitting and correlation effect on the electronic structure of A2IrO3. Phys. Rev. Lett. 110, 076402 (2013).
14. Comin, R. et al. Na2IrO3 as a novel relativistic Mott insulator with a 340-meV gap. Phys. Rev. Lett. 109, 266406 (2012).
15. Arita, R., Kunek, J., Kozhevnikov, A. V., Eguiluz, A. G. & Imada, M. Ab initio studies on the interplay between spin-orbit interaction and Coulomb correlation in Sr2IrO4 and Ba2IrO4. Phys. Rev. Lett. 108, 086403 (2012).
16. Li, Q. et al. Atomically resolved spectroscopic study of Sr2IrO4: Experiment and theory. Sci. Rep. 3, 3073 (2013).
17. Liu, X. et al. Long-range magnetic ordering in Na2Ir3O8. Phys. Rev. B 83, 220403(R) (2011).
18. Ye, F. et al. Direct evidence of a zigzag spin-chain structure in the honeycomb lattice: A neutron and x-ray diffraction investigation of single-crystal Na2IrO3. Phys. Rev. B 85, 180403 (2012).
19. Choi, S. K. et al. Spin waves and revealed crystal structure of honeycomb iridate Na2IrO3. Phys. Rev. Lett. 108, 127204 (2012).
20. Chaloupka, J., Jackeli, G. & Khaliullin, G. Zigzag magnetic ordering in the iridium oxide Na2IrO3. Phys. Rev. Lett. 110, 097204 (2013).
21. Mazin, I. I., Jeschke, H. O., Foyevtsova, K., Valenti, R. & Khomskii, D. I. Na2IrO3 as a molecular orbital crystal. Phys. Rev. Lett. 109, 197201 (2012).
22. Slater, J. Magnetic effects and the Hartree-Fock equation. Phys. Rev. 82, 538–541 (1951).
23. Ceperley, D. M. & Alder, B. J. Ground state of the electron gas by a stochastic method. Phys. Rev. Lett. 45, 566–569 (1980).
24. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
25. Cohen, A. J., Mori-Sánchez, P. & Yang, W. Insights into current limitations of density functional theory. Science 321, 792–794 (2009).
26. Mori-Sánchez, P., Cohen, A. J. & Yang, W. Localization and delocalization errors in density functional theory and implications for band-gap prediction. Phys. Rev. Lett. 100, 146401 (2008).
27. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened coulomb potential. J. Chem. Phys. 118, 8207–8215 (2003).
28. Krakau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. J. Chem. Phys. 125, 224106 (2006).
29. Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. Phys. Rev. B 48, 13115–13118 (1993).
30. Kresse, G. & Furthmüller, J. Efficient ab initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–16 (1996).
31. Sohn, C. H. et al. Mixing between Ia3 = 1/2 and 3/2 orbitals in Na2IrO3: A spectroscopic and density functional calculation study. Phys. Rev. B 88, 085125 (2013).
32. He, J. & Franchini, C. Screened hybrid functional applied to 3d → 3d transition-metal perovskites LaMnO3 (M = Sc–Cu): Influence of the exchange mixing parameter on the structural, electronic, and magnetic properties. Phys. Rev. B 86, 235117 (2012).
33. Giovannetti, G. & Capone, M. Electronic correlations stabilize the antiferromagnetic Mott state in Cs$_3$C$_6$O$_6$. *Phys. Rev. Lett.* **109**, 166404 (2012).
34. Lee, J.-H., Kim, H.-J. & Cho, J.-H. Ferrimagnetic Slater insulator phase of the Sn/Ge(111) surface. *Phys. Rev. Lett.* **111**, 106403 (2013).
35. Calder, S. *et al.* Magnetically driven metal-insulator transition in NaOsO$_3$. *Phys. Rev. Lett.* **108**, 257209 (2012).

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**Author contributions**

H.J.K. and J.H.L. carried out the DFT calculations and data analysis. J.H.C. was responsible for the planning and the management of the project. J.H.C. wrote the main manuscript text and H.J.K. prepared figures 1–4. All authors reviewed the manuscript.

**Additional information**

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