In-gap states with nearly free electron characteristics in layered structure trivalent iridates

Xing Ming,1* Carmine Autieri,2 Huanfu Zhou,3 Jiafeng Ma,1 Xin Tang,3 Xiaojun Zheng1

1. College of Science, Guilin University of Technology, Guilin 541004, People's Republic of China
2. International Research Centre Magtop, Polish Academy of Sciences, Aleja Lotników 32/46, PL-02668 Warsaw
3. Key Lab of New Processing Technology for Nonferrous Metal & Materials, Ministry of Education, School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China.

ABSTRACT

Iridium oxides (iridates) provide good platform to study the complex interplay of spin-orbit coupling (SOC) interactions, correlation effects, Hund coupling and lattice degree of freedom. However, previous studies primarily focus on tetravalent (Ir4+, 5d5) and pentavalent (Ir5+, 5d4) iridates. Here, we turn our attention to a recently reported unprecedented trivalent (Ir3+, 5d6) iridates, K0.75Na0.25IrO2, crystallizes in a triangular lattice with edge-sharing IrO6 octahedra and alkali ions intercalated [IrO2]- layers. We theoretically determine the preferred occupied positions of the alkali ions from energetic viewpoints, and reproduce the experimentally observed semiconducting behavior and nonmagnetic (NM) properties. The SOC interactions play a critical role in the band dispersion, resulting in NM $J_{\text{eff}} = 0$ states. More intriguingly, our electronic structure not only confirms the experimental speculation of the presence of in-gap states and explains the abnormal low activation energy in K0.75Na0.25IrO2, but also puts forward the in-gap states featured with nearly free electron characteristics. Our theoretical results provide new insights into the unconventional electronic structures of the trivalent iridates and imply its promising applications in nanoelectronic devices such as ideal electron transport channels.

* Email: mingxing@glut.edu.cn
I. INTRODUCTION

Due to the intricate interactions between Coulomb correlation, Hund exchange coupling, spin-orbit coupling (SOC) and crystal field splitting, novel phenomena and intriguing properties have emerged in iridium oxides (iridates).[1-8] Furthermore, the effective electronic correlations and SOC interactions increases with the decreasing geometry connectivity (connection between the polyhedral units) in iridates.[5-7] Depending on the relative strength of Coulomb repulsion and SOC interactions, exotic phases have been proposed and revealed in iridates,[1,4] such as spin-orbit coupled Mott insulators,[9,10] Weyl semimetals,[11,12] topological insulators,[4,13] giant magnetic anisotropy,[14,15] superconductors,[16-19] spin liquids and spin ices.[20,21]

In addition, the lattice degree of freedom and geometry connectivity play a crucial role in iridates and have renewed growing interests in iridates. The IrO$_6$ octahedra are arranged in a mixed corner- and edge-sharing network. The structural dimensionality and the octahedra stacking manner can be used to control the electronic structure in iridates.[6,22] For instance, the Ruddlesden-Popper series Sr$_{n+1}$Ir$_n$O$_{3n+1}$ compounds (n = 1, 2 and ∞) show dimensionality-controlled metal-insulator transition (MIT) and correlated metallic state.[5,23] A novel $J_{\text{eff}} = 1/2$ Mott insulating state has been proposed in single-layer quasi-two-dimensional Sr$_2$IrO$_4$ (n = 1) due to the cooperative interaction between electron correlations and SOC interactions.[9,10] In contrast, bilayer Sr$_3$Ir$_2$O$_7$ (n = 2) in close proximity to a MIT, and the three-dimensional counterpart, SrIrO$_3$ (n = ∞) is found to be semimetallic with unusually narrow bandwidths.[24]

Extensive investigations have been focused on iridates with 5$d^5$ (Ir$^{4+}$) or 5$d^9$ (Ir$^{5+}$) electronic configurations, far less attention have been paid to iridates with other valence states. Recently, an unprecedented trivalent iridate K$_{0.73}$Na$_{0.25}$IrO$_2$ was synthesized by Daniel Weber et al., where the Ir$^{3+}$ ions adopting a 5$d^6$ electron configuration.[25] In strong SOC limit, all six 5$d$ electrons are expected to fully occupy the $t_{2g}$ states, resulting in a diamagnetic property. As shown in Figure 1, K$_{0.73}$Na$_{0.25}$IrO$_2$ crystallizes in triangular lattice with a space group of P6$_3$/mmc. The IrO$_6$ octahedra are edge-sharing and form [IrO$_2$]$^-$ layers. The alkali ions act as intercalated ions, locating on two types of interlayer sites: A (1/3, 2/3, 1/4) and B (0, 0, 1/4), respectively. Experimentally, the Na ions almost only sit on the interlayer positions A, whereas two third (one third) of the K ions occupy the interlayer positions A (B), together with 25%/75% vacancies on the positions A/B.
The uncommon trivalent iridium ions and the triangular layered structure of $K_{0.75}Na_{0.25}IrO_2$ offer a promising platform to explore the interplay between electron correlations, SOC interactions, and lattice degree of freedom. Magnetic behavior and resistivity measurements show nonmagnetic (NM) character and semiconducting behavior in $K_{0.75}Na_{0.25}IrO_2$. However, the experimentally determined activation energy (85.7 meV) is very low for this semiconductor, which indicates the presence of in-gap states in $K_{0.75}Na_{0.25}IrO$. Although preliminary electronic structure has been reported in the original work, the authors just considered one case of the alkali ions occupancy in their theoretical calculations. The interlayer positions only occupied by K ions, whereas the Na ions have been completely neglected, corresponding to $KIR_2$. Furthermore, they didn’t definitely specify the positions A or B occupied by the K ions. Moreover, the band structure and density of states (DOS) show a big band gap of 0.973 eV, but detailed analysis are absent to clarify the abnormal activation energy. In present work, we not only consider the interlayer positions fully occupied by one type of alkali ions, but also consider occupancy of mixed alkali ions. Especially, in order to capture the real occupancy of the alkali ions and improve the description of the intrinsic characteristics of the title material $K_{0.75}Na_{0.25}IrO_2$, we have built supercell to consider the
distribution of the alkali ions and vacancies in the interlayer space. These settings of the structure model are more consistent with the real constitutions of the K_{0.75}Na_{0.25}IrO_{2} material. Based on density functional theory (DFT) first-principles electronic structure calculations, we try to provide new insights into the unique electronic structures of this rare trivalent iridates K_{0.75}Na_{0.25}IrO_{2}. We not only successfully reproduce the experimentally observed semiconducting behavior and NM properties, but also reveal the evolutions of the band structure along with the SOC interactions.

More interesting, in-gap states are discovered below the conduction bands, which provide clues to explain the experimentally observed abnormal low activation energy. Furthermore, the in-gap states feature with nearly free electron (NFE) characteristics around the conduction band minimum (CBM), which can be utilized as perfect transport channels without nuclear scattering for electron transport, suggesting potential applications in nanoelectronic devices.

II. COMPUTATIONAL DETAILS

Employed the projector augmented wave (PAW) method [29,30], first-principles calculations were performed in the framework of DFT with VASP code [31], together with the Perdew-Becke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) as the exchange-correlation functional.[32] We adopted the rotationally invariant DFT + U method introduced by Liechtenstein et al. to consider the correlations effects.[33] The onsite Coulomb interactions U and Hund coupling parameter J_{H} were set to 2 and 0.2 eV for the Ir atoms, respectively.[5,14,15] But we should note that the Coulomb repulsion is not the essential factor to manipulate the insulating nature in the title compound, and we will explain this issue later.

Regarding the layered structure and large interlayer distances along the c-axis, beyond traditional GGA, we took into account the van der Waals (vdW) interactions using semiempirical dispersion interaction correction methods (DFT-D) with optPBE-vdW functional.[34-36] Calculations have also taken into account the fully relativistic SOC interactions. The total energy was converged within 10^{-6} eV. The Brillouin zone was sampled using a k-point mesh of 14 × 14 × 3 for the crystallography unit cell, and the energy cutoff was set to 520 eV.

In order to unveil the preferred occupation positions of the alkali ions, first we considered ten configurations in the crystallographic unit cell (schematic shown in Figure S1 in Supplemental Material [37]), which are denoted as NaA (Na ions only occupy the interlayer positions A, and there are no K ions), NaB (Na ions only occupy the interlayer positions B, and there are no K
ions), NaANaB (Na ions occupy the positions A in one interlayer space, and occupy positions B in another interlayer space, and there are no K ions), KA (K ions only occupy the interlayer positions A, and there are no Na ions), KB (K ions only occupy the interlayer positions B, and there are no Na ions), KAKB (K ions occupy the positions A in one interlayer space, and occupy the positions B in another interlayer space, and there are no Na ions), KANaB (K ions occupy the positions A in one interlayer space, and Na ions occupy the positions B in another interlayer space), KBNaA (K ions occupy the positions B in one interlayer space, and Na ions occupy the positions A in another interlayer space), KANaA (K ions occupy the positions A in one interlayer space, and Na ions occupy the positions A in another interlayer space), KA (K ions only occupy the interlayer positions B, and there are no Na ions), KB (K ions only occupy the interlayer positions B, and there are no Na ions), KBNaB (K ions occupy the positions B in one interlayer space, and Na ions occupy the positions B in another interlayer space), KBNaA (K ions occupy the positions B in one interlayer space, and Na ions occupy the positions B in another interlayer space), respectively. Recognized the structural stability and experimental measured positions of the alkali ions, we did not consider the configuration that the alkali ions only occupy one interlayer position and left another interlayer position empty.

III. RESULTS AND DISCUSSIONS

Figure 2 (a) Theoretically calculated lattice constants with PBE or optPBE-vdW functionals and (b) relative energies calculated without or with SOC by optPBE-vdW + U calculations. The energies for the configurations of NaA, KA and KANaA are set as references (zero point).

As shown in Figure 2 (a), the vdW corrections play minor role in the lattice constants, the PBE and optPBE-vdW functionals nearly predict identical results. The in-plane lattice constant $a$ is almost independent on the alkali ions’ occupation positions. In contrast, the out-of-plane lattice constant $c$ obviously depends on the occupied positions, which is longer when the alkali ions occupy the interlayer position B. As shown in Figure 1 (b), these trends can be attributed to the
different local environments of the two interlayer positions, where positions A face to two hollows of the [IrO$_2$]$^-$ layers, whereas positions B face to two surfaces of the IrO$_6$ octahedra. In addition, owing to bigger ionic radius of the K ions, the lattice constant $c$ is obvious longer when the interlayer positions are only occupied by K ions. The experimentally observed preferred-occupancy of the alkali ions can be further inspected from the energetic point of view. As shown in Figure 2 (b), no matter there are one or two types of alkali ions, once the alkali ions occupy the interlayer positions A, the energies are apparent lower than they occupy the positions B, which are closely related to the hollows of the [IrO$_2$]$^-$ layers. Consequently, these two types of alkali ions prefer to occupy the interlayer positions A with much lower energy, which are in good agreement with the experimental results, where Na ions almost only occupy the positions A, whereas two third (one third) of K ions occupy positions A (B), coexisting with 25%/75% vacancies on the positions A/B.[25]

![Figure 3](image_url) Band structures around Fermi level calculated within optPBE-vdW + U for the alkali ions occupancy configuration of KBNaA: (a) without SOC, (b) including SOC. For better clarity, the energy-level splitting of the Ir 5$d$ orbitals are assigned to $t_{2g}$, $e_g$ states, and $J_{\text{eff}}$ states, respectively. Because spin-up and spin-down states are degenerate in the NM states, only spin-up subbands are depicted. It is worth noting that the four bands above $E_F$ are assigned to nominal $e_g$
states according to crystal-field theory, in fact, they are originated from the combinations of Ir $e_g$ states and alkali ions $s$ states as shown in the projected band structures (Figure S3 in Supplemental Material [37]).

In order to maximum extent approach the alkali ions occupancy in real material and reveal the impact of SOC interactions on the electronic structures of these iridates, according to the experimentally determined crystallographic structure, we show the electronic structure of the KBNaA case (corresponding to K$_{0.5}$Na$_{0.5}$IrO$_2$) in the main text (detailed electronic structures of all ten configurations are displayed in Supplemental Material [37]). We perform spin polarized calculations and consider the correlation interactions together with vdW corrections by optPBE-vdW + U calculations to check the basic electronic structure. In octahedral crystal field, the Ir 5$d$ orbitals split into the $t_{2g}$ and $e_g$ states. Even without onsite Coulomb corrections, the crystal-field splitting is sufficient to account for the insulating nature (Figure S2), the experimentally observed semiconducting behavior has been successfully reproduced (see Figure S3 for the band gap and Figure S4 for band structures of all ten cases in Supplemental Material [37]). According to traditional band theory scenario, these layered iridates can be classified as band insulator.[38,39] As shown in Figure 3 (a), in line with two Ir ions in the crystallographic unit cell, the isolated manifold of six pairs $t_{2g}$ bands below Fermi level ($E_F$) are fully occupied, and are distinctly split away from four pairs of fully empty $e_g$ states above $E_F$ by a large crystal-field splitting (about 4 eV), resulting in insulating band structures in these iridates. Due to the two-dimensional connectivity of the IrO$_6$ octahedra, the bandwidth of the $t_{2g}$ states (about 2 eV) are close to another quasi two-dimensional iridate Sr$_2$IrO$_4$.[5,9] The typical characteristics of the band structure shows NM 5$d^6$ $(t_{2g}^6, e_g^6)$ electronic configurations, agrees well with the magnetic measurement results.[25]

To shed more light on the underlying role of SOC in the electronic structure, the SOC interactions are included by optPBE-vdW + U + SOC calculations. As shown in Figure 3 (b), SOC interactions significantly influence the dispersion of the $t_{2g}$ states below $E_F$, but almost have no impact on the dispersion of the $e_g$ states. The SOC interactions lead to a broadening of the valence band and upward movement of the conduction band, resulting in enlargement of the band gap (see the band gap plot in Figures S3 for all ten cases in Supplemental Material [37]). Especially, attributed to large octahedral crystal-field splitting and strong SOC interactions in
iridates, triply degenerate $t_{2g}$ states evolve into $J_{\text{eff}} = 3/2$ quartet and $J_{\text{eff}} = 1/2$ doublet states.[1,9] Because the energy of the former is somewhat lower than that of the latter, the $J_{\text{eff}} = 3/2$ bands and $J_{\text{eff}} = 1/2$ bands are all fully occupied for $K_{0.75}Na_{0.25}IrO_2$ with obvious gap between them (Figure 3 (b)).[1,7,9] In the strong SOC scenario, four out of the six electrons of the trivalent Ir$^{3+}(5d^2)$ ions fully occupy the lower-energy $J_{\text{eff}} = 3/2$ quadruplet, and the remaining two electrons fully occupy the higher-energy $J_{\text{eff}} = 1/2$ doublet, leading to NM $J_{\text{eff}} = 0$ characteristics. Normally, a proper projection or down-folding should be carried out in order to distinguish $J_{\text{eff}}=1/2$ and $J_{\text{eff}}=3/2$ bands. But it is reasonable to distinguish $J_{\text{eff}}=1/2$ and $J_{\text{eff}}=3/2$ bands according to the energy bands arrangement. The energy scenario of the assignments of $J_{\text{eff}}$ state has been widely applied to classify the $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$ bands in the hexagonal iridates Ca$_2$IrO$_6$ [40], pentavalent iridium pyrochlore Cd$_2$Ir$_2$O$_7$ [41], Ruddlesden-Popper series iridates [5], and Rh and Ir Fluorides Rb$_2$IrF$_6$ and Rb$_2$RhF$_6$ [42]. In our previous study on Sr$_2$IrO$_6$ with Ir$^{4+}(5d^4)$ ions and Sr$_3$NaIrO$_6$ and Sr$_3$LiIrO$_6$ with Ir$^{5+}(5d^6)$ ions, we have also demonstrated the robustness of the classification of $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$ bands according to the band structure arrangement.[7]

**Figure 4** Hypothetical three mixed occupancy configurations of alkali ions according to statistical distribution in the interlayer space of iridate K$_{0.75}$Na$_{0.25}$IrO$_2$. The solid line denotes one $2\times2\times1$ supercell, and there are three K ions and one Na ion in one supercell, corresponding to formal compositions of K$_{0.75}$Na$_{0.25}$IrO$_2$. 1/4 (2/4) A positions (big balls) are occupied by Na (K) ions, whereas only 1/4 B positions (small balls) are occupied by K ions, resulting in 25%/75% vacancies on positions A/B (denoted as V(A) and V(B)).

In order to learn more information about the intrinsic nature of the electronic structure and clarify the abnormal low activation energy in K$_{0.75}$Na$_{0.25}$IrO$_2$, we build $2\times2\times1$ supercells and consider three different occupancy configurations of the alkali ions (as shown in Figure 4) to inspect the electronic structures of K$_{0.75}$Na$_{0.25}$IrO$_2$. Though the energy of the second case (Figure 4 (b)) is significantly lower than other two cases, the projected band structures show similar
characteristics for these three cases. As shown in Figure 5 (also refer to Figures S5-S6 in Supplemental Material [37]), strong hybridizations between Ir 5d and O 2p states give rise to the bonding bands of Ir 5d states ranging from -8 to -5 eV.[14,15,43-45] The O 2p states mainly locate at lower energy region above these bonding states, whereas the Ir 5d antibonding states dominantly contribute to the states around $E_F$. One notable feature is the almost flat band without dispersion for the Ir 5d valence bands along the high symmetry path of $\Gamma$-A direction (along the stacking direction of [IrO$_2$]$^-$ layers in real space), reflecting weakly interlayer interactions in these layered structure iridates.[46] Another noteworthy feature is the presence of in-gap states located at the bottom of the conduction bands, which confirms the experimental speculation and are consistent with the abnormal low activation energy.[25] Furthermore, the conduction band minimum (CBM) always located at the high symmetry point $\Gamma$, and the states around the high symmetry points $\Gamma$ and A primarily come from the interlayer alkali ions, rather than the Ir 5d states (see more detailed projected band structures of Figures S5-S6 in Supplemental Material [37]). Especially, these states have NFE characteristics with parabolic energy dispersions.[47] By fitting the energy band in the vicinity of the $\Gamma$ point, the effective masses $m^*$ along the $\Gamma$-A, $\Gamma$-K, and $\Gamma$-M directions are estimated to be 0.586, 0.493 and 0.557 $m_0$ ($m_0$ is the free-electron mass) for K$_{0.75}$Na$_{0.25}$IrO$_2$ calculated by optPBE-vdW + U without SOC. Including SOC interactions, the corresponding effective masses $m^*$ are 0.639, 0.513 and 0.603 $m_0$, respectively. The deviations of effective masses $m^*$ from free-electron mass $m_0$ widely exist in other NFE systems. For example, the $m^*$ of two NFE states in the bulk gap of silicon are 0.404 and 0.314 $m_0$,[48] and the $m^*$ of NFE states in carbon and boron nitride nanotubes are 1.2 $m_0$.[49] Effective masses $m^*$ for the lowest NFE band is 2.164, 1.029, 0.957, and 1.027 $m_0$ for monolayer Ca$_2$N, graphene, BN, and graphane, respectively.[50] By deposition of metallic indium on In$_2$O$_3$ (111) single crystals, ref. [51] detected the formation of a free-electron-like band with effective mass of 0.38 $m_0$. 
Figure 5 Projected band structures of K\textsubscript{0.75}Na\textsubscript{0.25}IrO\textsubscript{2} (corresponding to the case of Figure 4(b)) calculated within optPBE-vdW + U: (a) without SOC, (b) including SOC, which are projected onto K 4s, Na 3s, O 2p and Ir 5d states, denoted by cyan diamond, black circle, red hollow balls and blue solid balls. The size of the symbols is proportional to the contribution from the corresponding elements.

As shown in Figure 6, we can gain further insight into the nature of the NFE states by looking at the composition of the charge densities at Γ point for the CBM. The charge densities are delocalized, where the charge densities are not localized around alkali ions, but are distributed within whole interstitial region between two [Ir\textsubscript{2}O\textsubscript{4}]\textsuperscript{2-} layers. The NFE states have been proposed as ideal electron transport channels without nuclear scattering.[50] They are originally proposed to exist in graphite and alkali graphite intercalation compounds, display free-electron character parallel to the graphitic layers.[52] NFE states have been widely discovered in other carbon-based materials (such as graphene, nanotubes, and fullerenes [49,49,53,55]) as well as two-dimensional transition metal carbides and nitrides (MXenes,[47] hexagonal boron nitride,[46] and Ca\textsubscript{2}N monolayer [50]). The NFE states are usually unoccupied and located at high energy region, and unsuitable to be used as transport channel.[47] Fortunately, the NFE states in the title iridates are located at the CBM, which renders them more accessible for electron transport or other applications than other known two-dimensional systems.[47,50]
**Figure 6** Charge density maps (isosurface value is 0.008 e/Å³) of the CBM state at the Γ point for the K_{0.75}Na_{0.25}IrO₂ (corresponding to the case of Figure 4 (b)) calculated within optPBE-vdW + U.

**IV. CONCLUSIONS**

In summary, we have studied the electronic structure of the layered iridates K_{0.75}Na_{0.25}IrO₂ based on first-principles DFT calculations. The preferred-occupied positions of the alkali ions are theoretically reproduced from an energetic viewpoint. The crystal-field splitting is sufficient to rationalize the insulating nature, and the layered iridates K_{0.75}Na_{0.25}IrO₂ can be classified as band insulator. The SOC interactions play critical role in the band structure, resulting in NM $J_{\text{eff}} = 0$ states without magnetic moments for the trivalent Ir^{3+} (5d^6) ions. Intriguingly, the electronic structure calculations confirms the experimental speculation of the presence of in-gap states located below the conduction bands, which are responsible for the experimentally observed abnormal low activation energy in K_{0.75}Na_{0.25}IrO. In addition, the in-gap states with parabolic energy dispersions exhibit NFE characteristics, which primarily come from the interlayer alkali ions, rather than the Ir 5d states. The charge densities for these NFE states are delocalized distributed within the whole interstitial region between two [Ir₂O]⁻ layers. Present theoretical results provide new insights into the unique electronic structures of the layered structure iridates and imply promising applications in ideal electron transport channels, and will stimulate experimental works to further understand the unprecedented electronic structures and exploit potential applications in future nanoscience and engineering.

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