Surface States of Perovskite Iridates AIrO$_3$; Signatures of Topological Crystalline Metal with Nontrivial $\mathbb{Z}_2$ Index

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Motivated by a recent proposal of topological crystalline metal in perovskite iridates,[1] we perform first-principles calculations for epitaxially stabilized orthorhombic perovskite iridates with $Pbnm$ symmetry. In the presence of spin-orbit coupling, a ring-shape nodal Fermi surface composed of a set of Dirac points exists, hinting intriguing surface states. Two types of distinct topological surface states are found depending on the surface direction. On the side surfaces, flat surface states protected by the mirror symmetry emerge manifesting the topological crystalline character. On the top surface where mirror symmetry is broken, a Dirac cone appears indicating a non-trivial topology of the nodal metal. Indeed, there is a well-defined two dimensional topological $\mathbb{Z}_2$ index associated with time reversal symmetry leading to the Dirac surface state. Transitions to weak and strong topological insulators and implications of different surface states in light of angle resolved photoemission spectroscopy are also discussed.

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Introduction - Recently, a wide range of novel phases including topological Mott insulators, axion insulators, and Kitaev spin liquids was investigated in correlated electronic systems with strong spin-orbit coupling (SOC)[2]. Among various candidate materials, iridium oxides have provided an excellent playground to study such combined effects [3–19]. In particular, it was suggested that orthorhombic perovskite iridates AIrO$_3$ where A is alkaline earth metal fall into a new class of metal dubbed topological crystalline metal (TCM)[1]. TCM is distinguished by flat surface states protected by the crystal symmetry.

It is interesting to note that the bulk electronic band structure of orthorhombic perovskite SrIrO$_3$ was investigated earlier, and a ring-shape nodal Fermi surface (FS) due to SOC was identified[15, 16]. This ring FS is protected by the crystal symmetry, and has linear dispersion in both radial and longitudinal directions perpendicular to azimuthal direction along the ring. Each point on the ring is composed of two dimensional (2D) Dirac cone. It was further shown that breaking the mirror symmetry along c-axis leads to a three dimensional (3D) Dirac semimetal or a strong topological insulator depending on the strength of broken symmetry[16].

These previous studies imply that surface states may differ depending on surface direction of AIrO$_3$, since top (or bottom) surface naturally breaks the mirror symmetry. Furthermore, the TCM proposal was made based on a tight binding model assuming that only single band made of $j_{\text{eff}}=1/2$ orbitals is relevant near the Fermi level in AIrO$_3$.

To understand topological nature of these iridates and to check the validity of single band model, we perform first-principles calculations for AIrO$_3$ epitaxially stabilized on different substrates. In the bulk, we find that electronic interaction supports the $j_{\text{eff}}=1/2$ band model by enhancing the strength of SOC. On the surfaces, we observe flat surface states (flat in one-direction, and dispersing linear along the other direction) on (110) and (110) side surfaces. These are protected by the mirror symmetry, signalling the TCM character. On the other hand, on the top surface of (001) direction, where the mirror symmetry is broken, a Dirac surface state appears indicating a non-trivial nodal metallic state. Indeed, we find that this nodal metal is characterized by a topological $\mathbb{Z}_2$ index defined on a 2D side-plane in 3D Brillouin zone, and thus reinforces the Dirac surface state protected by time reversal symmetry (TRS).

SOC in iridates and effects of electronic interaction on bulk electronic band structures - In transition metal oxides with strong SOC, $t_{2g}$ states separate from $e_g$ states due to the crystal field split into $j_{\text{eff}}=1/2$ and $3/2$ states. As a result, the multiorbital $t_{2g}$ bands can be mapped to a single $j_{\text{eff}} = 1/2$ band for $d^5$ valence configuration. Due to narrowing of bandwidth, the effects of electronic interaction are amplified leading to magnetic insulators, as shown in layered iridates Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$[3, 4, 9]. However, SrIrO$_3$ shows a qualitative difference compared to those of its quasi-2D cousins. It exhibits a well-defined and protected line node with linear dispersion called a nodal ring featuring a semimetal bulk state, and the size of this ring depends on oxygen octahedra distortions[15, 16].

We study two AIrO$_3$ on two different substrates; orthorhombic perovskite phase of CaIrO$_3$ and SrIrO$_3$ stabilized on GdScO$_3$ (a=3.967Å) and SrTiO$_3$ (a=3.905Å) substrates with $Pbnm$ space group symmetry (No. 62). For each system, c-axis lattice constant and internal atomic coordinates are determined from the structural optimization. Since all of the systems share qualitatively same features, hereafter we show the results of CaIrO$_3$ on GdScO$_3$ substrate as a representative example, which
The effective Coulomb interaction parameter \( U_{\text{eff}} \equiv U - J \) (where \( J \) is Hund’s coupling) is increased up to 2 eV, and the paramagnetic semimetallic phase with the nodal line remains unchanged. One can see a cut of the nodal ring close to U-point where the location of the ring is shown as cyan circles in Fig. 1(a). Dark red and blue colors refer to \( j_{\text{eff}} = 1/2 \) and \( 3/2 \), respectively, and the size of circles represents their weight.

In the top four bands \( j_{\text{eff}} = 1/2 \) character is dominant, but there are non-negligible amount of \( j_{\text{eff}} = 3/2 \) states mixed into the bands over the BZ, which is also shown in the projected density of states (PDOS). However, it is important to note that the bands near U-point where the nodal ring exists is mainly composed of \( j_{\text{eff}} = 1/2 \), validating the effective single band model for the nodal FS used in Ref. 1. By comparing Fig. 1(b) and (c), the \( j_{\text{eff}} = 1/2 \) states are pushed up and enhanced near the Fermi level, and on the contrary, the \( j_{\text{eff}} = 3/2 \) states are pushed down in the presence of \( U_{\text{eff}} \), even though the nodal ring composition is minimally affected. Comparing the PDOS with nonzero \( U_{\text{eff}} \) to that with artificially increased SOC, inclusion of \( U_{\text{eff}} = 2 \) eV corresponds to approximately 30% enhancement of SOC. Such behavior can be understood as the enhancement of orbital polarization in terms of \( j_{\text{eff}} \) basis. In other words, fully occupied \( j_{\text{eff}} = 3/2 \) states are energetically favored in the presence of both \( U_{\text{eff}} \) and sizable SOC [23, 24]. Unless the Hund’s coupling becomes a dominant factor, such effect should persist in more general treatment of Coulomb interaction. For cross-checking purpose we performed another LDA+U calculations using Lichtenstein’s generalized LDA+U formalism as implemented in VASP code [25], which gives consistent results for \( U \leq 2.0 \) eV and \( J \leq 0.5 \) eV. It should be noted that, such behavior is also observed in recent dynamical mean-field theory calculations [7, 26], indicating that the enhancement of SOC by electronic interaction is a general feature of correlated electronic systems with SOC.

We consider three surface directions; (110), (110), and (001) surfaces in terms of the local coordinates, which are perpendicular to \( a_1 \), \( a_2 \), and \( a_3 \) as shown in Fig. 1(a), respectively. Among them, (110) and (110) contain the mirror symmetry, while (001) surface does not. Results on other sides such as (100) and (010) orientations are discussed in Supplementary material. Maximally-localized Wannier orbitals are used to construct the slab Hamiltonians from the bulk electronic structure, each of them having thickness of 30 unit cells along the surface normal directions [27, 29].

**Surface states when the mirror symmetry is preserved**

Fig. 2 shows the \( j_{\text{eff}} \)-projected electronic structures of CaIrO$_3$ on GdScO$_3$ substrate in the presence of SOC, where the bulk and surface Brillouin zones (BZ) are depicted in Fig. 1(a), and Fig. 1(b) and (c) show the band structure without and with on-site Coulomb interaction, respectively. The effective Coulomb interaction

![Fig. 1](image-url)

**FIG. 1.** (Color online) (a) Special \( k \)-points in the bulk and on the surfaces. Note that \( b_i \parallel a_i \) (\( i = 1, 2, 3 \)), where \( a_i \) are the Bravais lattice vectors. \( x, y, \) and \( z = x \times y \) are the local coordinates of IrO$_6$ octahedra in the absence of octahedral rotation. Bulk nodal lines are depicted as cyan circles near U points (size is exaggerated). Bulk \( j_{\text{eff}} \)-projected band structure and density of states of CaIrO$_3$ on GdScO$_3$ substrate with (b) \( U_{\text{eff}} = 0 \) and (c) 2 eV. The weight of \( j_{\text{eff}} = 1/2 \) and 3/2 states are denoted as the thickness of dark blue lines and size of red circular symbols, respectively.
FIG. 2. (Color online) Band structure of a slab geometry parallel to (110) surface (30 unit cell thickness) with (a) $U_{\text{eff}} = 0$ and (b) 2 eV. The thickness of red lines overlaid with the bands represents surface weight.

in the figures. The presence of these flat surface states is a manifestation of bulk TCM phase. Our result suggests that the single band $j_{\text{eff}} = 1/2$ tight binding model used in Ref. 1 is valid even though the bands near Fermi level involve $j_{\text{eff}} = 3/2$ states. This is because the mixing of $j_{\text{eff}} = 3/2$ states does not alter the topology of this nodal metal.

However, ideally the surface states perpendicular to $b_2$ for a fixed $k_z = \pi c$ should be completely flat along the $b_1$-direction, because of the presence of bulk chiral symmetry [1]: note that there are four sublattices in perovskite iridates leading to a sublattice chiral symmetry. Slight dispersion of this surface state is due to the presence of a small chiral symmetry breaking term such as a finite hopping integral between the same sublattice in the $a - b$ plane. The mixing of the $j_{\text{eff}} = 3/2$ states into the $j_{\text{eff}} = 1/2$ bands further breaks the chiral symmetry, but its effect is minor compared to the same sublattice hopping integral effects. Introducing electronic interaction pushes down the bulk $j_{\text{eff}} = 3/2$ states, and thus reveals the surface states more visible. The linear dispersing surface state along $\Gamma - Z - \Gamma'$ exists, but its weight is too small as it mixes with the bulk states.

Fig. 3 shows the band structure of (110) slab, depicted as the green side in Fig. 1(a). The band structure with $U_{\text{eff}} = 0$ and 2 eV are shown in Fig. 3(a) and (b), respectively. The separation of the bulk and surface bands owing to electronic interaction is also found. Unlike the (110) surface, bulk spectrum is gapped at $\bar{Z}$ point due to the absence of nodal ring projected onto (110) plane. Thus the linear dispersing surface state along $\Gamma - \bar{Z} - \Gamma'$ is observable and denoted by a light green color.

Note that, the chiral symmetry is also lifted, as the surface states split into two from $\bar{U}$ to $\bar{Z}$, but the degeneracy is recovered at $\bar{Z}$ due to the presence of the $n$-glide symmetry $\Pi_n$ on the (110) surface in addition to TRS. The one-dimensional (1D) Hamiltonian, parametrized by the surface momentum $k_{b_2}$, is applicable to represent the system with open (110) surface at $k_z = \frac{\pi}{c}$. The $n$-glide operation only reverses the sign of $k_{b_2}$ when acting on the 1D Hamiltonian, which suggested that $\Pi_n$ can be treated effectively as a spatial inversion operator. Accordingly, the degeneracy at $\bar{Z}$, which is a $n$-glide-symmetry-invariant momentum, is protected by the $n$-glide symmetry and TRS.

Surface states of top surface without the mirror symmetry - Now let us examine the (001) surface. Due to the loss of mirror symmetry, the theory of TCM does not apply here, and one does not expect any protected surface states on the (001) plane[1]. However, as shown in Fig. 4, a Dirac cone at $\bar{Y}$ point emerges, which carries rather weak but still finite surface weight. This surface state is an indication of a non-trivial bulk topological $Z_2$ invariant. While the 3D iridate is a semi-metal with the nodal ring FS, the 2D bands in $k_{b_1} = \frac{\pi}{a}$ plane have a gap across the Fermi level, and thus there exists a well-defined 2D topological $Z_2$ index, $\nu_{2D}$. This $\nu_{2D}$ can be obtained by multiplying the parity eigenvalues at each TRIM point in $k_{b_1} = \frac{\pi}{a}$ plane shown in the inset of Fig. 4(c). We find that $\nu_{2D} = 1$ which implies the presence of the 2D surface Dirac cone at $\bar{Y}$ point. [30, 31]. On the other hand, due to the existence of the gapless Dirac bulk points in $k_{b_1} = 0$ plane, we do not expect protected surface states at $\bar{X}$ point, which is indeed shown in Fig 4.

This nontrivial topology of nodal metal leads to other topological insulators via phase transition by lowering
resolved photoemission spectroscopy measurement will of perovskite iridates on various substrates [32–36]. Angle ing, there have been several reports on successful growth thin film or superlattices of CaIrO
the surface direction. While utilizing epitaxial growth of topological surface states can be realized depending on
Moreover, these iridates are unusual as different types of show that perovskite iridates possess such phenomena.
small FS pockets, lines, or points can exhibit topological excitations, it is not meaningful to investigate topologi-
smears surface states by mixing them with bulk gapless topological metallic states. Since a metal with large FS insulators including Z
-While various topological insulators can be realized by adding a small perturbation that does not invert the bands but breaks the mirror and inplane sublattice symmetries. This WTI has the weak Z
indices, (ν1, ν2, ν3) = (110) and exhibits two surface Dirac cones at both X and Y points (see Supplementary material). When the mirror symmetry breaking is large enough to invert the parity at R-point, the system becomes a strong topological insulator as reported in Ref. [15].
Remarkably, this iridate can hold both the crystal symmetry protected flat surface states (thus named topological crystalline metal), and TRS protected Dirac surface state indicated by a 2D topological Z2 index.
Discussion and Summary - While various topological insulators including Z2 and crystalline insulators are intensively studied, less efforts have been made to explore topological metallic states. Since a metal with large FS smears surface states by mixing them with bulk gapless excitations, it is not meaningful to investigate topological surface states. However, a non-trivial semimetal with small FS pockets, lines, or points can exhibit topological surface states separated from its bulk spectrum. Here we show that perovskite iridates possess such phenomena. Moreover, these iridates are unusual as different types of topological surface states can be realized depending on the surface direction. While utilizing epitaxial growth of thin film or superlattices of CaIrO3 or SrIrO3 is challenging, there have been several reports on successful growth of perovskite iridates on various substrates [32, 33]. Angle resolved photoemission spectroscopy measurement will reveal a novel metallic state, as the dispersion of these surface states differ depending on momentum direction in the BZ.
Another interesting result is the enhancement of SOC by electronic interaction. The states near the Fermi level contain non-negligible mixing of j_eff=3/2 states. However, when electronic interaction is taken into account, the effective SOC strength is enhanced supporting the j_eff=1/2 low-energy theory. While we have treated electronic interaction within a Hartree-Fock approximation, previous dynamical mean-field theory studies also show the enlarged SOC strength in addition to significant bandwidth reduction [26]. Such scenario may be realized in 4d-orbital systems such as α-RuCl3, spin-orbit-assisted Mott insulators [37].
In summary, we propose that the orthorhombic perovskite iridate is a topological semimetal characterized by both time reversal and crystal symmetry. Thus it hosts two distinct types of topologically nontrivial surface states; the flat surface states protected by the crystal symmetry, and the Dirac surface state protected by TRS associated with the 2D topological Z2 index. The electronic interaction cooperates with SOC, making such surface states more evident. Considering the recent successes in growing high-quality samples, these perovskite iridates could be an excellent platform in searching for uncovered topological metallic phases.

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