Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

The novel electronic and magnetic properties in 5*d* transition metal oxides system

Yongping Du, Xiangang Wan*

National Laboratory of Solid State Microstructures, School of Physics, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history: Received 19 May 2015 Received in revised form 5 September 2015 Accepted 15 September 2015 Available online 16 November 2015

Keywords: 5d transition metal oxides Spin-orbit coupling Electron correlation Weyl semimetal Fermi arc Axion insulator Slater insulator Metallic ferroelectricity

1. Introduction

It has been suggested that Coulomb interaction is of substantial importance in 3*d* and 4*d* electron systems [1], and these systems exhibit peculiar properties, such as metal-insulator transition [2], ferroelectric [3], colossal magnetoresistance [4] and high critical temperature superconductivity [5]. On the other hand, comparing with 3*d* and 4*d* state, the 5*d* orbitals are spatially more extended, consequently usually possess a broader bandwidth, thus it is natural to expect that correlation effects are minimal in 5*d* compounds and may be ignored. However, recently, both theory and experiment give the evidences of the importance of Coulomb interaction for 5*d* materials [6–9]. On the other hand, the spin–orbit coupling (SOC) in the 5*d* transition metal elements is expected to be strong due to the large atomic number [10]. Thus various anomalous electronic properties have been also observed/proposed in the 5d TMO such as $J_{eff} = 1/2$ Mott state [6–8], giant magnetoelectric effect [12], high *T_c* superconductivity [13,14], topological insulator [15,45–47], correlated metal [16], novel magnetic properties [20–22], Kitaev mode [17], Quantum spin liquid [18,19], etc.

In this review, we briefly summarize our theoretical works about the 5d TMO. In Section 2, we systematically discuss

ABSTRACT

In 5*d* transition metal oxides, novel properties arise from the interplay of electron correlations and spin–orbit interactions. In this paper, we briefly review our theoretical progress relating to 5*d* compounds. We focus on describing the topological Weyl-Semimetal in pyrochlore iridates, the Axion insulator in spinel osmates, the Slater insulator in perovskite osmates. We also discuss the anisotropic unscreened Coulomb interaction in ferroelectric metal LiOsO₃.

© 2015 Elsevier B.V. All rights reserved.

pyrochlore iridates [23]. We find that magnetic moments at Ir sites form a non-colinear pattern with moment on a tetrahedron pointing all-in or all-out from the center. We propose pyrochlore iridates are Weyl Semimetal (WSM), thus provides a condensedmatter realization of Weyl fermions that obey a two-component Dirac equation. We find Weyl points are robust against perturbation and further reveal that WSM exhibits remarkable topological properties manifested by surface states in the form of Fermi arcs, which are impossible to realize in purely two-dimensional band structures. In Section 3, we propose that spinel osmates show a large magnetoelectric coupling characteristic of axion electrodynamics [24]. In Section 4, we give a comprehensive discussion about the electronic and magnetic properties of Slater insulator NaOsO₃, and successfully predict the magnetic ground state configuration of this compounds [25]. We also discuss the novel properties of LiOsO₃, and suggest that the highly anisotropic screening and the local dipole-dipole interactions are the two most important keys to form LiOsO₃-type metallic ferroelectricity [26] in Section 5.

2. Weyl semimetal in pyrochlore iridates

 $A_2Ir_2O_7$ [27–32] (A = Y or rare-earth element), which crystallize in pyrochlore structure [33], is a geometrically frustrated iridate system. Experiment observe that depend on the A-site, $A_2Ir_2O_7$







shows a wide range of electrical properties [27-32]. For example, $Y_2Ir_2O_7$ shows insulating behavior [27]. With increasing the A-site ionic radii, the band gap will vary slightly, and eventually the system becomes metal for Nd₂Ir₂O₇ [28], and Pr₂Ir₂O₇ shows strong Kondo abnormal [32]. Moreover, it had been found that temperature will drive a insulator to metal transition for these systems, and this transition is associated with the magnetic abnormal meanwhile no structural changing has been found [28]. To clarify the effect of A-site, based on the full-potential, all-electron, linear-muffin-tin-orbital (FP-LMTO) method [34], we perform a constrained calculation with the 4*f* band shifted by a constrained potential [35]. Our calculations show that the rare earth element has only a small effect on the bands around the Fermi level. Therefore, we focus on $Y_2Ir_2O_7$ to discuss the properties of pyrochlore iridates.

2.1. All-in/all-out magnetic configuration

In Y₂Ir₂O₇, each of four Ir atoms is octahedrally coordinated by six O atoms, which makes the Ir 5d states split into doubly degenerate e_g and triply degenerate t_{2g} states. Due to the extended nature of Ir 5d orbital, the crystal-field splitting between t_{2g} and e_{g} is large, and our local-density functional (LDA) calculation shows that the e_g band to be 2 eV higher than the Fermi level. The bands near the Fermi level are mainly contributed by Ir t_{2g} and SOC has a considerable effect on these t_{2g} states: it lifts their degeneracy and produces 24 separate bands in the range from -2.3 to 0.7 eV. Same as in Sr_2IrO_4 [6,7], the bandwidth of these t_{2g} states in our LSDA + U + SO calculation (U = 2.0 eV) for ferromagnetic (FM) setup of $Y_2Ir_2O_7$ is also narrow. However, $Y_2Ir_2O_7$ is still metallic. Naively one may expect that using larger Coulomb U will result in an insulating state. However, our additional calculations show that increasing U cannot solve this problem, and even a quite large U (=5 eV) cannot open a band gap for the initial collinear (001) magnetic configuration setup.

With the pyrochlore structure, the Ir sublattice has a topology consisting of corner-sharing tetrahedra and is geometrically frustrated. To search the possible magnetic order and explore its effect on the electronic properties, we subsequently perform calculations with the initial magnetization aligning along (110), (120), (111) directions. We also perform the calculations with two sites in the Ir tetrahedron along and other two pointed oppositely to (001), (111), (110) or (120) direction in order to account for possible antiferromagnetism. It turns out that all of the above mentioned calculations give metallic states with large Fermi surface, which is not consistent with the experimental insulating behavior [29–31]. Also, all of them produce a considerable net magnetic moment in contrast to the experiment [29–31]. Carefully check these calculations, we notice that for all of considered collinear initial setup, the magnetic moments tend to rotate to the direction of pointing to the centers of the tetrahedron during the selfconsistency process. Motivated by that, we thus carry out several non-collinear calculations with the initial state to be "all-in/ all-out" (AIAO) (where all moments point to or away from the centers of the tetrahedron, see Fig. 1 for the moments configuration), "2-in/2-out" (two moments in a tetrahedron point to the center of this tetrahedron, while the other two moments point away from the center, i.e. the spin-ice [36] configuration), and "3-in/1-out" magnetic structures. Different from all of other considered magnetic configurations, during the self-consistency iterations the AIAO state will retain their initial input direction indicating a local energy minimum. While for other magnetic setup, even we obtain a very good total energy convergence, the calculated magnetic moments still slowly rotate. Consistent with the experiment, the band structure of AIAO configuration with U around 2.0 eV looks like insulating as shown in Fig. 2, while all of other configu-



Fig. 1. The pyrochlore crystal structure showing the Ir corner sharing tetrahedral network and the "all-in/all-out" magnetic configuration predicted to occur for iridates (from Ref. [23]).

rations give metal state with large Fermi surface. There is no net magnetic moment for AIAO setup. While in contrast to the experimental fact on the absence of the magnetic hysteresis loop [31], all of other magnetic orders produce a considerable net magnetic moment. Moreover, the Fermi surface from LDA + SO calculation does not show strong nesting feature, one can expect that the non-commensurate order is unlike although the possibility of complex larger *q* sates cannot be ruled out. Consider these facts, we thus believe AIAO is the ground state configuration of pyrochlore iridates.

Pyrochlore lattice has strong geometric frustration, moreover the 5*d* electron is quite itinerant and the effective magnetic model [37] may not suitable for pyrochlore iridates. Thus our work attracts attention [38–44], and AIAO magnetic configuration now had been confirmed by several experimental works [38–41]. AIAO has also been found as the magnetic configuration of Slater insulator Cd₂Os₂O₇ at 2012 [44].

Based on both strong sensitivity of the energy bands near the Fermi level on the orientation of moments, and proximity of various magnetic states in energy as shown in Table 1, it is natural to expect that an application of a magnetic field could have a big effect not only on the magnetic response but also on the conductivity in iridates. In particular, this should result in a large magnetoresistance effect if one is able to switch between insulating AIAO state and any collinear state. This simple idea has been proved by the numerical calculation. Starting from the AIAO ground state, we apply an external field along (001) direction. The result shows that the external field will rotate the magnetic moments meanwhile only slightly change their magnitude. A 5 T magnetic field along (001) induces a 0.07 μ_{B} net magnetic moment, which is in fact close to the experiment performed for Sm₂Ir₂O₇, where it was shown that a 4T magnetic field produces a 0.05 μ_{B} total moment [31]. Increasing the field further, the numerical calculation does find energy bands crossing the Fermi level, namely an insulator-to-metal transition at a field of 40 T, although there is already non-negligible density of states at *E*_f for a lower magnetic field. Notice the proximity of the ground and excited (or said metastable) states in energy, one can also understand that for the same compound Y₂Ir₂O₇, Taira et al. [31] observe no ferromagnetic ordering while Yanagishima et al. [29,30] claim a presence of a small net magnetic moment. One can also understand the observed temperature induced metal-insulator transition, as well as a large difference in temperature dependence of magnetization



Fig. 2. Evolution of electronic band structure of $Y_2Ir_2O_7$ shown along high symmetry directions, calculated using LSDA + *U* + SO method with three different values of *U* equal (a) 0 (metallic), (b) 1.5 eV, and (c) 2 eV (insulator with small gap). The magnetic configuration is AIAO. The Weyl point that is present in case (b), is not visible along high symmetry lines (from Ref. [23]).

Table 1

The spin $\langle S \rangle$ and orbital $\langle O \rangle$ moment (in μ_B) and the total energy E_{tot} per unit cell (in meV) for several selected magnetic configurations of Y₂Ir₂O₇ as calculated using LSDA + *U* + SO method with *U* = 1.5 eV. (E_{tot} is defined relative to the ground state.) The IDM (indirect Dzyaloshinsky–Moriya) is a coplanar configuration predicted for one sign of D–M interactions in Ref. [37] (from Ref. [23]).

Configuration:	(001)	(111)	2-in/2-out	IDM	All-in/out
$\left. \begin{array}{l} \left< S \right> \\ \left< O \right> \\ E_{tot} \text{ (meV)} \end{array} \right.$	0.08	0.10	0.09	0.06	0.13
	0.09	0.10	0.07	0.06	0.12
	5.47	1.30	3.02	2.90	0.00

measured under zero-field-cooled conditions (ZFC) and under field-cooled conditions (FC).

2.2. Weyl semimetal

We now discuss electronic properties of $Y_2Ir_2O_7$. A variety of phases ranging from normal metal at small *U* to Weyl semimetal at intermediate $U \sim 1.5$ eV and Mott insulating phase at *U* above 2 eV with non-collinear magnetic AIAO ordering are predicted based on the band structure calculation and effective model. Importance of electronic correlations for 5*d* orbitals has been recently emphasized [6–8] and estimates for the values of *U* have been recently obtained between 1.4 and 2.4 eV in layered Sr₂IrO₄/Ba₂IrO₄ [9]. Moreover, pressure or chemical substitution may alter the screening and the electronic bandwidth resulting in changes in *U*, we thus expect that these phases can be observed experimentally in iridates.

As mention above, the bands near the Fermi level are mainly contributed by Ir t_{2g} with some mixing with O 2*p* states. SOC has a considerable effect on these t_{2g} states: it lifts their degeneracy and produces quadruplet with $J_{eff} = 3/2$ and doublet with $J_{eff} = 1/2$ with the latter lying higher in energy [6]. Alternatively, one can view the *d*-shell in strong SOC limit which splits the 10-fold degenerate state onto lower lying J = 3/2 and higher lying J = 5/2 multiplets. A subsequent application of the cubic crystal field would leave the J = 3/2 multiplet degenerate but would split the 6-fold degenerate J = 5/2 state onto Γ_7 doublet and Γ_8 quadruplets. Since Ir occurs in its 4+ valence, its 5 electrons would fill completely J = 3/2 subshell and put an additional one electron into the Γ_7 dou-

blet thought as the state with $J_{eff} = 1/2$ in some previous work [6]. For the solid, we thus expect 8 narrow energy bands at half-filling to appear in the vicinity of the chemical potential that correspond to the Γ doublets of four Ir atoms.

Based on a tight-binding model, the non-magnetic phase of the pyrochlore iridates had been proposed as a topological insulator [45,46]. Our study of the nonmagnetic state by using LDA + SO scheme contradict this; instead we find a metallic phase. One can understand the discrepancy by analyzing the structure of energy levels at the Γ point (Brillouin Zone center) for the low energy 8-band complex, composed of the four $J_{eff} = 1/2$ states. In Ref. [45], these appear with degeneracies 4, 2, 2 (in order of increasing energy) which after filling with 4 electrons results in an insulating band structure. Our study of the non-magnetic state using LDA + SO method results, on the other hand, in the sequence 2, 4, 2 of degeneracies, which is necessarily metallic assuming 4 levels are filled. Thus, one needs either magnetic order, or a structural transition [47], to recover an insulating phase. Based on AIAO magnetic configuration, we thus perform LSDA + SO (with no U) calculation and as shown in Fig. 2(a) magnetic order alone cannot give insulating behavior. Considering the effect of Coulomb repulsion, LSDA + U + SO calculation indeed show that the band structure along high-symmetry lines appears to be insulating (see Fig. 2(b) and (c)). LDA + U method use a Hartree Fock approximation for Coulomb repulsion of correlated electron, and the calculated band gap usually increase with increasing the parameter U [48]. However, a very interesting feature appears in the band structure of Y₂Ir₂O₇, as shown Fig. 2 the band gap seems decrease with increasing U from 1.5 to 2.0 eV.

Since AIAO magnetic order preserves inversion symmetry, we thus calculate the band parity to study the evolution of the band structure and explore the possible novel properties related with the abnormal band behavior. At special momenta, called TRIMs (Time Reversal Invariant Momenta), that are invariant under inversion, we can label states by parity eigenvalues $\xi = \pm 1$. In the Brillouin zone (BZ) of the FCC lattice, TRIMs correspond to the $\Gamma = (0, 0, 0)$, and $X, Y, Z [= 2\pi/a(1, 0, 0)$ and permutations] points and four L points [$\pi/a(1, 1, 1)$ and equivalent points]. The parities of the top four occupied bands at TRIMs, in order of increasing energy, are shown in Table 2. Note, although by symmetry all L points are equivalent, the choice of inversion center at an

Table 2

Calculated parities of states at Time Reversal Invariant Momenta (TRIMs) for several electronic phases of the iridates. Only the top four filled levels are shown in order of increasing energy (from Ref. [23]).

Phase	Г	X, Y, Z	L'	$L(\times 3)$
<i>U</i> = 2.0, AIAO (Mott)	+ + + +	+ +	+	_ + + +
<i>U</i> = 1.5, AIAO (Weyl)	+ + + +	++	++	_ + + _

Iridium site singles out one of them, L'. With that choice the parities at L' and the other three L points are the opposite of one another. The parities of the AIAO state remains unchanged above $U > U_c \sim 1.8$ eV, and is shown in the top row under U = 2 eV. It is readily seen that these parities are the same as for a sitelocalized picture of this phase, where each site has an electron with a fixed moment along the ordering direction. Due to the possibility of such a local description of this magnetic insulator, we term it the Mott phase. For the same AIAO magnetic configuration, at smaller U = 1.5 eV, the parities reveals that a phase transition has occurred. At the L points, an occupied level and an unoccupied level with opposite parities have switched places. It can readily be argued that only one of the two phases adjacent to the U where this crossing happens can be insulating (see the Appendix of Ref. [23]). Since the large U phase is found to be smoothly connected to a gapped Mott phase, it is reasonable to assume the smaller U phase is the non-insulating one. A detailed analysis perturbing about this transition point (see the Appendix of Ref. [23]) allows us to show that there are 24 points where the conduction and valence band touch.

Without time reversal symmetry, the bands forming the crossing point are non-degenerate, thus the excitations near each touching point \mathbf{k}_0 can be described by an effective Hamiltonian:

$$H_W = \sum_{i=1}^{3} \mathbf{v}_i \cdot \mathbf{q} \sigma_i, \tag{1}$$

Energy is measured from the chemical potential, $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$ and σ_i are the three Pauli matrices. The velocity vectors \mathbf{v}_i are generically non-vanishing and linearly independent. Thus around the node,

system has a cone-like energy dispersion $\Delta E = \pm \sqrt{\sum_{i=1}^{3} (\mathbf{v}_i \cdot \mathbf{q})^2}$. This equation is closely related to the Weyl equation in particle physics [49]. One thus can assign a *chirality* (or chiral charge) $c = \pm 1$ to the fermions defined as $c = \text{sign}(\mathbf{v}_1 \cdot \mathbf{v}_2 \times \mathbf{v}_3)$, and the crossing points related by inversion have opposite chirality. Note, since the 2 × 2 Pauli matrices appear, our Weyl particles are two component fermions. In contrast to regular four component Dirac fermions, it is not possible to introduce a mass gap. The only way for these nodes to disappear is if they meet with another Weyl point with opposite chiral charge.

The stability of Weyl points can also been understood as following: a general Hamiltonian for two bands system is $H = \begin{pmatrix} A(k) & B(k) + iC(k) \\ B(k) - iC(k) & -A(k) \end{pmatrix}$, and the eigenvalues are $E(k) = \pm \sqrt{A^2(k) + B^2(k) + C^2(k)}$. The emergence of band crossing point

 $\pm \sqrt{A^2(k) + B^2(k) + C^2(k)}$. The emergence of band crossing point requires three equations A(k) = 0, B(k) = 0 and C(k) = 0. A 3D system has three parameters (namely k_x, k_y and k_z). This does not promise a band crossing point, but once such a node is formed, a small perturbation for Hamiltonian will only slightly change the location of the node, since one can always adjust k_x , k_y and k_z to satisfy the three equations [50].

The key point for Weyl nodes is the non-degenerate band, thus to obtain the Weyl points one need break either time reversal symmetry [23] or inversion symmetry [51–53]. The Weyl fermions here are rather different from the Dirac fermions in three dimensional semi-metals. The Weyl points are topological objects and robust against perturbations regardless of symmetry. However,

with inversion symmetry and time reverse symmetry, the Dirac Semimetal requires additional lattice symmetry [54–57].

For pyrochlore iridates, we note that near each *L* point there are three Weyl points related by the three fold rotation, which have the same chiral charge, as well as the inverse images with opposite chirality. Thus, there are 24 Weyl points, where the valence and conduction band line up, in the whole Brillouin zone (BZ). Since all Weyl points are at the same energy by symmetry, the chemical potential must pass through them. Therefore, for the case of intermediate correlations, relevant to $Y_2Ir_2O_7$, the electronic ground state is an unusual *Weyl semi-metal*, with linearly dispersing Weyl nodes *at* the Fermi level. The small density of states at Fermi level makes it an insulator at zero temperature and frequency (as seen experimentally for $Y_2Ir_2O_7$). The a.c. conductivity for a single node with isotropic velocity *v* in the free particle limit of the clean system is $\sigma(\Omega) = \frac{e^2}{12h} \frac{|\Omega|}{v}$.

In the LSDA + U + SO band structure at U = 1.5 eV, we find a 3D band crossing located at the k-vector (0.52, 0.52, 0.3) $2\pi/a$. There also are five additional Weyl points in the proximity of the point L related by symmetry. When U increases, these points move toward each other and annihilate all together at the L point close to U = 1.8 eV. This is how the Mott phase is born from the Weyl phase. Decreasing the value of U to 1 eV, the Weyl points with opposite chirality will meet and annihilate at X point. Unfortunately, within our LSDA + U + SO calculation, a metallic phase intervenes on lowering $U \leq 1.0$ eV, before the Weyl points annihilate to give the axion insulator (We will discuss this novel property at next section). Since we expect that for Ir 5d states the actual value of the Coulomb repulsion should be somewhere within the range 1 eV < U < 2 eV we thus conclude that the ground state of the Y₂Ir₂O₇ is most likely the semi-metallic state with the Fermi surface characterized by a set of Weyl points but in proximity to a Mott insulating state. Both phases can be switched to a normal metal if Ir moments are collinearly ordered by a magnetic field. Thus we expect magnetic-field induced semi-metal/insulator to normal metal transition to occur in pyrochlore iridates which should greatly affect their transport and optical properties.

2.3. Fermi arc surface states

We now discuss surface states that are associated with the presence of the Weyl fermions. The Weyl points behave like 'magnetic' monopoles in momentum space whose charge is given by the chirality; they are actually a source of "Berry flux" rather than magnetic flux [58]. The Berry connection, a vector potential in momentum space, is defined by $\mathcal{A}(\mathbf{k}) = \sum_{n=1}^{N} i \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$ where *N* is the number of occupied bands. As usual, the Berry flux is defined as $\mathcal{F} = \nabla_{\mathbf{k}} \times \mathcal{A}$ [58].

We now prove that the band topology associated with the Weyl point leads to a novel surface states. Consider a curve in the surface Brillouin zone encircling the projection of the bulk Weyl point, which is traversed counterclockwise as we vary the parameter $\lambda : \mathbf{0} \to 2\pi; \mathbf{k}_{\lambda} = (k_x(\lambda), k_y(\lambda))$ (see Fig. 3a). We show that the energy ϵ_{λ} of a surface state at momentum \mathbf{k}_{λ} crosses E = 0. Consider $H(\lambda, k_z) = H(\mathbf{k}_{\lambda}, k_z)$, which can be interpreted as the gapped Hamiltonian of a two dimensional system (with λ and k_z as the two momenta). The two periodic parameters λ , k_z define the surface of a torus in momentum space. The Chern number of this two dimensional band structure is given by the Berry curvature integration: $\frac{1}{2\pi} \int \mathcal{F} dk_z d\lambda$ which, by Stokes theorem, simply corresponds to the net monopole density enclosed within the torus. This is obtained by summing the chiralities of the enclosed Weyl nodes. Consider the case when the net chirality is unity, corresponding to a single enclosed Weyl node. Then, the two dimensional subsystem is a quantum Hall insulator with unit Chern number. When defined

on the half space z < 0, this corresponds to putting the quantum Hall state on a cylinder, and hence we expect a chiral edge state. Its energy ϵ_{λ} spans the band gap of the subsystem, as λ is varied (see Fig. 3b). Hence, this surface state crosses zero energy somewhere on the surface Brillouin zone \mathbf{k}_{λ_0} . Such a state can be obtained for every curve enclosing the Weyl point. Thus, at zero energy, there is a Fermi line in the surface Brillouin zone, that terminates at the Weyl point momenta (see Fig. 3c). An arc beginning on a Weyl point of chirality *c* has to terminate on a Weyl point of the opposite chirality. Clearly, the net chirality of the Weyl points within the (λ, k_z) torus was a key input in determining the number of these states. If Weyl points of opposite chirality line up along the k_z direction, then there is a cancellation and no surface states are expected.

For U = 1.5 eV, a Weyl node is found to occur at the momentum $(0.52, 0.52, 0.31)2\pi/a$ (in the coordinate system aligned with the cubic lattice of the crystal) and equivalent points. They can be thought of as occurring on the edges of a cube, with a pair of Weyl nodes of opposite chirality occupying each edge, as, e.g., the points $(0.52, 0.52, 0.31)2\pi/a$ and $(0.52, 0.52, -0.31)2\pi/a$. For the case of U = 1.5 eV, the sides of this cube have the length $0.52(4\pi/a)$. Thus, the (1 1 1) and (1 1 0) surfaces would have surface states connecting the projected Weyl points (see Fig. 4 for the (1 1 0) surface states). If, on the other hand we consider the surface orthogonal to the (001) direction, the Weyl points of opposite chirality are projected to the same surface momentum, along the edges of the cube. Thus, no protected states are expected for this surface.

To verify these theoretical considerations, we have constructed a tight-binding model which has features seen in our electronic structure calculations for $Y_2Ir_2O_7$. The calculated (110) surface band structure for the slab of 128 atoms together with the sketch of the obtained Fermi arcs is shown in Fig. 4. This figure shows Fermi arcs from both the front and the back face of the slab, so there are twice as many arcs coming out of each Weyl point as predicted for a single surface. We also display the expected surface states for the (111) surface. Note, no special surface states are expected for the (001) surface.

The tight-binding model considers only t_{2g} orbitals of Ir atoms in the global coordinate system. Since Ir atoms form a tetrahedral network (see Fig. 1), each pair of nearest neighboring atoms forms a corresponding σ -like bond whose hopping integral is denoted as t and another two π -like bonds whose hopping integrals are denoted as t'. To simulate the appearance of the Weyl point it is essential to include next-nearest-neighbor interactions between t_{2g} orbitals which are denoted as t''. With the parameters t = 0.2, t' = 0.5t and t'' = -0.2t, the value of the on-site spin–orbit coupling equal to 2.5t and the applied on-site "Zeeman" splitting of 0.1t between states parallel and antiparallel to the local quantization axis of the AIAO configuration we can roughly model the bulk Weyl semimetal state, when this model is solved on a lattice with a boundary, the surface states shown in Fig. 4 appear.

The theoretical phase diagram for pyrochlore iridates is summarized in Fig. 5 as a function of U and applied magnetic field, which leads to a metallic state beyond a critical field.

3. Axion insulator in spinel osmates

The orbital motion of electrons in a three-dimensional solid can generate a pseudoscalar magnetoelectric coupling θ , and this polarizability θ is the same parameter that appears in the "axion electrodynamics" Lagrangian $L_{\theta} = \frac{\theta e^2}{2\pi\hbar} E \cdot B$ [60,59,61,62]. This form implies that an electric field can induce a magnetic polarization, whereas a magnetic field can induce an electric polarization. The linear magnetoelectric polarizability α_{ij} ($\alpha_{ij} = \frac{\partial H_i}{\partial E_i}|_{B=0} = \frac{\partial P_i}{\partial B_i}|_{E=0}$, *E*

and *B* are electric and magnetic fields, *P* and *M* are the polarization and magnetization) can be expressed as $\alpha_{ij} = \alpha_{ij}^0 + \frac{\partial e^2}{2\pi\hbar} \delta_{ij}$. Thus the dimensionless "axion" field θ is a very important parameter for the magnetoelectric effect. Clearly the combination $E \cdot B$ in the expression of L_{θ} is odd under time-reversal T, while the electrodynamics is invariant under $\theta \rightarrow \theta + 2\pi$ [60,61]. Thus all timereversal invariant insulators fall into two distinct classes described by either $\theta = 0$ or $\theta = \pi$. $\theta = \pi$ corresponds to topological insulator and $\theta = 0$ denotes trivial insulators [60,61]. Actually, L_{θ} is also odd under any improper rotation, such as a simple mirror reflection or inversion *P*. Thus, one can obtain an insulator with quantized $\theta = \pi$ not only for time invariant systems, but also for inversion- and mirror-symmetric crystals regardless of time symmetry. When time reversal symmetry, as well as spatial symmetries are broken in the bulk, the θ parameter is no longer quantized [62]. However, in most known materials, it is extremely small, e.g. $\theta = 10^{-3}$, 10^{-4} in Cr₂O₃ and BiFeO₃ respectively [62]. Thus, achieving large values of the θ parameter, even at the absence of quantization, is an important materials challenge. For sufficiently large $\theta > \pi/2$, it has been proposed that magnetic domain walls will be associated with conducting channels at the sample surface [63].

Ideally, magnetic topological insulators would combine band topology with intrinsic magnetic order, leading to large surface energy gaps. Unfortunately, most of known/proposed topological insulators involve *p*-electron orbitals, whose Coulomb interaction is weak and cannot support magnetism. Elements with 3*d* and 4*d* electrons do have large electronic correlations, but only small SOC. While both strong Coulomb interaction and large SOC is found in 4*f* and 5*f* electron systems, they usually form narrow energy bands, thus making it also hard to realize topological insulator state of matter (see [64] for an exception).

As mentioned above, 5*d* electron has strong SOC and considerable electronic correlation, thus it is interesting to explore the possible magnetic Axion insulator in 5*d* TMO. At weak correlation region ($U \sim 1.0 \text{ eV}$), the Weyl points of pyrochlores A₂B₂O₇ will meet at the X point of BZ and annihilate. Unfortunately for such small *U* value, there is other band crossing the Fermi level, thus A₂B₂O₇ in weak correlation region is metal instead of Axion insulator. As in pyrochlores A₂B₂O₇, spinel compounds AB₂O₄ have their four B-sites forming a corner sharing tetrahedral network. Furthermore, it may be expected that 5*d* systems in the spinel structure will be more tunable by pressure, external fields or by doping as compared to the closely packed pyrochlore lattice. We therefore focus on spinel osmates AOs₂O₄ (A is alkali metal element such as Mg, Ca, Sr, Ba), and investigate their electronic structure and magnetic properties using DFT calculations with FP-LMTO [34].

Spinel structure forms space group $Fd\bar{3}m$. As the experimental lattice parameters are not available, we search for the stable crystal structures by using DFT calculation. Our numerical calculations show that Coulomb U has only a small effect on the crystal structure of AB₂O₄, thus based on LDA + SO scheme, we perform fully structural optimization and list the calculated structural parameter in Table 3. The structural stability has further been checked by studying various energy surfaces, chemical stability with possible reactants, other crystal structures and by calculating the phonon spectrum. All of these calculations suggest that spinel AB₂O₄ is at least metastable. For comparison, in Table 3 we also list the same parameters for the pyrochlore iridate Y₂Ir₂O₇. We see that the A-site element has a considerable effect on the Os-O bond angle and its length. As we discuss below, this allows us to control the electronic structure in Osmates and design exotic topological phases.

Our calculation predicts $MgOs_2O_4$ to be always metallic. We therefore do not discuss this compound here and concentrate our study on CaOs $_2O_4$. Although, the accurate value of *U* is not known



Fig. 3. Illustration of surface states arising from bulk Weyl points. (a) The bulk states as a function of (k_x, k_y) (and arbitrary k_z) fill the inside of a cone. A cylinder whose base defines a 1D circular Brillouin zone is also drawn. (b) The cylinder unrolled onto a plane gives the spectrum of the 2D subsystem $H(\lambda, k_z)$ with a boundary. On top of the bulk spectrum, a chiral state appears due to the non-zero Chern number. (c) Meaning of the surface states back in the 3D system: the chiral state appears as a surface connecting the original Weyl cone to a second one, and the intersection between this plane and the Fermi level gives a Fermi arc connecting the Weyl points (from Ref. [23]).



Fig. 4. Surface states. The calculated surface energy bands correspond to the (110) surface of the pyrochlore iridate $Y_2|r_2O_7$. A tight-binding approximation has been used to simulate the bulk band structure with three-dimensional Weyl points as found by our LSDA + *U* + SO calculation. The plot corresponds to diagonalizing 128 atoms slab with two surfaces. The upper inset shows a sketch of the deduced Fermi arcs connecting projected bulk Weyl points of opposite chirality. The inset below sketches the theoretically expected surface states on the (111) surface at the Fermi energy (surface band structure not shown for this case) (from Ref. [231).

for spinels, we generally expect screening to be larger in three dimensional systems than that of two dimensional systems like Sr_2IrO_4 [9]. Furthermore, the Os–Os bond length is shorter than that of $Y_2Ir_2O_7$, and one can expect that the *U* in CaOs₂O₄ is also smaller than in $Y_2Ir_2O_7$. We therefore believe that the *U* is in the range between 0.5 and 1.5 eV. As in the pyrochlore structure, the Os spinel sublattice is geometrically frustrated. Naively one may expect that the magnetic configuration of CaOs₂O₄ is also non-colinear as recently found in $Y_2Ir_2O_7$. However, a carefully theoretical study predicts that regardless of the value of *U*, the ferromagnetic (FM) configuration with magnetization along (010) is found to be the ground state, and the energy difference between this and other configurations is quite large.

For the values of U = 0.5 and 1.5 eV, electronic band structures along high symmetry lines appear to be insulating as shown in

Fig. 6b and c, respectively. To check a possibility of the gap closure and the metallic behavior away from the high symmetry lines of BZ, we perform the calculation with $100 \times 100 \times 100$ k-mesh. This very dense k-mesh confirms that both U = 0.5 and 1.5 eV calculations show the band gaps of 0.01 and 0.08 eV respectively.

Similar to the Fu and Kane criterion [65], which is designed for non-magnetic systems with inversion symmetry, one can still use the parity eigenvalues to classify the magnetic insulators with inversion symmetry and evaluate the magneto-electric coupling [66,67]: $\theta = \pi M \pmod{2}$, where $M = (\sum_k N_i)/2$, and N_i is the number of occupied states at the TRIM points *i* with odd parity. The local environment of Os ion in spinels is oxygen octahedron, and the crystal-field splitting of Os 5d states is large, which makes the e g band higher (about 2 eV) than the Fermi level. The bands close to the Fermi level are mainly contributed by t_{2g} mixed with O 2*p* orbitals. There are 4 Os per unit cell, thus the number of t_{2g} bands is 24. If all of 24 t_{2g} bands are fully occupied, the system cannot possess any topologically non-trivial properties. Noticing that Os occurs in its 3+ valence, for an insulator to occur, there are 20 occupied and 4 empty t_{2g} bands. Thus, instead of analyzing 20 occupied bands, we alternatively look at the parities of 4 empty bands.

For the spinel lattice, the eight TRIM points are Γ , *X*, *Y*, *Z*, and four *L* points. For the Γ point, all of the t_{2g} bands possess even parity, while for *X*, *Y*, and *Z* points, two of the 4 empty bands have even parity and the other two bands possess odd parity. Thus,



Fig. 5. Sketch of the predicted phase diagram for pyrochlore iridiates: Horizontal axis corresponds to the increasing interaction among Ir 5d electrons while the vertical axis corresponds to external magnetic field which can trigger a transition out of the non-collinear "all-in/all-out" ground state, which has several electronic phases (from Ref. [23]).

Table 3

Theoretically determined lattice parameters of spinel osmates. Angle denotes the Os– O–Os bond angle; Os–O and Os–Os denote the nearest neighbor Os–O bond length, and Os-Os bond length, respectively (from Ref. [24]).

	Angle (°)	Os–Os (Å)	Os–O (Å)
CaOs ₂ O ₄	98.5	3.07	2.04
SrOs ₂ O ₄	94.6	3.12	2.05
BaOs ₂ O ₄	103.1	3.28	2.11
Y ₂ Ir ₂ O ₇	129.7	3.60	1.99

regardless the value of *U*, the summation of the number of empty t_{2g} states with odd parities at Γ , *X*, *Y*, and *Z* points is 6. On the other hand, the Coulomb interaction has a significant effect on the parities of the bands around the *L* points. This is shown in Table 4, where the summation of the number of the odd states are 6 and 4 for U = 1.5 and 0.5 eV, respectively. Therefore, for U = 1.5 eV, we have $\theta = 0$, which corresponds to a normal insulator. However, for U = 0.5 eV, we have $\theta = \pi$, which leads us to the axion insulator with novel magnetoelectric properties.

Topological insulators must be separated from trivial insulators by a semi-metallic state [23]. To find the boundary between semimetal and Axion insulator as well as between semi-metal and Mott insulator we perform LSDA + U + SO calculations for a number of intermediate values of U. Our calculations for U's varying from 1.0 to 1.3 eV show that there are 3D Weyl crossings close to (0.02, x, 0.02) $2\pi/a$ and its symmetry related points of the BZ, where the value of x changes with U. With both decreasing and increasing U, the Weyl points move and annihilate by meeting with each other, thus opening the energy gap and forming either the $\theta = \pi$ Axion insulator or normal insulator, respectively.

Replacing Ca by Sr, both the Os–O–Os bond angle and the bond length will change as shown in Table 3. However, similar with $Y_2Ir_2O_7$, both CaOs₂O₄ and SrOs₂O₄ show the same rich phase diagram (see Fig. 7) as a function of *U*.

We finally study $BaOs_2O_4$ which has both the largest bond angle and bond length as shown in Table 3. These differences significantly affect its band structure: the LDA + SO calculation with U = 0 gives that at the Γ point the eight $J_{eff} = 1/2$ states have degeneracies 4-2-2 and not 2-4-2 as found in Ca and Sr cases. Note that this sequence of levels is the same as recently suggested by

Table 4

Calculated parities of states at Time Reversal Invariant Momenta (TRIMs) for CaOs₂O₄. Only 4 empty t_{2g} bands are shown in order of increasing energy. L_x denotes $2\pi/a$ (-0.5, 0.5, 0.5), L_y denotes $2\pi/a(0.5, -0.5, 0.5)$, L_z denotes $2\pi/a(-0.5, 0.5, 0.5)$ and L denotes $2\pi/a(0.5, 0.5, 0.5)$ (from Ref. [24]).

	L_x	L_y	Lz	L
<i>U</i> = 0.5 eV	+ + + +	+ + + +	+ + + +	
<i>U</i> = 1.5 eV	_ + + +	_ + + +	_ + + +	+



Fig. 7. Sketch of the predicted phase diagram for spinel osmates (from Ref. [24]).

Pesin and Balents to realize topological insulating in pyrochlore iridates [45]. Unfortunately, the bands crossing the Fermi level exist and cannot be removed by slight adjusting the lattice constant. Same with $CaOs_2O_4$ and $SrOs_2O_4$, considering the Coulomb interaction *U* will induce magnetism, but we do not find axion-insulator or Weyl-metal state for $BaOs_2O_4$ for any reasonable *U*.

4. Electronic structure and magnetic properties of Slater insulator NaOsO₃

In addition to the novel topological properties discussed at previous sections, the unusual metal-insulator transition (MIT) had also been found in 5*d* TMO. In 1951, Slater proposed that antiferromagnetic (AFM) order alone can open a gap in the half-filled state regardless of the magnitude of the Coulomb interaction [68]. Usually, the formation of AFM ordering can only affect a small fraction of Fermi surface, thus three dimensional (3D) Slater insulator is very rare. As the first well-documented example of 3D Slater insulator, 5*d* transition metal oxide $Cd_2Os_2O_7$ has attracted research



Fig. 6. Electronic band structure of CaOs₂O₄ shown along high symmetry direction. (a) LDA + SO; (b) LSDA + SO + U, with U = 0.5 eV; (c) LSDA + SO + U, with U = 1.5 eV (from Ref. [24]).

attention since 2001 [69–72]. However, due to the strong geometric frustration of the pyrochlore structure, until 2012 its magnetic ground-state configuration had been determined as AIAO [44] and this compound had been finally confirmed as a Slater insulator [44].

In 2009, by using high-pressure technique, Shi et al. synthesized another osmate: $NaOsO_3$ [73]. It has been found that $NaOsO_3$ is metallic at high temperature, while undergoing a MIT at about 410 K [73]. Experiments reveal that this MIT is continuous and purely electronic. Moreover, it is coincident with a magnetic transition of AFM character [73]. Therefore, $NaOsO_3$ provides a unique platform to understand the temperature-induced and magnetic-related MIT, and a comprehensive investigation of the mechanism of this MIT is an interesting problem.

Based on the full potential linearized augmented planewave method [74], we first perform non-magnetic LDA calculation to see the basic band-structure features. Due to the octahedral environment, the Os 5*d* bands split into the t_{2g} and e_g states. Our LDA results show that the crystal splitting between t_{2g} and e_g states is large, the bands around the Fermi level are basically contributed by t_{2g} states and all of other states are far from Fermi level. LDA calculation produces a metallic state in contrast to the experimental insulating behavior.

SOC usually changes the 5*d* band dispersion significantly and plays an essential role in the gap opening of 5*d* TMO. We thus compare the results obtained in the presence and absence of SOC, which are given in Fig. 8. The difference between the bands with and without SOC is small, as demonstrated in Fig. 8. For $5d^5$ electronic configuration of SrIr₂O₄ [6], A₂Ir₂O₇ (A = Y or rare earth) [23] and AOs₂Os₄ (A = Ca, Sr) [24], where $J_{eff} = 1/2$ picture is valid, SOC has a dramatic effect on the band structure. In NaOsO₃, Os occurs in its 5+ valence and there are 3 electrons in its t_{2g} band. Since t_{2g} band is half filled, it is natural to expect the effect of SOC to be small. We then perform a spin polarized calculation but find that the FM state is not stable for this compound, as our LSDA + SO calculation with initial FM setup converges to the non-magnetic state.

We generally expect the screening to be larger in three dimensional systems than in two dimensional ones, and one can image that U in NaOsO₃ should be smaller than that in Sr₂IrO₄/Ba₂IrO₄ [9]. We perform LDA + U + SO calculation, which is adequate for magnetically ordered insulating ground states [2]. Varying parameter U between 0.5 and 2.0 eV, numerical results show that the electronic correlations can stabilize the FM configuration and narrow the Os t_{2g} band. However, as shown in Fig. 9(a), our



Fig. 8. Band structure of NaOsO₃, shown along the high symmetry directions. Fermi energy E_F is set to zero. (a) LDA, (b) LDA + SO (from Ref. [25]).

LDA + U + SO calculation with U = 2.0 eV still gives a metallic solution. Naively, one may expect that using larger Coulomb U will result in an insulating state. However, similar with the case in Y₂Ir₂O₇, our additional calculations show that increasing U cannot solve this problem, and even a quite large U(=6.0 eV) cannot open the band gap. Therefore, electronic correlations alone cannot explain the insulating behavior, and the MIT in NaOsO₃ is definitely not of a Mott-type.

After studying the effect of SOC and U, we subsequently investigate the effect of various magnetic orders. We considered four AFM configurations besides the FM state: A-type AFM state (A-AFM) with layers of Os ions coupled ferromagnetically in a given set of (001) planes but with alternate planes having opposite spin orientation; C-type AFM state (C-AFM) with lines of Os ions coupled ferromagnetically in a given direction (001) but with alternate lines having opposite spin orientation: G-type AFM state (G-AFM) with Os ions coupled antiferromagnetically with all of their nearest neighbors; D-type AFM state (D-AFM) where Os ions lying within alternating planes perpendicular to [001] direction are coupled ferromagnetically along either [010] or [100] directions while different lines are coupled antiferromagnetically. Same as with the FM setup, the LSDA + SO calculation with U = 0 for all considered AFM setups converges to the nonmagnetic metallic state.

The Coulomb interaction *U* of Os 5*d* is found to stabilize the AFM configuration. Our calculation confirms that the magnetic order has a significant effect on the band structure, and for a reasonable $U (\leq 2.0 \text{ eV})$, G-AFM configuration is the only insulating solution as shown in Fig. 9. The comparison of the total energy shows that regardless the value of *U*, the G-AFM configuration is



Fig. 9. Electronic density of states (DOS) from LDA + SO + U (U = 2.0 eV) calculation. Fermi energy E_F is set to zero. (a) FM configuration, (b) G-AFM (c) C-AFM, (d) A-AFM (e) D-AFM. The black/red line is for up/down-spin, respectively. For AFM configurations, spin-up is the same as spin-down, thus only one spin channel is plotted (from Ref. [25]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

always the ground state. With increasing U the band structure will change, but only when U is larger than 1.0 eV, the G-AFM solution becomes insulating. It is found that the magnetic moment is mainly located at Os site, and despite of strong hybridization between Os 5d and O 2p, O site is basically non-magnetic (less than 0.003 $\mu_{\rm B}$). The numerical data for *U* = 2.0 eV are given in Table 5. For the $5d^5$ electronic systems such as BaIrO₃, Sr₂IrO₄, pyrochlore iridates, etc, it has been found that due to the strong spin-orbit entanglement in 5d states, the magnetic orbital moment is about twice larger than the spin moment [6,7,23,20], even in the presence of strong crystal field and band effects. Contrary to 5d⁵ systems, the obtained orbital moment for NaOsO₃ is much smaller than its spin moment, showing again that SOC effect is small for this $5d^3$ electronic configuration case. As shown in Table 5, the magnitude of magnetic moment is sensitive to the magnetic configuration, indicating the itinerant nature of magnetism. For the same U value, the G-AFM configuration always has the largest magnetic moment among the considered states. As shown in Table 5, our numerical magnetic moment is 0.83 μ_B , while based on the Curie–Weiss fitting of magnetic susceptibility $\chi(T)$, the magnetic moment was estimated to be 2.71 $\mu_{\rm B}$ [73]. For an itinerant magnet, one may still fit the $\gamma(T)$ curve by the Curie–Weiss law, but cannot estimate the magnetic moment accurately based on the Curie–Weiss constant [75]. Thus, the experimental magnetic moment may not be reliable. The energy difference between various magnetic configurations is large, which is consistent with the observed high magnetic transition temperature (about 410 K) [73], although here one cannot estimate the interatomic exchange interaction and T_N based on the difference between total energies accurately as in the local moment systems [76]. Since the G-AFM configuration is the only insulating state, it is easy to understand that both magnetic and electronic phase transitions occur at the same temperature and our calculation indeed confirms that the MIT of NaOsO₃ is a Slater-type transition.

The agreement between our theory and recent experiment [77] is fairly good: (1) Our theoretical magnetic ground state configuration has been confirmed by the experiment; (2) numerical magnetic moment at Os (0.83 μ_B) is close to the neutron result (1.01 μ_B); (3) SOC is not important for NaOsO₃, this theoretical result agrees with the experimental measurement; (4) Our theoretical conclusion (the MIT of NaOsO₃ is a Slater-type transition) is also consistent with the experimental result.

5. Anisotropic unscreened Coulomb interaction in metallic ferroelectricity LiOsO₃

Very recently, another important 5*d* TMO LiOsO₃ had been synthesized by high-pressure technique [78]. LiOsO₃ remains metallic behavior while it undergoes a second-order phase transition from the high temperature centrosymmetric $R\overline{3}c$ to a ferroelectric (FE) like R3*c* structure at $T_s = 140$ K [78]. It is well accepted that FE instability can be explained by a delicate balance between short-range elastic restoring forces supporting the undistorted paraelectric (PE) structure and long-range Coulomb interactions favoring the FE phase [79]. Itinerant electrons can screen the

Table 5

Spin $\langle S \rangle$ and orbital $\langle O \rangle$ moment (in μ_B) as well as the total energy E_{tot} per unit cell (in eV) for several magnetic configurations, as calculated using LDA + U + SO method with U = 2.0 eV (E_{tot} is defined relative to the G-AFM configuration) (from Ref. [25]).

Configuration	G-AFM	FM	C-AFM	A-AFM	D-AFM
E_{tot} $\langle S \rangle$	0 0.94	0.243 0.22	0.186 0.54	0.282 0.29	0.205 0.20
$\langle \mathbf{U} \rangle$	-0.11	-0.01	-0.04	-0.05	-0.05

electric fields and inhibit the electrostatic forces, metallic systems are thus not expected to exhibit FE like structural distortion. Therefore as the first convincing FE metal [80], LiOsO₃ receives extensive research attention [78,81–84].

Neutron and X-ray diffraction studies showed that the structural phase transition involves the displacements of Li ions accompanying also a slight shift of O ions [78]. The electronic structure and lattice instability were studied by several groups [82–84]. It was found that the local polar distortion in LiOsO₃ is solely due to the instability of the A-site Li ion [82–84]. Despite these efforts devoted to understanding the origin of the FE like structural transition in this metallic system, there are still two fundamental issues have not been clearly clarified. The first is the origin of the ferroelectric instability: is it displacive or order–disorder? Second, as FE-like phase transition of LiOsO₃ occurs at a relatively high temperature (140 K), how can these local dipoles lined up to form long-range order, as if there is no conduction electrons to screen the dipole interactions.

The atomic arrangements of LiOsO₃ are sketched in Fig. 10. In the $R\overline{3}c$ PE structure, the Os atoms are at the centers of the oxygen octahedrons, while Li atoms are centered between two adjacent Os atoms along the polar axis on average. The FE structural phase transition mainly involves the displacements of Li atoms: Li atoms shift along the polar axis about $d \sim 0.47$ Å from the mean positions of the PE phase (see gray arrow d in Fig. 10(a)) and O atoms slightly displace about 0.056 Å [78,82,84].

Based on Vienna *ab initio* simulation package [85,86], we first perform standard generalized gradient approximation (GGA) calculation and show the total and partial density of states (DOS) in Fig. 11. The energy range, -9.0 to -2.4 eV is dominated by 0-2porbital with an additional contribution from the Os-5*d* state indicating hybridization between them. As shown in Fig. 11(b), Li is highly ionic and its bands are far from the Fermi level. The Os atom is octahedrally coordinated by six O atoms, making the Os 5*d* bands split into the t_{2g} and e_g states, and the t_{2g} bands are located around the Fermi level (from -2.2 to 1.2 eV), as shown in Fig. 11(c). As shown in the comparison of DOS of PE and FE, the electronic structures almost do not change during the phase transition, which is consistent with the previous theoretical work [82]. It is worthy to mention that this is quite different from prototype FE systems such as BaTiO₃, in which hybridization is necessary for the FE



Fig. 10. Primitive unit cell of (a) PE and (b) FE phases of $LiOsO_3$. The green, blue and red balls are the Li, Os and O ions respectively. *d* and -d correspond to the displacements of Li ions along the polar axis (from Ref. [26]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. (a) The total DOS patterns of $LiOsO_3$ in PE(blue) and FE(pink) phases. The partial DOS of (b) Li-1s (c) Os-5d and (d) O-2p states in PE(blue) and FE(pink) phases respectively. The Fermi energy is positioned as zero (from Ref. [26]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

phase transitions [3,87,88]. Thus we conclude the hybridization is not the major driving force for the structural instability in LiOsO₃.

As shown in Fig. 11, the O-2*p* orbitals are almost fully occupied, while the bands of Li are mainly empty, thus Os occurs in its 5+ valence state and there are basically three electrons in its t_{2g} band. Since t_{2g} band is half filled, the effect of SOC is small despite the large strength of SOC [25,77].

The Os–Os bond length of LiOsO₃ is shorter than that of NaOsO₃, thus we expect that the *U* in LiOsO₃ is even smaller than in NaOsO₃, for which *U* is around 1 eV [25]. Here, we estimate the Sommerfeld coefficient based on the numerical DOS at Fermi level. Our numerical result (6.1 mJ mol⁻¹ K⁻²) is just slightly less than that of experimental one ($\gamma = 7.7$ mJ mol⁻¹ K⁻²) [78] which indicates the electronic correlation is indeed weak in LiOsO₃.

One fundamental issue about this system is the mechanism for the ferroelectric instability: is it displacive or order–disorder? We first calculate the potential energy profile along different displacive soft modes, i.e. the evolution paths from the PE to FE structures. The results, as shown in Fig. 12, suggest that the energy difference between the PE and FE structures is majorally contributed by Li ions movements. The depth of double wells resulting from the motion of Li ions only and both of the Li and O ions are 27 and 44 meV, respectively, which is in consistent with several previous works [82,84]. Note that we find it is important to adopt the optimized structure to obtain the correct potential energy surfaces. Adopting experimental coordinates will obtain unreasonable results, as the well depth caused by the sole Li ion movements is even larger than that of considering both the Li and O moments (see Appendix of Ref. [26].).

We notice that the experimental transition temperatures of $LiOsO_3$ is 140 K and much lower than the depths of double wells.



Fig. 12. The olive, blue and red curves represent the potential energy changes with respect to O displacements only. Li displacements only and the coupled displacements of the Li and O ions. The total energy and displacements of PE states are set as zero. The displacements of corresponded FE states are set as 100% (from Ref. [26]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This indicates the transition in LiOsO₃ is most probably orderdisorder like [89]. This may also explain the experimentally observed incoherent charge transport above the transition temperature [78], which is possibly caused by the scattering induced by disorder of Li off-center displacement. For order-disorder transition, the Li atoms oscillate between the double wells and the potential wells remain basically unchanged throughout the phase transition, thus we expect there is no softening mode in the Raman spectra of LiOsO₃. Therefore, a Raman measurement is useful to clarify this issue.

As mentioned above, the Li ions in LiOsO₃ favor an off-center displacement and form local dipoles as shown in Fig. 10. Thus it is a puzzle why the local electric dipoles in different unit cell can interact with each other and form a long range order at 140 K, noticing that the distance between them is far (even the nearest neighbor dipole distance is larger than 3.5 Å) and the DOS at the Fermi level is rather large (Fig. 11). We find that the bands located below -10 eV are quite narrow and have negligible hybridization with other bands. The electrons at these bands are tightly bounded with the ion, thus almost do not change with the motion of Li ion, namely these electrons almost have no contribution to the electric screening effect. On the other hand, the displacements of Li ions just slightly affect the Os-5d and O-2p electrons as shown in Fig. 11. To have a straightforward view of the charge distribution, we sketched the electron densities of PE LiOsO₃ arising from states between -10 eV and the Fermi level in Fig. 13(a) and (b). There are two distinctive characters in these two figures. One is that the electronic density is relevant high between the Os and O ions, which again indicates the strong hybridization between Os-5p and O-2p states. The second is that there is almost no conduction charge at all in a relative large space around the Li ions, i.e. the Li ion is literally bare ion. We will demonstrate later that the later character directly results in incomplete electric screening of dipole-dipole interactions and forms long range dipole ordering.

The screening effect actually can be described as the electron charge difference induced by a perturbation such as the change of the dipole or external electric field. Yet seldom efforts have been carried out to study the screening effect in the bulk metal, as people generally believe there is no macroscopic electric field inside metals. Actually this effect can be done by analyzing the charge difference before and after the local dipole is introduced. Such strategy provides a explicit picture on the exact behavior of the screening effect in metallic systems. Since the FE like transition



Fig. 13. Partial electron densities contour maps for PE LiOsO₃ taken through (a) [1–10] and (b) [2–10] plane. Contour levels shown are between 0 (blue) and 0.3 e/Å³ (red). (c) Charge density difference between FE and PE structures for Li pair 1, 3 and 5 through [1–10] plane. See text for details. Contour levels shown are between -0.004 (blue) and 0.004 e/Å³ (red). The (001) direction here is the same as the (111) direction in Fig. 10 (from Ref. [26]) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

basically involves displacements of Li ion, the change of local dipole can be approximated by the Li movement from the PE structure and the dipole interactions can be labeled as Li-Li pairs. In Fig. 13, we use symbol 1, 2, 3, etc. to denote the Li–Li pairs with the first, second and third nearest distance between them. As is clear in Fig. 13(a), there is almost no conduction charge distribution between pair 1 (red solid line), thus it is natural to expect the screening effect for the nearest dipole-dipole interaction is small. This had been confirmed by the calculation of the charge difference induced by the Li motions. We first construct a $3 \times 3 \times 1$ supercell containing 270 atoms in hexagonal phase. The PE structure is taken as background. Then we move Li ions in pair 1 to their FE positions, and all other atoms are fixed. In this way we can see what happened when the two local dipoles are formed. The charge density change (namely $\Delta \rho = \rho_{\rm FE} - \rho_{\rm PE}$) is then plotted in the left panel of Fig. 13(c), which clearly demonstrates the screening of these two dipoles. As can be seen from this plot, significant conduction electron responses only occur around Os ions, and they form local dipoles to against the Li dipoles, this is exactly the screening effect which is expected in metallic systems. Whereas the charge distribution near O remains almost unchanged, indicating the Os-5d and O-2p hybridization is neither important for the electric dipole interaction, nor will be affected by the Li dipoles. The most interesting thing is, as shown in the left panel of Fig. 13(c), that is almost no modification of charge distribution between pair 1 at all. This clearly demonstrates that dipole interaction between pair 1 is only slightly screened. We then apply the same strategy to study other Li pairs. For pair 2 (Fig. 13(b)), as there is O atom between two Li ions, we observe noticeable screening to prevent the direct dipole interaction. Yet for pair 3, the dipole interaction is again not fully screened as shown in the middle panel of Fig. 13(c). Detailed analysis indicates that this is because this Li pair is 0.65 Å away from the O ion plane. For other pairs, as there is either O or Os atoms between two Li ions, the electric screening effect is strong. The example of pair 5, which is also at the [1-10] plane like pair 1 and 3, is shown in the right panel of Fig. 13(c) for comparison.

6. Summary

In this review, we briefly summarize representative theoretical work of our group in this booming and fascinating research branch. We discuss the unusual properties in pyrochlore iridates, propose this system is WSM and possess a exotic surface states in the form of Fermi arcs. We suggest the spinel osmates are the insulator with a large magnetoelectric coupling characteristic of axion electrodynamics. We give a comprehensive discussion about the electronic and magnetic properties of NaOsO₃, and successfully determine the magnetic ground state configuration for this compound. We also discuss LiOsO₃, and propose that highly anisotropic screening and local dipole–dipole interactions are the two most important keys to form LiOsO₃-type metallic ferroelectricity.

In 5*d* TMO, the electron correlation and the SOC are of comparable magnitude, hence, the interplay of electron correlations and strong spin–orbit interactions makes the 5*d* transition metal oxides (TMO) of special interest for possible novel properties [11]. To find novel properties in 5*d* TMO is of both fundamental and technological importance and deserves special attention.

Acknowledgements

We would like to acknowledge our collaborators: Sergey Savrasov, Ashvin Vishwanath and Ari M. Turner. This work was supported by National Key Project for Basic Research of China (Grant No. 2011CB922101), NSFC (Grants No. 91122035, No. 11374137, and No. 11174124), and Doctoral Fund of Ministry of Education of China (Grant No. 20130091110003). The project is also funded by Priority Academic Program Development of Jiangsu Higher Education Institutions and supported by the program B for Outstanding PhD candidate of Nanjing University.

References

- [1] M. Imada, A. Fujimori, Y. Tokura, Rev. Mod. Phys. 70 (1998) 1039.
- [2] G. Kotliar, S.Y. Savrasov, K. Haule, V.S. Oudovenko, O. Parcollet, C.A. Marianetti, Rev. Mod. Phys. 78 (2006) 865.
- [3] R.E. Cohen, Nature (London) 358 (1992) 136.
- [4] S. Jin et al., Science 264 (1994) 413;
 - P. Schiffer et al., Phys. Rev. Lett. 75 (1995) 3336; Y. Tokura, N. Nagaosa, Science 288 (2000) 462.
- 5] W. Pickett, Rev. Mod. Phys. 61 (1989) 433.
- [6] B.J. Kim et al., Phys. Rev. Lett. 101 (2008) 076402;
- B.J. Kim et al., Science 323 (2009) 1329.
- [7] H. Jin, H. Jeong, T. Ozaki, J. Yu, Phys. Rev. B 80 (2009) 075112.
- 8] H. Watanabe, T. Shirakawa, S. Yunoki, Phys. Rev. Lett. 105 (2010) 216410.
- [9] R. Arita, J. Kuneš, A.V. Kozhevnikov, A.G. Eguiluz, M. Imada, Phys. Rev. Lett. 108 (2012) 086403.
- [10] L.F. Mattheiss, Phys. Rev. B 13 (1976) 2433.
- [11] W. Witczak-Krempa, G. Chen, Y.B. Kim, L. Balents, Annu. Rev. Condens. Matter Phys. 5 (2014) 57.
- [12] S. Chikara, O. Korneta, W.P. Crummett, L.E. DeLong, P. Schlottmann, G. Cao, Phys. Rev. B 80 (2009) 140407(R).
- [13] F. Wang, T. Senthil, Phys. Rev. Lett. 106 (2011) 136402.
- [14] Y.J. Yan, M.Q. Ren, H.C. Xu, B.P. Xie, R. Tao, H.Y. Choi, N. Lee, Y.J. Choi, T. Zhang, D.L. Feng, 2015. Available from: <arXiv:1506.06557>.
- [15] A. Shitade, H. Katsura, J. Kuneš, X.-L. Qi, S.-C. Zhang, N. Nagaosa, Phys. Rev. Lett. 102 (2009) 256403.
- [16] K. Maiti, R.S. Singh, V.R.R. Medicherla, S. Rayaprol, E.V. Sampathkumaran, Phys. Rev. Lett. 95 (2005) 016404;
- J.-G. Cheng et al., Phys. Rev. B 80 (2009) 104430.
- [17] G. Jackeli, G. Khaliulin, Phys. Rev. Lett. 102 (2009) 017205.
- [18] T. Okamoto, M. Nohara, H. Aruga-Katori, H. Takagi, Phys. Rev. Lett. 99 (2007) 137207.
 [19] P.A. Lee, Science 321 (2008) 1306;
 - L. Balents, Nature (London) 464 (2010) 199.

- [20] M.A. Laguna-Marco, D. Haskel, N. Souza-Neto, J.C. Lang, V.V. Krishnamurthy, S. Chikara, G. Cao, M. van Veenendaal, Phys. Rev. Lett. 105 (2010) 216407.
- [21] G. Cao, T.F. Qi, L. Li, J. Terzic, S.J. Yuan, L.E. DeLong, G. Murthy, R.K. Kaul, Phys. Rev. Lett. 112 (2014) 056402.
- [22] T. Dey, R. Kumar, A.V. Mahajan, S.D. Kaushik, V. Siruguri, Phys. Rev. B 89 (2014) 205101.
- [23] X. Wan, A.M. Turner, A. Vishwanath, S.Y. Savrasov, Phys. Rev. B 83 (2011) 205101;
 - L. Balents, Physics 4 (2011) 36.
- [24] X. Wan, A. Vishwanath, S.Y. Savrasov, Phys. Rev. Lett. 108 (2012) 146601.
- [25] Y. Du, X. Wan, L. Sheng, J. Dong, S.Y. Savrasov, Phys. Rev. B 85 (2012) 174424. [26] H.M. Liu, Y.P. Du, Y.L. Xie, J.-M. Liu, C.-G. Duan, X. Wan, Phys. Rev. B 91 (2015) 064104.
- [27] R.S. Singh, V.R.R. Medicherla, K. Maiti, E.V. Sampathkumaran, Phys. Rev. B 77 (2008) 201102.
- [28] K. Matsuhira et al., J. Phys. Soc. Jpn. 76 (2007) 043706.
- [29] D. Yanagishima, Y. Maeno, J. Phys. Soc. Jpn. 70 (2001) 2880.
- [30] H. Fukazawa, Y. Maeno, J. Phys. Soc. Jpn. 71 (2002) 2578;
- M. Soda et al., Physica B 329 (2003) 1071.
- [31] N. Taira, M. Wakeshima, Y. Hinatsu, J. Phys.: Condens. Matter 13 (2001) 5527.
- [32] S. Nakatsuji et al., Phys. Rev. Lett. 96 (2006) 087204.
- [33] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid St. Chem. 15 (1983) 55;
 - S.T. Bramwell, M.J.P. Gingras, Science 294 (2001) 1495;
 - A.P. Ramirez, Ann. Rev. Mater. Sci. 24 (1994) 453;
 - S. Gardner, M.J.P. Gingras, J.E. Greedan, Rev. Mod. Phys. 82 (2010) 53.
- [34] S.Y. Savrasov, Phys. Rev. B 54 (1996) 16470.
- [35] X. Wan, J. Zhou, J. Dong, Europhys. Lett. 92 (2010) 57007;
- Y. Du, H. Ding, L. Sheng, S.Y. Savrasov, X. Wan, C. Duan, J. Phys.: Condens. Matter 26 (2014) 025503.
- [36] R. Siddharthan, B.S. Shastry, A.P. Ramirez, A. Hayashi, R.J. Cava, S. Rosenkranz, Phys. Rev. Lett. 83 (1999) 1854;
 - M.J. Harris, S.T. Bramwell, D.F. McMorrow, T. Zeiske, K.W. Godfrey, Phys. Rev. Lett. 79 (1997) 2554-2557.
- [37] M. Elhajal, B. Canals, R. Sunyer, C. Lacroix, Phys. Rev. B 71 (2005) 094420.
- [38] S.M. Disseler, C. Dhital, A. Amato, S.R. Giblin, C. de la Cruz, S.D. Wilson, M.J. Graf, Phys. Rev. B 86 (2012) 014428.
- [39] S.M. Disseler, Phys. Rev. B 89 (2014) 140413(R).
- [40] K. Tomiyasu et al., J. Phys. Soc. Jpn. 81 (2012) 034709.
- [41] E. Lefrancois, V. Simonet, R. Ballou, E. Lhotel, A. Hadj-Azzem, S. Kodjikian, P. Lejay, P. Manuel, D. Khalyavin, L.C. Chapon, 2015. Available from: <arXiv:1502. 00787>.
- [42] G. Chen, M. Hermele, Phys. Rev. B 86 (2012) 235129.
- [43] A. Go, W. Witczak-Krempa, G.S. Jeon, K. Park, Yong Baek Kim, Phys. Rev. Lett. 109 (2012) 066401.
- [44] H. Shinaoka, T. Miyake, S. Ishibashi, Phys. Rev. Lett. 108 (2012) 247204.
- [45] D.A. Pesin, L. Balents, Nat. Phys. 6 (2010) 376.
- [46] H.-M. Guo, M. Franz, Phys. Rev. Lett 103 (2009) 206805.
- [47] B.J. Yang, Y.B. Kim, Phys. Rev. B 82 (2010) 085111.
- [48] V.I. Anisimov, F. Aryasetiawan, J. Lichtenstein, J. Phys.: Condens. Matter 9 (1997) 767.
- [49] H. Weyl, Zeitshrift fur Physik 56 (1929) 330.
- [50] A.M. Turner, A. Vishwanath, 2013. Available from: <arXiv:1301.0330>.
- [51] S. Murakami, New J. Phys. 9 (2007) 356.
- [52] G.B. Halasz, L. Balents, Phys. Rev. B 85 (2012) 035103.
- [53] H. Weng, C. Fang, Z. Fang, B.A. Bernevig, X. Dai, Phys. Rev. X 5 (2015) 011029. [54] S.M. Young, S. Zaheer, J.C.Y. Teo, C.L. Kane, E.J. Mele, A.M. Rappe, Phys. Rev. Lett.
- 108 (2012) 140405.

- [55] Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, Z. Fang, Phys. Rev. B 85 (2012) 195320.
- [56] Z. Wang, H. Weng, Q. Wu, X. Dai, Z. Fang, Phys. Rev. B 88 (2013) 125427.
- [57] Y. Du, B. Wan, D. Wang, L. Sheng, C.-G. Duan, X. Wan, 2014. Available from: <arXiv:1411.4394>.
- [58] D. Xiao, M.-C. Chang, Q. Niu, Rev. Mod. Phys. 82 (2010) 1959.
- [59] F. Wilczek, Phys. Rev. Lett. 58 (1987) 1799.
- [60] X.L. Qi, T. Hughes, S.C. Zhang, Phys. Rev. B 78 (2008) 195424.
- [61] R. Li, J. Wang, X.L. Qi, S.C. Zhang, Nat. Phys. 6 (2010) 284;
- J. Wang, R. Li, S.C. Zhang, X.L. Qi, Phys. Rev. Lett. 106 (2011) 126403.
- [62] A. Malashevich, I. Souzo, S. Coh, D. Vanderbilt, New J. Phys. 12 (2010) 053032; A.M. Essin, A.M. Turner, J.E. Moore, D. Vanderbilt, Phys. Rev. B 81 (2010) 205104:
- A.M. Essin, J.E. Moore, D. Vanderbilt, Phys. Rev. Lett. 102 (2009) 146805.
- [63] J.C.Y. Teo, C.L. Kane, Phys. Rev. B 82 (2010) 115120.
- [64] M. Dzero, K. Sun, V. Galitski, P. Coleman, Phys. Rev. Lett. 104 (2010) 106408.
- [65] L. Fu, C.L. Kane, Phys. Rev. B 76 (2007) 045302.
- [66] A.M. Turner, Y. Zhang, R.S.K. Mong, A. Vishwanath, 2010. Available from: <arXiv:1010.4335>.
- [67] T.L. Hughes, E. Prodan, B.A. Bernevig, 2010. Available from: <arXiv:1010.4508>.
- [68] J.C. Slater, Phys. Rev. 82 (1951) 538.
- [69] D. Mandrus, J.R. Thompson, R. Gaal, L. Forro, J.C. Bryan, B.C. Chakoumakos, L.M. Woods, B.C. Sales, R.S. Fishman, V. Keppens, Phys. Rev. B 63 (2001) 195104; W.J. Padilla, D. Mandrus, D.N. Basov, Phys. Rev. B 66 (2002) 035120.
- [70] Y.H. Matsuda, J.L. Her, S. Michimura, T. Inami, M. Suzuki, N. Kawamura, M. Mizumaki, K. Kindo, J. Yamauara, Z. Hiroi, Phys. Rev. B 84 (2011) 174431.
- [71] A. Koda, R. Kadono, K. Ohishi, S.R. Saha, W. Higemoto, S. Yonezawa, Y. Muraoka, Z. Hiroi, J. Phys. Soc. Jpn. 76 (2007) 063703.
- [72] D.J. Singh, P. Blaha, K. Schwarz, J.O. Sofo, Phys. Rev. B 65 (2002) 155109; H. Harima, J. Phys. Chem. Solids 63 (2002) 1035.
- [73] Y.G. Shi, Y.F. Guo, S. Yu, M. Arai, A.A. Belik, A. Sato, K. Yamaura, E. Takayama-Muromachi, H.F. Tian, H.X. Yang, J.Q. Li, T. Varga, J.F. Mitchell, S. Okamoto, Phys. Rev. B 80 (2009) 161104(R).
- [74] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Technische Universitat Wien, Austria, 2001).
- [75] T. Moriya, Spin Fluctuations in Itinerant Electron Magnetism, Springer-Verlag, 1985.
- [76] X. Wan, M. Kohno, X. Hu, Phys. Rev. Lett. 94 (2005) 087205.
- [77] S. Calder, V.O. Garlea, D.F. McMorrow, M.D. Lumsden, M.B. Stone, J.C. Lang, J.-W. Kim, J.A. Schlueter, Y.G. Shi, K. Yamaura, Y.S. Sun, Y. Tsujimoto, A.D. Christianson, Phys. Rev. Lett. 108 (2012) 257209.
- [78] Y. Shi, Y. Guo, X. Wang, A.J. Princep, D. Khalyavin, P. Manuel, Y. Michiue, A. Sato, K. Tsuda, S. Yu, M. Arai, Y. Shirako, M. Akaogi, N. Wang, K. Yamaura, A.T. Boothroyd, Nat. Mater. 12 (2013) 1024.
- [79] W. Cochran, Adv. Phys. 9 (1960) 387.
- [80] P.W. Anderson, E.I. Blount, Phys. Rev. Lett. 14 (1965) 217.
- [81] V. Keppens, Nat. Mater. 12 (2013) 952.
- [82] H. Sim, B.G. Kim, Phys. Rev. B 89 (2014) 201107(R).
- [83] H.J. Xiang, Phys. Rev. B 90 (2014) 094108.
- [84] G. Giovannetti, M. Capone, Phys. Rev. B 90 (2014) 195113.
- [85] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) R558.
 [86] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [87] N.A. Hill, J. Phys. Chem. B 104 (2000) 6694.
- [88] P. Ghosez, J.-P. Michenaud, X. Gonze, Phys. Rev. B 58 (1998) 6224.
- [89] I. Inbar, R.E. Cohen, Phys. Rev. B 53 (1996) 1193.