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

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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 $LiOsO_3$.

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 5*d* 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 5*d* TMO. In Section 2, we systematically discuss 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 condensed-matter 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 $NaOsO_3$, and successfully predict the magnetic ground state configuration of this compounds [25]. We also discuss the novel properties of $LiOsO_3$, and suggest that the highly anisotropic screening and the local dipole–dipole interactions are the two most important keys to form $LiOsO_3$-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, $A_2Ir_2O_7$

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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 $Nd_2Ir_2O_7$ [28], and $Pr_2Ir_2O_7$ 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 $Y_2Ir_2O_7$, each of four Ir atoms is octahedrally coordinated by six O atoms, which makes the Ir 5*d* states split into doubly degenerate e_g and triply degenerate t_{2g} states. Due to the extended nature of Ir 5*d* 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 self-consistency 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 configurations 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.

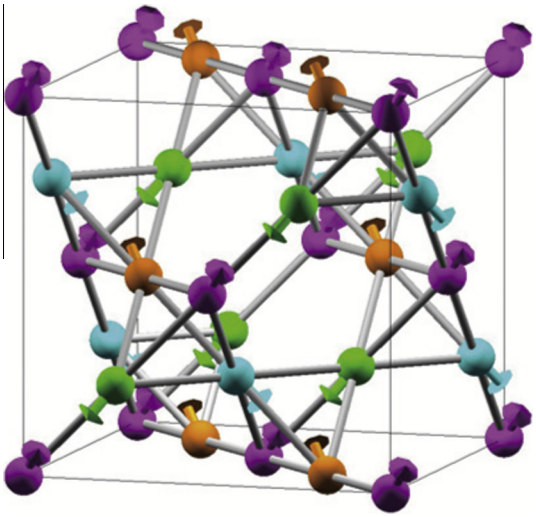

Fig. 1. The pyrochlore crystal structure showing the Ir corner sharing tetrahedral network and the "all-in/all-out" magnetic configuration predicted to occur for iridates (from Ref. [23]).

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 $Cd_2Os_2O_7$ 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 $Sm_2Ir_2O_7$, where it was shown that a 4 T 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 $Y_2Ir_2O_7$, 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