Computational Design of Axion Insulators Based on 5d Spinels Compounds

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Based on density functional calculation with LDA+U method, we propose that hypothetical Osmium compounds such as CaOs₂O₄ and SrOs₂O₄ can be stabilized in the geometrically frustrated spinel crystal structure. They also show some exotic electronic and magnetic properties in a reasonable range of on-site Coulomb correlation $U$ such as ferromagnetism and orbital magnetoelectric effect characteristic to Axion electrodynamics. Other electronic phases including 3D Dirac metal and Mott insulator exist and would make perspective 5d spinels ideal for applications.

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Recently, a theoretical work has played a key role in discovery of novel topological insulators (TI), where time reversal symmetry protects unusual surface states which could lead to electronic devices with new functionalities [13]. Unlike other fields of condensed matter physics, where most compounds are found haphazardly, here a number of new materials has been suggested based on band structure calculations [4,6], some of which have been confirmed experimentally [4,5].

In addition to these unusual electronic properties, introducing magnetic order on the surface of TIs can lead to a gap for surface states, leading to completely insulating behavior. Here, novel phenomena such as the half quantum Hall effect [9] and quantized magnetoelectric effect [10] appear. The latter is parameterized by the quantized value of the Axion electrodynamics parameter $\theta = \pi, \frac{\pi}{2}$. When time reversal symmetry, as well as spatial symmetries like inversion are broken in the bulk, the $\theta$ parameter is no longer quantized [12, 13]. However, in most known materials, it is extremely small eg. $\theta \approx 10^{-3}, 10^{-4}$ in Cr₂O₃ and BiFeO₃ respectively [13]. Thus, achieving large values of the $\theta$ parameter, even in the absence of quantization, is an important materials challenge. For sufficiently large $\theta$, $\theta > \pi/2$, it has been proposed that magnetic domain walls will be associated with conducting channels at the sample surface [10]. Recent experimental progress in introducing magnetism via dopants [14, 15] in Bi₂Se₃ has been reported, as well as tuning of chemical potential into the small gap induced on surface states [15]. Ideally however, magnetic topological insulators would combine band topology with intrinsic magnetic order, leading to large surface energy gaps. Unfortunately, most of known/proposed TIs 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 TI state of matter (see [17] for an exception).

Due to the interplay of strong SOC and moderate electronic correlations, very recently systems with 5$d$ electrons have received a lot of research attention [18, 23]. It has been suggested that pyrochlore iridates exhibit novel phases such, e.g., TI [21, 22], and topological semi-metal (TSM) [24] behavior. As in pyrochlores $A_2B_2O_7$, spinel compounds $AB_2O_4$ 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. Previous studies suggested that electronic $d^5$ configuration can realize an insulating state in 5$d$ compounds [19]. Based on valence arguments we therefore focus on spinel osmates $AO_2S_2O_4$ ($A$ is alkali metal element such as Mg, Ca, Sr, Ba), and investigate their electronic structure and magnetic properties using theoretical density functional calculations. Our numerical results reveal that the spinel structure can at least be a metastable crystallographic state for 5$d$ elements which is additionally supported by a very recent synthesis of an empty iridium spinel compound Ir₂O₄ [24]. Most interestingly, we find that the ground state is ferromagnetic and the electronic properties are sensitive to the $A$-site. Depending on Coulomb correlation, they show some exotic properties, and for the $U$ relevant to osmate, we predict $CaOs₂O₄$ and $SrOs₂O₄$ behave as magnetic axion insulators with $\theta = \pi$. The quantized value is protected by the inversion symmetry of the lattice. However, since the surfaces break inversion, typically they are gapped allowing us to define $\theta$. Unlike other proposals for generating large $\theta$, which exploit proximity to a topological insulator state [15], here a generalized parity criterion [25, 26] allows us to obtain large $\theta$ even when no proximate TI state exits.

We perform our electronic structure calculations for the spinel Osmates based on local spin density approximation (LSDA) to density functional theory (DFT) with
the full-potential, all-electron, linear-muffin-tin-orbital (LMTO) method\cite{27}. Despite the 5$d$ orbitals are spatially extended, recent theoretical and experimental work has given the evidence on the importance of Coulomb interactions in 5$d$ compounds\cite{19}. We utilize LSDA+U scheme\cite{28} to take into account the effect of Coulomb repulsion, and vary parameter $U$ between 0 and 1.5 eV. We use a $24 \times 24 \times 24$ k–mesh to perform Brillouin zone integration, and switch off symmetry operations in order to minimize possible numerical errors in studies of various (non–)collinear configurations. As the experimental lattice parameters are not available, we search for the stable crystal structures by locating the minimum in the calculated total energy as a function of the lattice constant and internal atomic coordinates.

Spinel structure (see Fig. 1) forms space group $Fd\bar{3}m$. In order to allow its relaxation, we change the lattice constant from 13 a.u. to 18 a.u. and vary the Os-O-Os bond angle from 90° to 120° with a step of 1°. We confirm that the choice of Coulomb $U$ has only small effect on the determination of lattice parameters, and list the lowest energy structures obtained by LDA+SO ($U$=0) calculations in Table I. For comparison, we also list the same parameters for the pyrochlore iridate $Y_2Ir_2O_7$. 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.

The 3$s$ band of Mg is lower in energy, and appears around the Fermi level, which makes MgOs$_2$O$_4$ always metallic. We therefore do not discuss this compound here and concentrate our study on CaOs$_2$O$_4$. Its band structure from non-magnetic LDA+SO calculation is found to be metallic and shown in Fig.2a. The energy bands around the Fermi level appear as $J_{\text{eff}}=1/2$ states similar to the ones found in Sr$_2$IrO$_4$\cite{19}, and also in $Y_2Ir_2O_7$\cite{23}, where a metal rather than the interesting topological insulator scenario of \cite{21} was obtained due to a 2–4–2 sequence of degeneracies at the $\Gamma$ point. As importance of electronic correlations for 5$d$ orbitals has been recently emphasized \cite{19}, we therefore perform LSDA+U+SO calculations. Although, the accurate value of $U$ is not known, the Os-Os bond length of spinel osmates is shorter than that of $Y_2Ir_2O_7$, and one can expect that the $U$ in CaOs$_2$O$_4$ is 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 CaOs$_2$O$_4$ is also non-collinear as recently found in $Y_2Ir_2O_7$\cite{23}. To search for possible magnetic ground states, we perform calculations by starting with a number of different collinear and noncollinear magnetic configurations including ferro– and antiferromagnetic (FM/AFM) collinear (010), (110), (111), as well as non–collinear all-in/all-out, 2-in/2-out, 3-in/1-out and some perpendicular configurations promoted by Dzyaloshinsky–Moriya interactions\cite{29}. We find that when $U$ is less than 1.3 eV, only the FM-(010)-configuration retains its initial input magnetization direction; in all other configurations the moments depart from their input orientation. We also consider a two-up, two-down state which is suggested by the strong coupling limit where Os-O bond is nearly 90°. As shown in \cite{30}, this leads to a 'Kitaev type' ferromagnetic interaction for spin components perpendicular to the plane. Although this structure is found to be stable for $U < 0.8$ eV, it is higher in energy than the ferromagnetic state as shown in Table II. Regardless of the value of $U$, the 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.

This is understood by examining lattice parameters in Table I, where the main difference between pyrochlore iridates and spinel osmates is the Os–Os bond angle and the Os–Os bond length. Due to the extended nature of 5$d$ orbitals, the 5$d$–2$p$ hybridization is strong and important for the inter–atomic exchange interaction. In $Y_2Ir_2O_7$, the Ir–O–Ir bond angle is much larger than 90° and Ir–O–Ir antiferromagnetic (AFM) superexchange interaction is dominant. This results in a strong magnetic frustration and non–collinear ground state magnetic configuration\cite{23}. In contrast to pyrochlores, the

\begin{table}[h]
\centering
\caption{Theoretically determined structure 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.}
\begin{tabular}{ccc}
\hline
& Angle & Os-O & Os-Os \\
\hline
CaOs$_2$O$_4$ & 98.5° & 3.07 Å & 2.04 Å \\
SrOs$_2$O$_4$ & 94.6° & 3.12 Å & 2.05 Å \\
BaOs$_2$O$_4$ & 103.1° & 3.28 Å & 2.11 Å \\
$Y_2Ir_2O_4$ & 129.7° & 3.60 Å & 1.99 Å \\
\hline
\end{tabular}
\end{table}
Os–O–Os angle in spinel osmates is close to 90°, while Os 5d orbitals have stronger overlap, making a direct ferromagnetic exchange to be important for CaOs$_2$O$_4$.

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.2b and Fig.2c, 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 100×100×100 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.

In order to examine whether the system becomes an Axion insulator, we recall that similar to the Fu and Kane criterion[5], which is designed for non–magnetic systems with inversion symmetry, one can still use the parity eigenvalues for the states at eight Time Reversal Invariant Momenta (TRIMs) of CaOs$_2$O$_4$. For the values of U=0.5 and 1.5 eV, the summation of the number of empty $t_{2g}$ states with odd parity at Γ, X, Y, and Z points is 24. If all of 24 $t_{2g}$ bands are fully occupied, the system cannot possess any topologically non–trivial properties. Thus, 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.

Since topological insulators must be separated from trivial insulators by a semi–metallic state[23], with 3D Dirac like dispersion, we additionally perform calculations for a number of intermediate values of $U$ to find out the boundary between semi-metal and Axion insulator as well as between semi-metal and Mott insulator. Our calculations for $U$‘s varying from 1.0 to 1.3 eV show that there are 3D Dirac crossings close to (0.02, x, 0.02)2π/a points of the BZ, where the value of x will change with $U$. With both decreasing and increasing the $U$, the Dirac crossings are expected to be close to (0.02, x, 0.02)2π/a points of the BZ.

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, the value of U, the summation of the number of empty $t_{2g}$ states with odd parity 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 III, where the summation of the number of the odd states are 6 and 4 for U=1.5 and 0.5 eV, respectively. Therefore, according to Eq.1 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.

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point moves and annihilates by meeting with other Dirac points, thus opening the energy gap and forming either the \( \theta = \pi \) Axion insulator or normal insulator, respectively. To summarize, our electronic phase diagram (see Fig. 3) for \( U < 0.4 \text{ eV} \), predicts CaOs\(_2\)O\(_4\) to be a metal; for \( 0.4 < U < 0.9 \text{ eV} \), an axion insulator; for \( 0.9 < U < 1.4 \text{ eV} \), a topological semi-metal; for \( U > 1.4 \text{ eV} \), a Mott insulator. Note, unlike in the cubic pyrochlore iridates [21], where the topological semi-metal has Dirac points exactly at the Fermi energy, here, because of lower symmetry of the magnetic order, the Dirac points are slightly above or below the Fermi energy. To see the sensitivity of these results to the lattice parameters we perform calculations with increasing and decreasing the volume by 6%, as well as adjusting the internal coordinates and performing small changes in Os-O-Os bond angle. We confirm that while there are some little changes in calculated energy bands, our predictions on Axion insulator behavior are robust.

Replacing Ca by Sr, both the Os-O-Os bond angle and the bond length will change as shown in Table I. However, same as CaOs\(_2\)O\(_4\), SrOs\(_2\)O\(_4\) shows the same rich phase diagram as a function of \( U \).

We finally study BaOs\(_2\)O\(_4\) which has both the largest bond angle and bond length as shown in Table I. These differences significantly affect its band structure: the LDA+SO calculation with \( U=0 \) gives that at the \( \Gamma \) point the eight \( J_{\text{eff}} = 1/2 \) 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 Pesin and Balents to realize topological insulating scenario in sequence of levels is the same as recently suggested by Pesin and Balents to realize topological insulating scenario in perovskite manganites [22]. Unfortunately, the bands crossing the Fermi level exist and cannot be removed by slight adjusting the lattice constant. Same with CaOs\(_2\)O\(_4\) and SrOs\(_2\)O\(_4\), considering the Coulomb interaction \( U \) will induce magnetism, but we do not find axion-insulator or Dirac-metal state for BaOs\(_2\)O\(_4\) for any reasonable \( U \).

To summarize, using density functional based electronic structure calculations, we have found that depending on the strength of the Coulomb correlation among the 5d orbitals several exotic electronic phases may be realized in Os based spinel compounds. In particular a magnetic topological insulating phase (axion insulator) may be realized in CaOs\(_2\)O\(_4\) and SrOs\(_2\)O\(_4\) with large orbital magneto–electric parameter \( \theta = \pi \). This research suggests that new functionalities such as controlling electrical[13] and optical [31] properties via magnetic textures, can be found in the new 5d spinel materials that we propose.

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