Topological insulators in filled skutterudites

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We propose new topological insulators in cerium-filled skutterudite (FS) compounds based on *ab initio* calculations. We find that two compounds, $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$, are zero gap materials with band inversions between Os-d and Ce-f orbitals, similar to HgTe. Both compounds are predicted to become topological Kondo insulators at low temperatures, which are Kondo insulators in the bulk but with robust Dirac surface states on the boundary. Furthermore, this family of topological insulators has more unique features. Due to similar lattice parameters there will be a good proximity effect with other superconducting FS compounds, which may realize Majorana fermions. Additionally, the experimentally observed antiferromagnetic phase of $CeOs_4Sb_{12}$ at very low temperature provides a way to realize the massive Dirac fermion with topological magnetoelectric effects.

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I. INTRODUCTION

The topological insulator (TI), a new quantum state, has attracted recent attention[1–4] for both fundamental physics and technological applications. TIs have an energy gap in the bulk and metallic edge or surface states on the boundary which are protected by time-reversal symmetry (TRS). With a TRS breaking perturbation on the surface, the effective electromagnetic response is described by the topological term $S_\theta = (\theta/2\pi)(\alpha/2\pi)\int \mathrm{d}^3x\mathrm{d}t\mathbf{E}\cdot\mathbf{B}$, with α being the fine-structure constant. The parameter θ is equal to π for a topological insulator and 0 for a trivial insulator.[5] This topological response supports many topological phenomena, such as an image magnetic monopole induced by a point charge,[6] topological Faraday and Kerr effects,[5] and the realization of the axion field in condensed-matter physics.[7] Therefore magnetically doped TIs with magnetic impurities and ferromagnetism are of particular interest. In addition, superconducting proximity effects on the surface states of a three-dimensional (3D) TI have been proposed[8] to realize the Majorana fermion, which is a promising candidate for quantum computation application. We theoretically predict new TI materials which could realize both the antiferromagnetic (AFM) TI and the Majorana fermion. We furthermore predict them to be topological Kondo insulators, since they are known to be Kondo insulators at low temperatures.

The first TIs, HgTe quantum wells, were predicted theoretically[9] and subsequently observed experimentally.[10] The basic mechanism of band inversion driven by spin-orbit coupling (SOC) served as a template for most TIs discovered later. Shortly after this, many TIs were proposed and experimentally measured, e.g., Bi_2Se_3, Bi_2Te_3, Sb_2Te_3,[11–13] and $TlBiTe_2$.[14,15] Most of them have been known as good thermoelectric materials. At the same time theoretical calculations have predicted many other TIs which are waiting for experimental verification.[3,4] We propose $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$ within the filled skutterudite (FS) class to be TIs. The FS compounds[16] have the chemical formula RT_4X_{12} (R = rare earth; T = Fe, Ru, or Os; and X= P, As, or Sb), in which heavy elements are expected to induce strong SOC. Similar to Bi_2Se_3, they are also known for excellent thermoelectric properties.[17,18] Moreover, they exhibit a rich variety of electronic and magnetic ground states at low temperature,[19–21] including superconductivity, ferromagnetism, antiferromagnetism, and Kondo insulating behavior. Among these compounds, most Ce-based FSs are reported to be insulators.[19,22] All these reasons motivate us to investigate the Ce-based FSs as TI candidates, which can accommodate both magnetism and superconductivity proximity effects.

II. CRYSTAL STRUCTURE AND CALCULATION METHODS

The FSs crystallize in the bcc structure (Im3) shown in Fig. 1 and have inversion symmetry. The R atoms, the inversion centers, are located at the body center and corners of the cubic structure and are surrounded by a cage of corner-sharing T_4X_{12} octahedra. We calculated the electronic properties of CeT_4X_{12} by density-functional theory (DFT) within a Perdew-Burke-Ernzerbof-type generalized gradient approximation (GGA).[23] Using the Vienna *ab initio* simulation package (VASP)[24] with the projected augmented wave method, we adopted the experimental lattice constants (see Ref. 19) and fully optimized the atomic positions in the unit cell. The optimized atomic positions agree well with experimental values.[25] SOC is included in our calculations. In addition, the WIEN2K package[26] was also used for cross-checking.

III. RESULTS AND DISCUSSION

The calculated GGA band gap as well as the experimental values are shown in Table I. Our results are well consistent with previous calculations for $CeFe_4P_{12}$, $CeFe_4Sb_{12}$,[27] and $CeOs_4Sb_{12}$.[28] Most materials have a small gap while $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$ are gapless semimetals, as can be seen in the band structures in Fig. 2. $CeOs_4P_{12}$ is a good example of the class of gapped materials. The Ce-4f states hybridize with both Os-5d and P-3p states near the Fermi energy and a band gap opens due to the hybridization. The lower conduction bands are mainly composed of Ce-4f orbitals, while the highest valence band mainly consists of Os-5d orbitals. Since GGA tends to underestimate the interatomic correlation of Ce-4f electrons and thereby underestimates the bandwidth, the energy gap between f and d bands could

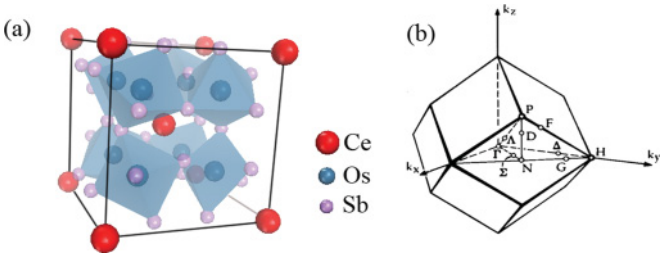

FIG. 1. (Color online) (a) Crystal structures of the filled skutterudites RT_4X_{12} (R = rare earth; T = Fe, Ru, or Os; and X= P, As, or Sb) in a bcc lattice and (b) the corresponding first Brillouin zone, in which Γ, N, and H are time-reversal invariant momenta.

be overestimated[27] in this way, in contrast to the usual gap underestimation of DFT calculation. This can explain why our calculated band gap is larger than the experimental one. On the other hand, $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$ have a d-f band inversion near the Fermi energy. The d band moves into the conduction band. Both the lowest conduction band and the highest valence band are composed of f orbitals and are degenerate at the Γ point as a result of the cubic symmetry. Therefore they have a zero energy gap, similar to HgTe.

In order to determine their topological features, we use the parity criteria proposed by Fu and Kane[29] to calculate the $\mathbb{Z}_2$ topological index. The $\mathbb{Z}_2$ index is determined by the parity of occupied bands on each time-reversal invariant momentum. The bcc Brillouin zone has eight time-reversal invariant points, including the Γ point, six points equivalent to $N(\pi/a,\pi/a,0)$ by the point-group symmetry, and one H point $(2\pi/a,0,0)$. Here k points are denoted in Cartesian coordinates with a being the lattice constant, while N points can also be labeled as (0.5,0,0) or (0.5,0,5,0), and H points can be labeled as (0.5,0.5,0.5) in units of reciprocal lattice vectors. We listed the product of parities for all occupied states at these k points and corresponding $\mathbb{Z}_2$ invariants in Table I. Among these FSs $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$ are found to be topologically nontrivial with $\mathbb{Z}_2$ (1;000). Compared to those topologically trivial FSs, e.g., $CeOs_4P_{12}$, a band inversion between Os-d (Γ_5^+) and Ce-f (Γ_{67}^-) bands can found in the band structures, as shown in Fig. 2. In order to understand the band structure better and to provide a comparison with experiment, we show

TABLE I. Calculated and experimental (see Ref. 21) band gap in units of eV as well as $\mathbb{Z}_2$ topological invariants. The products of parities for time-reversal invariant points in the bcc Brillouin zone are shown, including the Γ point, one H point, and six N points.

FSs	E_g(calc.)	E_g(exp.)	Parity	$\mathbb{Z}_2$
$CeFe_4P_{12}$	0.38	0.13		
$CeFe_4As_{12}$	0.16	0,0.01		
$CeFe_4Sb_{12}$	0.08	0	1 Γ(−)	
$CeRu_4P_{12}$	0.12	0.086	1 H(−)	(0;000)
$CeRu_4As_{12}$	0.13	0,0.0043	6 N(−)	
$CeRu_4Sb_{12}$	0.12	0		
$CeOs_4P_{12}$	0.12	0.034		
			1 Γ(+)	
$CeOs_4As_{12}$	0.00	0.0047	1 H(−)	(1;000)
$CeOs_4Sb_{12}$	0.00	0.0009	6 N(−)	

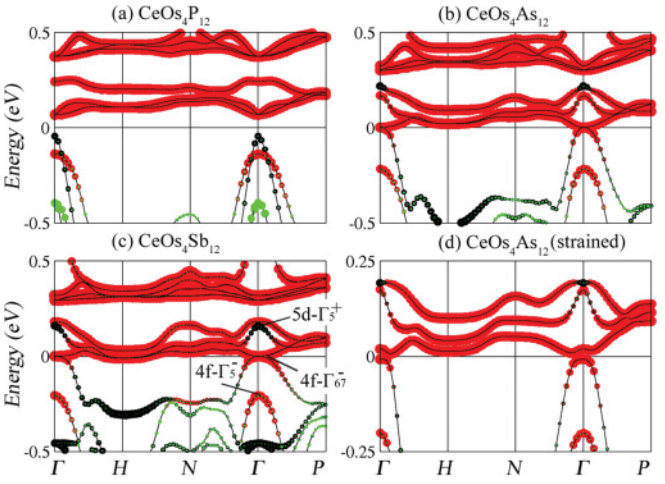

FIG. 2. (Color online) Band structures of (a) $CeOs_4P_{12}$, (b)$CeOs_4As_{12}$, (c) $CeOs_4Sb_{12}$, and (d) $CeOs_4As_{12}$ under 2% uniaxial strain. Red/gray dots stand for the components of Ce-f states, black dots stand for Os-d states, and green/light gray stand for p states. The size of the dots represents the relative amplitude of corresponding components. The Fermi energy is set to zero.

the Fermi surface at $E_F = 0.0$ and -0.1 eV for $CeOs_4Sb_{12}$ in Fig. 3. There are two small electron pockets around H from the conduction f states and a small hole pocket at Γ from the valence f state at $E_F = 0.0$ eV, since the points of degeneracy do not coincide at the Fermi level. The electron and hole pockets are compensated by each other. For $E_F = -0.1$ eV, there is only a hole pocket around the Γ point with a little anisotropy, which is due to the top valence band.

As seen above, $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$ have a zero energy gap. To drive them into fully gapped topological insulators, the degeneracy at the Γ point needs to be lifted.

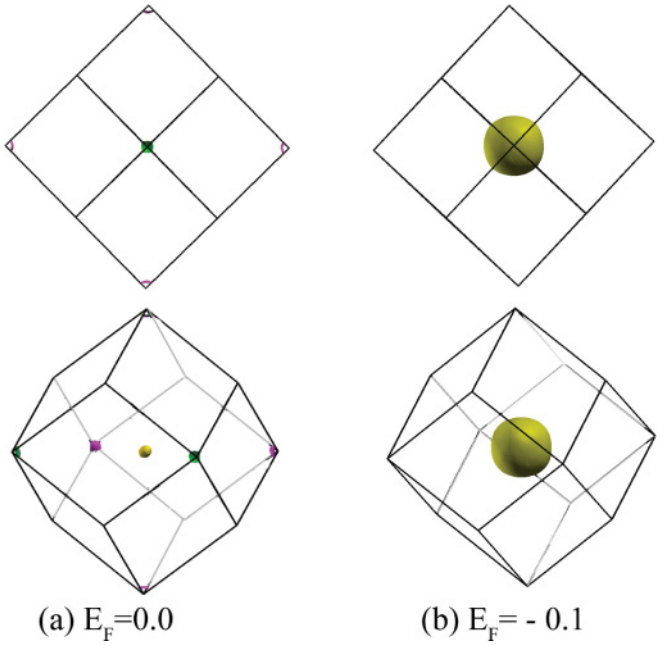

FIG. 3. (Color online) Fermi surface in the first Brillouin zone for $CeOs_4Sb_{12}$ at E_F = (a) 0.0 and (b) −0.1 eV. The top and side views are shown in the upper and lower panels, respectively.

There are several possible ways to open a gap. One possibility is to fabricate quantum wells using $CeOs_4As_{12}$ or $CeOs_4Sb_{12}$ together with the above-mentioned topologically trivial FSs as barrier layers, similar to HgTe-CdTe quantum wells.[9,10] The quantum well will still have an inverted band structure together with an energy gap. Then the two-dimensional (2D) TI (the quantum spin Hall effect) can be realized. In addition, strain can break the cubic symmetry and thereby lift up the Γ_{67}^- degeneracy. Then a gap opens at Γ, and these two materials will become 3D topological insulators, similar to strained HgTe.[29–31] In our calculations, 2% uniaxial strain along the (001) direction can open an energy gap at Γ for $CeOs_4As_{12}$. It should be noted that here applied strain does not change the parity and the ordering of these bands and therefore the $\mathbb{Z}_2$ invariants remain the same, which can be seen in Fig. 2(d) as the d-f band inversion feature does not change. Finally, a new feature in these two materials compared to previously proposed TI materials is that they can be 3D topological Kondo insulators.[32] At low temperature ($T < 135$ K for $CeOs_4As_{12}$ and $T < 50$ K for $CeOs_4Sb_{12}$), both materials are reported to be Kondo insulators.[33,34] Though the GGA band gap is zero, at low temperature the residual carriers in the system can form Kondo singlets with localized f states, leading to a Kondo insulating behavior in transport. Moreover, both materials have p-type carriers with a low carrier density,[35,36] so that the Fermi level cross the highest valence band and does not affect the band inversion between f and d bands; thus the $\mathbb{Z}_2$ does not change. Consequently, when the carriers become insulating due to the Kondo effect, the topological surface states due to the band inversion are expected to remain robust on the surface, so that the system becomes a "topological Kondo insulator" rather than an ordinary Kondo insulator. The topological Kondo insulator has a Kondo gap in the bulk but topological metallic surface states. It is also characterized by the $\mathbb{Z}_2$ topological invariants. In contrast, if the carrier is n type, the bands involved in band inversion will be buried below the Fermi level, so that the topologically nontrivial nature of the system is lost for a high enough carrier density. If the carrier density in this system can be tuned, we expect to see a topological phase transition between the topological Kondo insulator phase for p doping and the ordinary Kondo insulator phase for n doping. It should be noticed that the topological Kondo insulators studied here are different from those proposed by Dzero *et al.*[32] Since the residual carrier density in the FS compounds is low, the Kondo effect leading to a Kondo insulator state is expected to be induced by magnetic impurities, rather than a Kondo lattice formed by f electrons.[32] These magnetic impurities will be screened by residual carriers when the Kondo insulator forms. Therefore TRS still remains in the system. At first glance the Ce-filled FSs have a similar electronic structure to the rare-earth containing Heusler compounds, which were also recently predicted to be HgTe-like TIs (see Refs. 37 and 38 and references therein). Among them, heavy-fermion systems (e.g., YbPtBi) and superconductivity (e.g., in LaBiPt) are closely related to f electrons. However, the topological features of the Heusler compounds are related to a s-p band inversion, different from these FSs. Even though we did not take the strong correlation effect of $4f$ electrons into account, we believe our GGA calculations still reveal the salient features of these materials. From Fig. 2, $CeOs_4As_{12}$ has a $4f$ occupancy close to one and $CeOs_4Sb_{12}$ has a $4f$ occupancy a little larger than one. In metallic Ce systems, a tiny deviation from one is known to produce Kondo-type physics. Our results agree well with this picture. In principle, one can take into account correlation effects by performing local-density-approximation-plus-U (LDA + U) or GGA + U calculations. We indeed found that d-f band inversion remains in GGA + U for a fair $U = 3.0$-eV to Ce-$4f$ orbital[39] in these two compounds, preserving the nontrival topological feature. But it should be noted that f states are pushed far above when $U > 4.0$ eV, resulting in a large energy gap. This is not in agreement with experiments, where both materials become Kondo insulators with a small gap at low temperature (see Table I). Moreover, our DFT calculations show the same band alignments as the recent photoemission experiment:[40] $4f - \Gamma_5^-$ and $4f - \Gamma_{67}^-$ are close to E_F and mixed with the conducting bands, in which $4f - \Gamma_5^-$ is lower. For the systems discussed here f electrons appear near the Fermi level and hybridize with the conducting electrons. Methods beyond LDA + U, such as dynamical mean-field theory (DMFT), could be an option, because this method takes correlations into account and allows hybridization. However, we do not expect that DMFT will change the d-f band inversion, similar to the case in a recent prediction of topological Mott insulators.[41] In Ref. 41 DFT calculations give a d-f band inversion, consistent with DMFT.

Recent experiments reveal that $CeOs_4Sb_{12}$ has a AFM phase below 1 K.[42] (It should be noted that in the above calculations we constrained the magnetic moments as zero to keep the TRS, since the total-energy difference with and without magnetic moments is negligibly small and beyond the accuracy of DFT calculations.) The existence of AFM order provides a possible way to realize the massive Dirac fermion state with many exotic topological phenomena without requiring magnetic doping. For example, axions were predicted to exist inside magnetic doped TIs,[7] which are weakly interacting particles originally postulated in the standard model of particle physics to explain the missing dark matter of the universe.[43,44] In the TI $CeOs_4Sb_{12}$, the AFM order breaks the TRS and then the massless Dirac fermions on the surface will become massive with a gap opening at the Dirac point. Due to the topological electromagnetic response S_θ, the spin wave inside the AFM material is expected to couple to the electromagnetic field exactly like axions, realizing the dynamical axion field. Such an "axionic" spin wave couples to the electric field of photons with the coupling strength tuned by a background magnetic field. This leads to a new kind of tunable optical modulator.[7] On the other hand, the existence of many superconductors in the FS family, e.g., LaT_4X_{12}, offers the possibility to realize Majorana fermions. Different from Dirac fermions, Majorana fermions are their own antiparticles, so that a pair can annihilate each other. They attract great interest in condensed-matter physics, because they could be utilized to realize a fault-tolerant topological quantum computer. Recently an ordinary s-wave superconductor combined with a TI has been proposed by Fu and Kane[8] to realize Majorana fermions. When a superconductor is close to the surface of a 3D TI, the topological surface states become superconducting due to the proximity effect. The superconducting state has half degrees of freedom compared to the superconductor. This is

exactly what is required to host Majorana fermions, which are predicted to exist inside vortices. Up to now, several materials have been proposed to realize them, such as Cu doped Bi_2Se_3[45] and p-type $TlBiTe_2$.[14] In this work we present the possibility to use a superconducting FS material to form an interface with $CeOs_4As_{12}$ or $CeOs_4Sb_{12}$. Then topological surface states of either the TI or the topological Kondo insulator could become superconducting. This offers a new possibility to realize Majorana fermions.

IV. CONCLUSIONS

In summary, we proposed two FS compounds, $CeOs_4As_{12}$ and $CeOs_4Sb_{12}$, to be new topological insulators. They have a zero band gap due to band inversion driven by spin-orbit coupling, similar to HgTe. It is possible to form quantum wells to open the gap and make them 2D TIs. Applied strain can also open a gap and turn them into 3D TIs. Up to now the experimentally measured TI materials include only s-p band inversion such as HgTe and p-p band inversion such as Bi_2Se_3. In contrast, the two TIs proposed here have d-f band inversion. They furthermore have two advantages compared to previous ones. First, they could have good proximity with other superconducting FS compounds for the possible realization of Majorana fermions. Second, the antiferromagnetism of $CeOs_4Sb_{12}$ at low temperature provides a way to realize the massive Dirac fermion with exotic topological phenomena. Moreover, their rich physics offers a platform for topological Kondo effects. At low temperature, both compounds are predicted to become topological Kondo insulators; i.e., they are Kondo insulators in the bulk but have robust metallic surface states. After the completion of this work, we became aware of recent work on $CoSb_3$,[46] which also belongs to the skutterudite family and has a crystal structure similar to FSs. It is found to be near the phase-transition point between the topological insulator and the trivial insulator.

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