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 CeOs₄As₁₂ and CeOs₄Sb₁₂ are zero gap materials with band inversion between Os-σ and Ce-f orbitals, which are thus parent compounds of two and three-dimensional topological insulators just like bulk HgTe. At low temperature, both compounds become topological Kondo insulators, which are Kondo insulators in the bulk, but have robust Dirac surface states on the boundary. This new family of topological insulators has two advantages compared to previous ones. First, they can have good proximity effect with other superconducting FS compounds to realize Majorana fermions. Second, the antiferromagnetism of CeOs₄Sb₁₂ at low temperature provides a way to realize the massive Dirac fermion in an important class of topological phenomena.

The topological insulator (TI) is a new state of quantum matter attracting extensive attention[1][4] for both fundamental physics and technical applications recently. TIs have insulating energy gap in the bulk and accommodate gapless edge or surface states which are protected by time-reversal symmetry (TRS). With TRS broken on the surface of a three-dimensional (3D) insulator, the effective electromagnetic response is described by the topological term \( S_0 = (\theta/2\pi)(\alpha/2\pi) \int d^3x d\mathbf{E} \cdot \mathbf{B} \), with \( \alpha \) the fine-structure constant and the parameter \( \theta = 0 \) or \( \pi \) for trivial insulator and TI, respectively[5]. This topological response supports many novel topological phenomena, such as image magnetic monopole induced by a point charge[6], topological Faraday and Kerr effects[5] and the realization of axion field in condensed matter physics[7]. Therefore magnetically doped TI for magnetic impurities and ferromagnetism effects are of particular interest. In addition, superconducting proximity effects on the surface states of a 3D TI[8] have been proposed to realize the Majorana fermion which is a promising candidate for quantum computation application. In this letter we report new TI materials which could realize both the antiferromagnetic (AFM) TI and the Majorana fermion. Furthermore they are found to be topological Kondo insulators at low temperature.

HgTe quantum wells were the first TI predicted theoretically[9] and subsequently observed experimentally[10]. The basic mechanism of band inversion driven by spin-orbit coupling (SOC) was discovered in this work and provides a template for most TIs discovered later. Thereafter, many TIs have been proposed and experimentally measured, e.g. Bi₂Se₃ and Bi₂Te₃ crystals[11][13] and TIBiTe₂[14][15] crystals. Most of them are known as thermoelectric materials[16].

FIG. 1: (Color online) (a) Crystal structures in bcc lattice for filled skutterudites \( RT₄X₁₂ \) (\( R \)= rare-earth, \( T \)= Fe, Ru or Os, and \( X \)= P, As or Sb) in a bcc lattice and (b) corresponding first Brillouin zone, in which \( \Gamma, N \) and \( H \) are time-reversal-invariant points.

dated(FS) class are TI materials. The FS compounds[10] have a chemical formula \( RT₄X₁₂ \) (\( R \)= 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 Bi₂Se₃ materials, 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 insulator behavior with hybridization gaps. Among these compounds, most of 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 magnetism and superconductivity proximity.

The FSs crystallize in the bcc structure (Im3) shown in Fig.1 and have inversion symmetry. The \( R \) atoms, the inversion centres, are located at the body centre and corners of the cubic structure and surrounded by a cage of corner-sharing \( T₄X₁₂ \) octahedra. We calculated the electronic properties of CeT₄X₁₂ by density-functional theory (DFT) within Perdew-burke-Ernzerhof
TABLE I: The calculated band gap and the $Z_2$ topological index. We listed the calculated band gap $E_g$(calc.) together with the experimental value $E_g$(exp.) (see ref. [21]) in unit of $\text{eV}$. The products of parities for time-reversal invariant points in the $bcc$ Brillouin zone are shown, including the $\Gamma$ point and one $H$ point and six $N$ points.

| FSs          | $E_g$(calc.) | $E_g$(exp.) | Parity | $Z_2$ |
|--------------|--------------|-------------|--------|-------|
| CeFe$_4$P$_{12}$ | 0.38         | 0.13        | $\Gamma$(-) |      |
| CeFe$_4$As$_{12}$ | 0.16         | 0.001       | $\Gamma$(-) |      |
| CeFe$_4$Sb$_{12}$ | 0.08         | 0           | $\Gamma$(-) |      |
| CeRu$_4$P$_{12}$ | 0.12         | 0.086       | $H$(-) (0:000) |    |
| CeRu$_4$As$_{12}$ | 0.13         | 0.00043     | $N$(-) (0:000) |    |
| CeRu$_4$Sb$_{12}$ | 0.12         | 0           | $H$(-) (1:000) |    |
| CeOs$_4$P$_{12}$ | 0.12         | 0.034       | $\Gamma$(-) |      |
| CeOs$_4$As$_{12}$ | 0.00         | 0.0047      | $H$(-) |      |
| CeOs$_4$Sb$_{12}$ | 0.00         | 0.0009      | $N$(-) |      |

type generalized gradient approximation (GGA). The Vienna ab initio simulation package (VASP) [23] with the projected augmented wave method are employed. We adopted the experimental lattice constants (see ref. [19]) and fully optimized the atomic positions in the unit cell. SOC is included in our calculations. In addition, WIEN2k package [24] was also used for cross-checking.

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$_4$P$_{12}$ and CeFe$_4$Sb$_{12}$ [27] and CeOs$_4$Sb$_{12}$ [26]. Most materials have a small gap while CeOs$_4$As$_{12}$ and CeOs$_4$Sb$_{12}$ have a zero gap. We show the band structure of CeOs$_4$X$_{12}$ in Fig.2. Take CeOs$_4$P$_{12}$ as an example. The Ce-4$f$ states hybridize with both Os-5$d$ and P-3$p$ states near the Fermi energy. A band gap opens due to their hybridization. The hybridization can be overestimated, since GGA tends to underestimate the inter-atomic correlation of Ce-4$f$ electrons. Then the calculated band gap is expected to be overestimated [25], which is different from the usual gap underestimation of DFT calculation. This can explain why our calculated band gap is larger than the experimental one. For all these three FSs in Fig.2, the Ce-4$f$ states exist near the valence top and becomes dominant as the narrow spin-orbit splitting bands at the conduction bottom.

In order to determine their topological features, we use the parity criteria proposed by Fu and Kane [27] to calculate the $Z_2$ topological index. The $Z_2$ index is determined by the parity of occupied bands on each time-reversal invariant momenta. The $bcc$ Brillouin zone has eight time-reversal-invariant points, including the $\Gamma$ point, six $N$ points equivalent to $(\pi,0,0)$ or $(\pi,\pi,0)$ by point group symmetry, and one $H$ point $(\pi,\pi,\pi)$. We listed the product of parities for all occupied states at these $k$-points and corresponding $Z_2$ index in Table I. Among them FSs CeOs$_4$As$_{12}$ and CeOs$_4$Sb$_{12}$ are found to be topological nontrivial with $Z_2$(1:000). Compared to those topological trivial FSs, e.g. CeOs$_4$P$_{12}$, a band inversion between Os-$d$ $(\Gamma_-^+)$ and Os-$f$ $(\Gamma_5^+)$ bands is found in the band structures, as shown in Fig. 2. The $d(\Gamma_5^+)$ state enters the conduction bands. Both the valence band maximum and conduction band minimum at $\Gamma$ are $f$ $(\Gamma_6^-)$ states and touch with each other. The degeneracy induces a zero band gap. This is similar with HgTe which has $s$ $(\Gamma_6^-)$-$p$ $(\Gamma_8^-)$ band inversion. In order to understand the band structure better, we showed in Fig.3 the Fermi surface at $E_F$ = 0.0 and -0.1 eV cases for CeOs$_4$Sb$_{12}$. At the Fermi surface, there is a small electron pocket around $H$ point from $f$ bands and a tiny hole pocket at $\Gamma$. For $E_F$ slightly below zero, there is a hole packet around $G$ with a little anisotropy, which is due to the top valence band.

To drive CeOs$_4$As$_{12}$ and CeOs$_4$Sb$_{12}$ into real topological insulators, the degeneracy at $\Gamma$ point needs to be lifted. There are several possible ways to lift the degeneracy. Firstly, it is possible to fabricate quantum wells using CeOs$_4$As$_{12}$ or CeOs$_4$Sb$_{12}$ together with above topological trivial FSs as barrier layers, like HgTe-CdTe quantum wells [28, 10]. Then the 2D TI (quantum spin hall effect) can be realized. Secondly, strain can lift up the $\Gamma_6^-$ degeneracy and open a gap at $\Gamma$. Then these two materials will become 3D topological insulators, similar to strained HgTe [27, 29]. For example, 2% uniaxial strain along $(001)$ direction can open an energy gap at $\Gamma$ for CeOs$_4$As$_{12}$ in our calculation, as shown in Fig. 2(d). Thirdly, a new feature in these two materials compared to previously proposed TI materials is that they can be 3D topological Kondo insulators [30]. At low temperature ($T < 135$ K for CeOs$_4$As$_{12}$ and $T < 50$ K for CeOs$_4$Sb$_{12}$), both materials are reported to be Kondo insulators [31, 32]. 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 insulator behavior in transport. Moreover, both materials have $p$-type carrier [33, 34], so that the Fermi level does not cross the bands involved in the band inversion. Consequently, when the carriers become insulating due to Kondo effect, the topological surface state due to the band inversion are expected to remain robust on the surface, so that the system becomes a “topological Kondo insulator” rather than ordinary Kondo insulators. On the contrary, if the carrier is $n$-type, the bands involved in band inversion will be buried below the Fermi level, so that the topological nontrivial nature of the system is lost for 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. [31], since the residual carrier density in the FS compounds is low, so that 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. On a first view the Ce filled FSs have similar electronic structure like the rare earth containing Heusler compounds, which are also predicted to be HgTe-like TIs recently [35, 36]. Among them the heavy-fermion behavior (e.g. YbPtBi) and superconductivity (e.g. LaBiPd) are closely related to $f$ electrons. However, the topological feature of the Heusler compounds are related to a $s-p$ band inversion, different from these FSs.

Recent experiments reveal that CeOs$_4$Sb$_{12}$ has a AFM phase below 1 K [37]. (It should be noted in above calculations we constrained the magnetic moments as zero to keep the TRS, since the total energy difference between with and without magnetic moments is negligible small and beyond the accuracy of DF 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, the spin wave in the AFM phase is expected to have “axionic” coupling to photons, leading to the axion polariton effect and a new kind of tunable optical modulator [7]. Moreover, in proximity with their superconducting FS neighbors, e.g. LaT$_4$X$_{12}$, both CeOs$_4$As$_{12}$ and CeOs$_4$Sb$_{12}$ can help to realize the topological superconductivity as both 3D and 2D TIs.

In summary, we proposed two FS compounds CeOs$_4$As$_{12}$ and CeOs$_4$Sb$_{12}$ as new topological insulators. 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$_2$Se$_3$ family. Different from them, these two TIs have $d$-$f$ band inversion. They have two advantages compared to previous ones. Firstly, they can have good proximity with other superconducting FS compounds to realize Majorana fermions. Secondly, the antiferromagnetism of CeOs$_4$Sb$_{12}$ 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 become topological Kondo insulators, i.e. they are Kondo insulators in the bulk, but have robust Dirac surface states on the boundary. After the completion of this work, we became aware of recent work on the skutterudite CoSb$_3$ [38], which is near the topological critical point.

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FIG. 3: (Color online) Fermi surface for CeOs$_4$Sb$_{12}$ at $E_F = (a) 0.0$ and (b) $-0.1$ eV. The top and side views are shown in upper and lower panels, respectively.

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