Pyrite-type OsX$_2$ (X = Se, Te) Crystals: A Novel Topological Material for Selective Control of Surface Spin Current

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Abstract

Understanding spin textures of the surface states of topologically nontrivial materials is essential for realizing their potential for applications such as spintronics. Here we propose the existence of symmetry-protected energy- and direction-dependent surface spin textures on the (001) surface of pyrite-type crystals OsX$_2$ (X= Se, Te) using first principles calculations. We show that the formation of these low-energy states is a consequence of a transformation from a topologically trivial to nontrivial state induced by spin orbit interactions. The unconventional spin textures of these surface states feature an in-plane to out-of-plane spin polarization transition in the momentum space. Moreover, the surface spin direction and magnitude can be selectively filtered in specific energy ranges. In addition, we have observed the existence of three-dimensional nodal lines in these crystals surviving the spin orbit coupling effect. Our findings are expected to provide new avenues for experimentalists to detect the surface spin textures in topologically nontrivial materials and can reveal new insights to designing novel spin-based nanoelectronic devices.
INTRODUCTION

Materials with nontrivial topological properties provide a rich playground for discovering unconventional fermions as well as unveiling novel physical phenomena such as giant magnetoresistance and superconductivity [1, 2]. Over the last few years, topological states of matter have been revealed in a diverse spectrum of electronic structures from insulators [3] to semimetals [4, 5] and metals [6, 7]. Several strategies have been proposed to effectively predict new materials with nontrivial topology by combining the knowledge of dimensionality, crystal symmetry and band theory [2, 8]. In particular, seeking materials that can demonstrate highly orientational and controllable spin structures is rapidly emerging as an active area of research [9, 10]. These materials have the potential of exhibiting exotic spin-dependent transport properties, such as inverse spin Hall effect and spin-transfer torque on the surface states [11, 12], which can be beneficial for the development of spintronics and spin detection devices [13, 14].

Each class of topological materials possesses unique spin textures associated with their surface states and spin orbital coupling (SOC) [15, 16]. In topological insulators (TIs), the spin textures of the surface states exhibit a strong spin-momentum locking behavior, where the direction of the spin of a Dirac fermion is locked perpendicular to its momentum [17, 18], typically lying in the plane of the surface. This character changes significantly for Dirac/Weyl semimetals (DSM/WSM). The spin textures of these materials are altered by the presence of the nodal points, i.e. the crossing points of valence and conduction bands in the bulk. In DSM such as Na$_3$Bi, the spin polarization tends to vanish at these nodal points due to the recovery of spin degeneracy [19, 20]. In WSM, the spin texture is less constrained compared to TI or DSM, and can be significantly affected by crystal symmetries [16, 21]. In recent years, complicated spin textures have been observed in nodal-line semimetals/metals [7, 22]. Moreover, external means such as strain and magnetic fields have been explored to achieve a tunable spin texture so that topological materials can be used to fabricate electronic nanodevices [23]. Despite these promising developments, the search for a topological material with highly energy- and orientation-dependent spin character remains a challenge. Pyrite structure is one of the common crystal structures found in nature [24]. A few pyrite-type materials have been theoretically predicted to show topologically nontrivial semi-metallic behavior [25]. The preservation of 3D nodal points under SOC in these materials provides
a plausibility for interesting physical phenomena. Recent experiments have confirmed that these topologically nontrivial phases can lead to extremely large magnetoresistance and the emergence of superconductivity [26, 27]. Motivated by these findings, here we investigate the family of pyrite-type noble metal selenides and tellurides. Most of these compounds are non-magnetic and reported as either semiconducting with a small band gap or metallic [28]. Among these materials, OsSe$_2$ and OsTe$_2$ are good candidates for exploring the topologically nontrivial electronic structure due to the strong SOC effects of the outermost 5d electrons of Os [29]. Moreover, they have the least magnitude of band gap opening between the conduction and the valence bands compared with other noble metal compounds [28]. This feature implies a possible band inversion due to a strong SOC in the vicinity of the Fermi level, an indication of the topologically nontrivial electronic structure. Most interestingly, the 5d electrons of Os have shown significant spin anisotropy in oxides due to a combination of a strong SOC and electronic correlation effects [30]. This observation indicates that osmium-based compounds can potentially be used for spin-based devices.

Here we report existence of unconventional three-dimensional energy- and direction-dependent spin textures in the surface of pyrite-type OsX$_2$ (X= Se, Te) crystals. OsSe$_2$ and OsTe$_2$ are semimetallic with a small energy overlap between conduction and valence bands. The characters of conduction and valence bands are inverted at Γ with nontrivial topological indices 1;(000) under strong SOC. The conduction and valence bands are separated everywhere in momentum space by an energy gap. In sharp contrast to the largely in-plane spin texture observed for surface states of other topological insulators, the surface bands of OsSe$_2$ and OsTe$_2$ show a novel texture of both in-plane and out-of-plane spin components, with nearly perfect coupling of one momentum direction to the out-of-plane spin component at certain energies. This unconventional spin texture opens new possibilities for injecting or detecting the out-of-plane spin component in topological spintronic devices. Finally, we have also discovered the presence of bulk nodal lines in the crystals surviving the strong SOC, owing to the protection of screw rotation and spatial inversion symmetry. This observation may open a new avenue for searching for similar symmetry-demanded nodal-line metals.
COMPUTATIONAL DETAILS

The optimized geometry and the electronic structure of OsSe\textsubscript{2}/OsTe\textsubscript{2} are obtained using density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP) \cite{31}. The Perdew-Burke-Ernzehof (PBE) form of the generalized gradient approximation (GGA) is used to describe electron exchange and correlation \cite{32}. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid potential is employed to check for possible overestimation of band inversion within GGA \cite{33}. The kinetic energy cutoff for the plane-wave basis set is set to 400 eV. The standard PBE pseudopotential is adopted in all calculations, treating eight valence electrons for Os (5\textit{d}\textsuperscript{6}6\textit{s}\textsuperscript{2}) and six valence electrons for Se/Te (Se: 4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}, Te: 5\textit{s}\textsuperscript{2}5\textit{p}\textsuperscript{4}). We use a 9 \times 9 \times 9 \Gamma-centered k-point mesh for sampling the Brillouin zone. All structures are fully relaxed until the ionic forces are smaller than 0.01 eV/Å. The surface states spectrum is calculated using the open-source code WANNIERTOOLS, based on the Wannier tight-binding Hamiltonian obtained from wannier90 \cite{34, 35}. Os \textit{d} and Se/Te \textit{p} orbitals are used as initial projectors for tight-binding Hamiltonian construction. To confirm the surface states obtained by tight-binding projections, we also explicitly calculated the surface electronic structure using a slab model with a 1 \times 1 \times 8 supercell. A 20 Å vacuum separates the periodic image to avoid any spurious interactions. The surfaces are also fully relaxed with the energy convergence up to 10\textsuperscript{−7} eV and a force tolerance up to 0.01 eV/Å.

RESULTS AND DISCUSSIONS

Crystal Structure and Bulk Electronic Band Structure

OsSe\textsubscript{2} and OsTe\textsubscript{2} are both transition metal dichalcogenides crystallized in pyrite-type structure. The single crystals of pyrite-type OsSe\textsubscript{2} and OsTe\textsubscript{2} can be synthesized via chemical vapor transport and are shown to be stable in ambient conditions \cite{36}. Other crystalline forms of these two materials have not been reported. The pyrite structure of OsSe\textsubscript{2} and OsTe\textsubscript{2} is chemically stable and robust against high temperature and pressure \cite{36, 37}. The crystal structure of OsSe\textsubscript{2} and OsTe\textsubscript{2} belongs to the space group \textit{P}\textacuted{\textit{a}}\textsubscript{3} (SG 205) and is shown in Figure 1 (a). The Os atoms are located at face-centered-cubic (FCC) sites. Each Se/Te atom is coordinated with three Os atoms and one Se/Te atom, forming a distorted
The lattice parameters optimized using DFT calculations are $a = b = c = 6.08 \, \text{Å} \ (\text{OsSe}_2) / 6.47 \, \text{Å} \ (\text{OsTe}_2)$. These values are close to the values reported by previous experimental investigations [36, 38].

First we study the electronic properties of OsSe$_2$/OsTe$_2$ by examining the projected density of states (PDOS) and the electronic band structure in the absence of SOC. In case of OsSe$_2$ (see Figure 2 (a)), the states near the Fermi level are mainly from Os $d$ states and Se $p$ states. The Os $d$ states are dominant below the Fermi level, while Se $p$ states dominate from the Fermi level up to 1.07 eV above the Fermi level (inset graph of Figure 2 (a)). These features are well reflected in the band structure diagram shown in Figure 2 (b). The band structure of OsSe$_2$ shows a semimetallic character, with the conduction band near Γ partially filled, accompanied by a hole pocket along Γ - Y in the valence band. We further divide the contribution from Os $d$ orbitals split into Os $d t_{2g}$ and $d e_g$ states due to the ligand field splitting effect. We find that the partially-filled low-energy conduction band across the Fermi level near Γ is parabolic and mainly has Se $p$ states. The adjacent valence bands around Γ are predominantly from Os $d e_g$ orbitals, whereas other low-lying valence bands below the Fermi level are of largely Os $d t_{2g}$ character. We also note the existence of multiple degeneracy points below the Fermi level at high symmetry points or along high symmetry lines. These band structure characteristics are consistent with previous investigations on other pyrite-type chalcogenide compounds (e.g. FeS$_2$, RuSe$_2$) [28].

Upon inclusion of spin orbit coupling (SOC), the electronic states near Γ point change significantly as presented in Figure 2 (c). The bottom of the partially occupied conduction band is now occupied by Os $d$ states and becomes flat near Γ point. The Se $p$ states are now pushed under the fourfold degenerate highest occupied valence bands (considering the spin), around -0.22 eV below the Fermi level. The Os $d$ states are pushed up to not just the bottom flat section of the conduction band, they are also found in adjacent regions up to the Fermi level. This change in band ordering is different from the conventional band inversion in that the band inversion in this case occurs between adjacent bands. This can be explained by the energy pinning of the highest occupied valence bands. We note that without SOC effects, the highest occupied bands are sixfold degenerate at Γ point. This degeneracy becomes fourfold upon consideration of SOC and is resulted from crossing of bands with different pairs of $C_3$ eigenvalues. The fourfold degenerate bands consist of two bands with $C_3$ eigenvalues of $\pm e^{i\pi/3}$ and two bands with $C_3$ eigenvalues of -1. The energy
position of this band degeneracy does not move with SOC, therefore the inverted Se $p$ band is located further below the fourfold degenerate bands. This band inversion feature is a strong signal of the existence of nontrivial topological phases in OsSe$_2$. It should be emphasized that since GGA functional is often known to underestimate the energy alignment between conduction bands and valence bands, we employed hybrid functional HSE06 to confirm the existence of the non-trivial band structure [33]. Our HSE06 calculations show that the band inversion between Os $d$ states and Se $p$ states is retained. Therefore we can conclude that the band order of OsSe$_2$ possesses nontrivial features.

SOC also has a significant impact on band crossings at high symmetry points and high symmetry lines in momentum space. Among all band crossings in the band structure diagram observed without SOC, most of them are gapped with SOC turned on owing to band repulsion. However, along the $C_3$-invariant $\Gamma - R$ line, some band crossings can survive the SOC effects. We also observe $C_3$-protected sixfold degenerate bands at R point. These features agree well with previous theoretical predictions that pyrite-type materials can have six-fold fermions stabilized by space group symmetries [8, 39]. Moreover, the band dispersion along $Y - M$ forms four-fold degenerate nodal lines with the presence of two-fold screw rotations about the x, y and z axes $\bar{C}_2 \alpha$, while along $X - M$ the bands are still two-fold degenerate (Figure 2 (d)). This anisotropy behavior suggests that nodal points can exist under strong SOC effects with the protection of nonsymmorphic crystal symmetries such as screw rotation [39].

Figure 2 (e) and (f) present the band structure diagram for OsTe$_2$ with and without SOC effects using the same approach for OsSe$_2$. The orbital composition of conduction and valence bands is similar to that observed in OsSe$_2$. The electronic structure of OsTe$_2$ is also semi-metallic (the unfilled hole packet is find along $\Gamma - M$. A key difference between OsSe$_2$ and OsTe$_2$ without SOC is that there is an accidental Dirac-like touching point between the low-energy conduction band of Te $p$ states and adjacent valence bands of Os $d$ states. We also find degeneracy of bands near $\Gamma$ and R point consisted of Te $p$ states at about 1.1 eV below the Fermi level. This is in contrast to clear separation of Os $d$ states and Se $p$ states in OsSe$_2$. The difference in the electronic structure between OsSe$_2$ and OsTe$_2$ can be attributed to the bonding between chalcogen dimers. The Te-Te covalent bond distance (2.87 Å) in OsTe$_2$ is much larger than Se-Se bond distance (2.57 Å) in OsSe$_2$. The increase in the bond distance tends to downshift the conduction band minimum and affect the shape
of the band. These results indicate that the electronic structure of these chalcogenides can be tuned dynamically via manipulating internal atomic coupling. The band structure of OsTe$_2$ also undergoes significant changes with SOC (Figure 2 (f)). The conduction band minimum near $\Gamma$ becomes flat and is of Os $d_{e_g}$ character. The Te $p$ states are inverted inside the valence bands. Degeneracy points are found along the $\Gamma$ – $R$ line. All these features qualitatively agree with the electronic structure OsSe$_2$, especially in the low energy region, therefore in the remaining part of the paper we will focus on OsSe$_2$ (discussion on OsTe$_2$ can be found in Supplementary Information).

We next calculate the $Z_2$ topological invariants based on the evolution of Wannier charge centers to confirm the existence of topological nontrivial phases in OsSe$_2$ and OsTe$_2$ [40]. The $Z_2$ topological invariants for the 3D bulk OsSe$_2$/OsTe$_2$ crystal $\nu_0; (\nu_1 \nu_2 \nu_3)$ are obtained by tracing the evolution of Wannier charge centers of fully occupied Bloch bands for six time-reversal invariant momentum planes ($k_1 = 0$ and $\pi$, $k_2 = 0$ and $\pi$, $k_3 = 0$ and $\pi$). To demonstrate this, we show the evolution of Wannier charge centers along $k_2$ for planes $k_3 = 0$ and $\pi$ for OsSe$_2$ with SOC as an example (Figure 3). Results for other planes can be found in Fig. S1. It can be clearly seen that $Z_2 = 1$ for $k_3 = 0$ plane since the reference line has odd number of intersections with the evolution lines (Figure 3 (a)), whereas even number of crossings between the reference line and evolution lines indicates that $Z_2 = 0$ for $k_3 = \pi$ plane (Figure 3 (b)). We find the $Z_2$ indices for both OsSe$_2$ and OsTe$_2$ are 1; (000), proving that these pyrite crystals are topologically nontrivial.

Our results show that the lowest conduction band and neighboring valence bands for OsSe$_2$ and OsTe$_2$ are completely gapped along high symmetry lines, providing a possible venue for the emergence of nontrivial surface states between them. Previous investigations have implied that these states can be linked with novel physical properties such as giant magnetoresistance[26] and superconductivity[27]. Another interesting electronic feature is the formation of inverted flat band at the bottom of the conduction band near $\Gamma$. This is similar to the profile of the well-known topological Kondo insulators such as SmB$_6$ [41]. Currently the flat band has only been realized in materials with strong correlated $f$ electrons through hybridization [42]. Therefore the stability of this flat band in OsSe$_2$/OsTe$_2$ consisting of hybridized Os $d$ states may need to be further assessed with advanced computational schemes [43]. Finally, we have identified a bulk nodal line along $Y$–$M$ and this nodal line can survive strong SOC effects owing to the protection of nonsymmorphic symmetries.
This anisotropic nodal line character could potentially result in more complicated electronic features on the surface.

**Surface Electronic Structure**

Next we discuss the surface correspondence of the bulk nontrivial electronic structure in detail. The morphology and electronic structures of the surfaces of pyrite crystals have been well studied before by both experiments and theoretical calculations\[44–46\]. The (001), (110), (111) and (210) surfaces have all been reported as possible cleavage surfaces in pyrite systems \[45\]. The rich symmetry of the pyrite crystal also allows the existence of multiple surface terminations for each cleavage surface \[45\]. Here we selected the appropriate surface to investigate based on two important factors: thermodynamic stability and extent of surface reconstruction \[37\]. The (001) surface is known to be the most common cleavage surface in pyrite-type crystals and thermodynamically the most stable. The most stable termination of (001) surface can well retain the bulk-like atomic configurations with little surface reconstruction \[45\]. The (110) surface is much less stable than the (001) surface, but the atom displacement at the surface is small. The (111) and (210) surfaces can be more stable than (110), but at the cost of significant surface reconstructions to compensate for the loss of coordination on the surface. Due to the considerable computational cost in obtaining optimal reconstructed surfaces involving heavy Os atoms, here we mainly consider the (001) surface and briefly discuss the characteristics of the (110) surface. Given the symmetry of the crystal, the (001) surface of OsSe2 can have three possible surface terminations: Se-Se terminated, Se terminated and Os terminated (see Fig. S2). Our slab cell calculations and previous investigations have shown that the Se-Se terminated and Os-terminated surfaces are less energetically favorable compared to Se-terminated surface \[44, 45\]. In addition, Se-Se terminated and Os-terminated surfaces have significant surface reconstructions upon relaxation. In the following, we will focus on the electronic structure of Se-terminated (001) surface.

The relaxed Se-terminated (001) surface OsSe2 and OsTe2 (see Figure 4 (a)) retains the bulk atomic configurations, consistent with earlier theoretical predictions on other pyrite-type crystals \[45\]. The Se-terminated (001) surface preserves the surface stoichiometry and only features rupture of Os-Se bonds normal to the (001) plane upon cleavage (i.e. no
Se-Se bonds are broken). As a consequence the coordination of surface Os atoms changes significantly. In the pristine lattice, each Os atom is surrounded by six Se atoms, forming a distorted octahedral (point group $O_h$). On the other hand, the coordination of each Os on (001) surface atom changes to square-planar pyramidal (point group $C_{4v}$) due to the loss of one Se ligand. The loss of coordination normally leads to further splitting of Os $d$ states (between $d_{x^2−y^2}$ and $d_{z^2}$) and formation of spin polarized surface states, as indicated in previous reports [37].

To effectively obtain the topologically nontrivial surface electronic structures of OsSe$_2$ and OsTe$_2$, we perform surface state calculations by the Green’s function approach using a tight-binding model Hamiltonian derived from our first principles calculations [47]. As seen from Figure 4 (b,c), we see different band dispersions along the lines connecting $\bar{X}$ (0.5,0) with $\Gamma$ (0,0) ($\bar{M}$ (0.5,0.5)) and lines connecting $\bar{Y}$ (0,0.5) with $\Gamma$ ($\bar{M}$). (i.e. $\bar{X}$ and $\bar{Y}$ are not equivalent.) This reflects the anisotropy observed in the bulk band structure. Moreover, the lowering symmetry of surface Os atoms results in a complicated electronic structure at the surface under the influence of strong SOC interactions near the Fermi level. In the vicinity of the Fermi level (ranging from -0.03 eV to -0.09 eV), we can observe hole-like surface bands around $\Gamma$ point (denoted by S1 ($\Gamma – M$), S2 ($\Gamma – X$) and S3 ($\Gamma – Y$) in Figure 4). These surface bands are partly buried in the partially occupied bulk conduction bands and connect with the underlying bulk valence bands.

The anisotropy in the surface electronic structure prompts us to further examine the spin structure by analyzing spin components $S_x$, $S_x$ ad $S_z$ along surface band S1, S2 and S3 in Figure 4 (d). We find that each surface band shows a distinctive energy- and orientation-dependent spin texture profile. For the S1 band (along $\Gamma – M$), we observe a strong $S_z$ polarization near the Fermi level (~0.04 eV below the Fermi level). For energies deeper below the Fermi level, the $S_y$ component of the S1 band tends to decrease and the magnitude of the $S_x$ component gradually increases. At $E_F−0.08$ eV, the $S_y$ component of the S1 band reduces to only 10% of the $S_x$ component. For the S2 band (along $\Gamma – X$), the surface spins are composed of little in-plane spin component and a large out-of-plane spin component. The total magnitude of the spin reduces significantly as the energy level decreases. Finally, the S3 band (along $\Gamma – Y$) has a strong spin polarization along the x axis and almost no spin component in other two directions. These distinct surface spin textures shown in Figure 4 (d) indicate the presence of novel topological nontrivial phases in OsSe$_2$. 
We also used slab calculations based on first principles DFT methods to verify the unusual surface spin textures shown in Figure 4 (d) near the Fermi level as the tight binding model usually leads to small difference in energy alignment when compared to DFT results. As shown in Figure 4 (e), the slab calculation reveals that the \( d \) orbital electronic states from top layer Os atoms are the dominant contributors to the surface bands observed in Figure 4 (b,c). The orbital character of the surface bands shows a further splitting of Os \( t_{2g} \) and Os \( e_g \) states as well as change of energy ordering compared to the bulk electronic states (see Fig. S3). The S1 band (\( \Gamma - M \)) is mainly comprised of a near equal fraction of \( d_{yz} \) and \( d_{xz} \) states, followed by \( d_{x^2-y^2} \). The orbital contributions from \( d_{z^2} \) and \( d_{xy} \) are much weaker compared to other \( d \) states. The S2 band (\( \Gamma - \bar{X} \)) shows a slight change in the ordering. \( d_{yz} \) and \( d_{xz} \) are still the strongest \( d \) characters in the surface band, while \( d_{z^2} \) becomes the next strong \( d \) states, surpassing \( d_{x^2-y^2} \). In the S3 band (along \( \Gamma - \bar{Y} \) \( d_{x^2-y^2} \) states become the second most contribution following \( d_{yz} \), while the projection from \( d_{xz} \) orbital decreases rapidly. The \( d_{z^2} \) character becomes negligible. The contribution from \( d_{xy} \) is weak in all surface bands. This anisotropic behavior in orbital splitting can be used to explain the strong direction-dependent spin split in the surface bands as shown in Figure 4 (e). The S1, S2 and S3 bands are separated from their spin splitted counterpart in the bulk by \( \sim 90 \) meV, \( 120 \) meV and \( 30 \) meV, respectively. The out-of-plane orbital character features of the S2 band (\( d_{yz} \), \( d_{xz} \) and \( d_{z^2} \)) is a key factor for obtaining such a sizable splitting effect. The significant in-plane \( d_{x^2-y^2} \) character leads to a small band splitting in the S3 band. We note that similar spin splitting behavior has been realized in layered materials with doped surface where the surface symmetry is broken by dopants [48]. Here we find that symmetry breaking at the pristine pyrite surface can achieve the same effect by inducing different orbital screening along each high symmetry line. This observation indicates a new approach of spin control at the surface from a spintronics viewpoint. Overall, the slab calculations results reaffirm the key electronic features discovered in tight binding models in Figure 4 (b–d).

The complex surface spin texture can be visualized by a three-dimensional perspective view of the constant energy contour at 0.07 eV below the Fermi level in Figure 5 (a). It is evident that the spin direction and magnitude vary in the momentum space and the transition from out-of-plane spin polarization to in-plane polarization can be clearly observed. Figure 5 (b) shows the evolution of the in-plane spin character by plotting the spin texture in the iso-energy surface spectral function projected on to the 2D Brillouin zone using the
Wannier tight-binding Hamiltonian. We select three representative energies: 0.05 eV, 0.07 eV and 0.09 eV below the Fermi level. The surface bands are projected in the iso-energy surface spectral function map of $E_F - 0.05$ eV and $E_F - 0.07$ eV as a ring-like contour surrounding the bulk states. At $E_F - 0.05$ eV, the spin texture shows the helical spin texture similar to that observed in topological insulators around the $\Gamma - Y$ axis, where the $S_x + S_y$ spin orientation is tangential to the iso-energy surface contour (i.e. spin-momentum locking). The magnitude of the in-plane spin component gradually decreases from $\Gamma - Y$ axis to the $\Gamma - X$ axis, and finally vanishes at the the $(\pm k_x, 0)$ point. For the out-of-plane spin component ($S_z$), the magnitude is nearly zero at the intersection with the $\Gamma - Y$ axis. The trend of the magnitude of $S_z$ along the surface contour is opposite to the in-planar spin component. When the in-plane spins disappear, the out-out-plane spins reach maximum. The spin texture shows a slightly different behavior at $E_F - 0.07$ eV, with the in-plane spins no longer tangential to the surface contour. As the energy reaches $E_F - 0.09$ eV, parts of the surface bands are now touching the bulk and the contour breaks into linear segments. The in plane spin texture on these segments is mostly $S_x$ polarized, with the out-of-plane texture shows a strong positive $S_z$ polarization. This kind of highly energy- and direction-dependent surface spin texture is yet to be observed in topologically nontrivial materials.

To effectively demonstrate the distinct spin behavior of the surface band structure, we next construct a three-dimensional view of the surface cone in an energy range of [-0.10, 0] eV below the Fermi level (see Figure 5 (c)). The shape of the surface contour is significantly reshaped by intersecting with the bulk states. Along the x axis in the range of [-0.035, 0] eV below the Fermi level, we can see a near-rectangular valley cut in the cone (denoted by black dashed lines). The width of the cut agrees well with the projection of the bulk flat conduction band. However, this cut is not observed along the y axis in the same energy range. Another special feature in the cone is the arc cut along the y axis near 0.08 eV below the Fermi level (denoted by the green dashed line). This surface cut eliminates the surface states near $k_y = 0$ starting from 0.082 eV below the Fermi level. A similar small cut is found along the x axis near 0.09 eV below the Fermi level. This means another asymmetrical surface dispersion between 0.082 eV and 0.09 eV below the Fermi level. This feature is opposite to the signal on the upper side of the cone as it screens out the $k_y = 0$ states instead of $k_x = 0$ states. These results indicate a possible way of selectively modulating spin texture from in-plane (near $Y$) to out-of-plane (near $X$) by a combination of energy and
momentum direction.

Finally, Figure 5(d) shows the magnitudes of spin polarizations $S_x$, $S_y$ and $S_z$. The circular and arc-like contour from inside to outside in Figure 5 (d) refer to the iso-energy surface spectral function at $E_F-0.03/0.04/0.05/0.06/0.07/0.08/0.09/0.095$ eV. The opposing colors in $S_x$, $S_y$ and $S_z$ graphs indicate the preservation of TR symmetry in the crystal. The spin flips its sign when comparing states at $k$ and $-k$. The total spin polarization gradually decreases as the surface states approach the bulk valence band.

The above analysis on the electronic structure of OsSe$_2$ (001) surface has already shown promising potentials for OsSe$_2$ as a novel topological material. We also calculate surface electronic structure of (011) surface (See Figure S4). The (110) surface is less stable than (001) surface and is not a common cleavage surface observed in pyrite system. The surface morphology of (011) surface is much complicated than (001) surface. The (011) surface can be either (Os+Se)-terminated or Se-terminated. The biggest difference between (001) and (011) surfaces is that visible surface states can be found near and slightly above the Fermi level in pairs, possessing opposite spin textures. In (001) surface, only positive $S_z$ polarized surface bands (S1 – S3) are found, while the other spin split bands are buried in the bulk. Another difference observed in (011) surface is that the surface states below the Fermi level are largely merged with the bulk states.

**Nodal line structures in OsSe$_2$**

Apart from the surface bands near $\Gamma$, we also find existence of exotic surface states further down below the Fermi level associated with the bulk nodal lines. For example, as shown in Figure 4 (b), we can see two near-flat surface bands around $0.27$ eV below the Fermi level along $X - \Gamma$. These drumhead-like surface states are often clear signs of presence of bulk nodal lines [49, 50]. During the investigation of bulk band structures we have already revealed the nodal line along $Y - M$. To further clarify the details of the nodal lines, we can find other nodal points in the Brillouin zone between the $N$ and $(N-1)$ energy bands using the Wannier tight binding model (i.e. $\delta(k) = E_N(k) - E_{N-1}(k)$). Figure 6 (a) shows the location of nodal points in the first Brillouin zone if $N$ is set to the highest occupied valence band. We can see three nodal lines along the high symmetry lines: $Y - M$, $X - U$ (0.5, 0, 0.5) and $Z - T$ (0, 0.5, 0.5). These lines are equivalent owing to additional threefold rotational
symmetry in the crystal. We also note that there are three curved nodal lines in the $k_i = \pi$
(i = x, y and z) planes, connected at R point. These curved nodal lines also share the same
physical origin with the three high-symmetry nodal lines and are protected by combination of
screw rotation and inversion symmetry. Moreover, the energy of these nodal points is spread
over a wide range from -0.04 eV (X, Y or Z point) to -0.85 eV (R point). When projected
into the surface Brillouin zone, surface states tend to emanate from the projection of these
bulk nodal lines. This is seen in Figure 4 (a,b) as multiple lines connecting projected bulk
cones below the Fermi level along $\overline{X} - \Gamma(\overline{M})$ and $\overline{Y} - \Gamma(\overline{M})$ including the drumhead states
we mentioned earlier. These surface states are reflected in iso-energy as eye-shaped rings and
disconnected arcs as shown in Figure 6 (b). The appearance of the nodal line structure is
in good agreement with previous theoretical predictions that the pyrite structure symmetry
can protect the nodal-line fermions when including SOC effects [39].

**Surface spin textures and nodal lines in OsTe$_2$**

Finally, we find OsTe$_2$ shares most features with that found in OsSe$_2$, with differences in
the energy alignment (see Figure S5). The surface bands S1 – S3 connecting the bulk valence
bands and bulk conduction bands are found in the vicinity of the Fermi level. The Surface
bands also possess highly anisotropy behavior. The S1 band ($\overline{X} - \Gamma$) is the most visible
band, while the S3 band ($\overline{Y} - \Gamma$) is significantly overshadowed by bulk bands. The spin
anisotropy behavior is also seen in these surface bands, with the in-plane spin polarization
dominating near $\overline{Y}$ and out-of-plane spin polarization prevailing near $\overline{X}$. These results agree
qualitatively well with those observed in OsSe$_2$. Compared to OsSe$_2$, the bulk screening
effect on the surface bands is more significant in OsTe$_2$. The full ring-like iso-energy contour
only exists in the range of $E_F - 0.03$ eV to $E_F - 0.06$ eV, only half of that in OsSe$_2$. Further below this energy range, the surface contours become segments linking the bulk
counterparts (Figure S6). This suggests that OsTe$_2$ could also be a feasible candidate for
selecvively mouldating the nontrivial surface spin structure. In addition, we also find nodal
lines further down below the Fermi level in OsTe$_2$, manifested by the multiple drumhead
surface states as shown in the surface band diagram (Figure S5).
CONCLUSION

In summary, using density functional theory calculations, we show novel anisotropic spin textures near the Fermi level on the low energy surfaces of topological nontrivial compounds OsX$_2$ ($X =$ Se, Te). The electronic structure of these pyrite-type crystals in the bulk form is nonmagnetic and semi-metallic. The low-energy energy bands near $\Gamma$ show significant band inversion due to SOC interactions. These states are found to be topologically nontrivial and stable owing to the presence of crystal symmetries. For stable cleavage surface (001) of these crystals, we observe exotic spin-anisotropic surface bands connecting the partially occupied conduction and valence bands. These surface bands have negligible in-plane spin polarization near $\bar{X}$, while around $\bar{Y}$ the in-plane spin components become dominant. The spin texture evolution of the surface bands is heavily influenced due to the energy screening by bulk bands. In addition, we have indicated that OsX$_2$ possess nodal-line structure below the Fermi level. This leads to the formation of highly direction-dependent bulk electronic structure and drumhead surface states. We anticipate that the anisotropic surface spin textures in topologically nontrivial pyrite crystals as predicted here could be verified by the spin and angle resolved photoemission spectroscopy (ARPES) measurements. These measurements can also provide experimental evidence for the exotic surface states associated with the bulk nodal line structures. Such unconventional energy- and direction-dependent spin texture could be beneficial for potential spintronics applications. Moreover, discovery of these novel physical phenomena on a pristine surface of a strong topological material could inspire new strategies of searching for exotic topological nontrivial properties.

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COMPETING INTERESTS

The authors declare no competing interests.

DATA AVAILABILITY

The data and codes that support the findings of this study are available from the authors upon request.

AUTHOR CONTRIBUTIONS

Y.Y. and N.V.M. conceived the work and were responsible for the overall research planning and direction. Y.Y did the first principles calculations and analysis. Y.Y and N.V.M wrote the main text. Y.Y wrote the Supplementary Information and plot all figures and tables. M.S.F. contributed to the revision of the manuscript. All authors contributed to the discussion.

SUPPLEMENTARY INFORMATION

Supplementary Information accompanying the paper is available at npj Quantum Materials’ website.
FIG. 1. (a) Crystal structure of OsSe$_2$/OsTe$_2$. (b) The bulk Brillouin zone and the projected surface Brillouin zones for (001) and (110) surfaces.
FIG. 2. (a) Total and projected electronic density of states of OsSe$_2$ in the absence of SOC, projected onto the Os $d$ orbitals and Se $p$ orbitals. (b-c) Band structure diagrams of OsSe$_2$ without SOC (b) and with SOC (c). The projections of Os $d\,e_g$, $d\,t_{2g}$, and Se $p$ states are labelled in yellow, green and red circles, respectively. (d) Band dispersion of OsSe$_2$ along X–M direction with SOC. (e-f) Band structure diagrams of OsTe$_2$ (e) without SOC and (f) with SOC.
FIG. 3. The evolution of Wannier charge centers along $k_2$ in (a) $k_3 = 0$ and (b) $k_3 = \pi$ planes with SOC. The evolution line cross the reference line (dashed line) odd and even times in $k_3 = 0$ and $\pi$ planes, respectively.
FIG. 4. (a) Side and top view of Se-terminated OsSe$_2$ (001) surface. (b-c) Surface band diagrams for OsSe$_2$ obtained using non equilibrium Green’s functions calculations. (d) Spin polarization along the surface bands S1, S2 and S3. (e) Corresponding surface band diagrams obtained from slab calculations.
FIG. 5. Complex surface spin texture in OsSe$_2$. (a) Three-dimensional vector representation of the surface spin texture at 0.07 eV below the Fermi level. (b) Spin textures at 0.05, 0.07 and 0.09 eV below the Fermi level. (c) Surface band structure near the Fermi level ($E_F$-0.1 eV, $E_F$). The color difference represents the level of surface localization. (d) Evolution of surface spin polarization ($S_x$, $S_y$, $S_z$ and total spin polarization).
FIG. 6. (a) Nodal line structure of OsSe$_2$. (b) Iso-energy contour at $E_F - 0.28$ eV.
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