Node-Surface and Node-Line Fermions From Nonsymmorphic Lattice Symmetries

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We propose a kind of novel topological quantum state of semimetals in a quasi-one-dimensional (1D) crystals BaMX\(_3\) (M = V, Nb or Ta; X = S or Se) family by using symmetry analysis and first principles calculation. We find that in BaVS\(_3\) the valence and conduction bands are degenerate in the \(k_z = \pi/c\) plane (c is the lattice constant along \(\hat{z}\) axis) of the Brillouin Zone (BZ). These nodal points form a node-surface and they are protected by a nonsymmorphic crystal symmetry consisting of a two-fold rotation about the \(\hat{z}\) axis and a half-translation along the same \(\hat{z}\) axis. The band degeneracy in the node-surface is lifted in BaTaS\(_3\) by including strong spin-orbit coupling (SOC) of Ta. The node-surface is reduced into 1D node-lines along the high-symmetry paths \(k_y = 0\) and \(k_x = \pm \sqrt{3}k_y\) on the \(k_z = \pi/c\) plane. These node-lines are robust against SOC and guaranteed by the symmetries of \(P6_3/mmc\) space group. These node-line states are entirely different from previous proposals which are based on the accidental band touchings. We also propose a useful material design for realizing topological node-surface and node-line semimetals.

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I. INTRODUCTION

Searching for new topological states of matters becomes an active field since the discovery of topological insulators (TI)\(^{12}\). Recently, much attention has been drawn to the topological semimetal (TSM) due to the stimulation of successful design and experimental observations of Weyl semimetal (WSM) in transition-metal monoprophides\(^{15}\). WSM are topological metallic states in which the Fermi surfaces are consisted of discrete two-fold-degenerate Weyl points. These Weyl points are topologically robust since they carry nontrivial chiral charges. The idea of TSMs has also been extended to node-line semimetal (NLS) hosting one-dimensional (1D) contacts of conduction and valence bands\(^9\). The node-line fermions have been proposed in realistic materials such as Graphene-network\(^2\), Cu\(_3\)N\(_2\), Cu\(_3\)PdN\(_2\) and Ca\(_3\)P\(_2\)\(^{10}\). Experimental characterization of topological properties of NLSs was carried out for PbTaSe\(_2\)\(^{11}\). One of the important topological properties of NLSs is that they support “drumhead” like flat surface bands\(^{12}\) which may potentially enhance the superconductivity transition temperature\(^{12}\).

In previous proposals,\(^9\)\(^{10}\) ring-like node-line contacts are fragile against spin-orbit coupling (SOC). Including SOC lifts the node-line contacts and drives the systems into topological insulators or WSM. Therefore, searching for stable NLSs robust to SOC\(^{10}\) is of great interest and importance. Recently, materials design principles involving a layer-stacking process of topological insulators and magnetic insulators are given for WSM\(^{11}\) and NLS\(^{12}\). Alternatively, in the present work we provide a new route to realize such exotic TSM state by arranging one-dimensional ionic chains in parallel. By using first principles calculations and symmetry consideration, we show that the quasi-one-dimensional crystal BaVS\(_3\) exhibits a two-dimensional (2D) touching of valence and conduction bands, namely a node-surface, at the \(k_z = \pi/c\) plane with \(c\) being the \(\hat{z}\)-axis lattice constant. In a cousin compound BaTaS\(_3\), the large SOC of Ta atom lifts the 2D degeneracy and reduces it into 1D node-lines which are robust to SOC. The node-lines found in the present work locate at the high-symmetry paths \(k_y = 0\) and \(k_x = \pm \sqrt{3}k_y\) on the \(k_z = \pi/c\) plane, demonstrating their purely symmetrical origin that is different from the accidental-band-degeneracy mechanism of previous node-lines\(^{11}\)\(^{12}\).

II. CRYSTAL STRUCTURE

The BaMX\(_3\) (M = V, Nb or Ta; X = S or Se) is a group of quasi-one-dimensional crystals adopting hexagonal structure with the space group of \(P6_3/mmc\) (No. 194)\(^{13}\)\(^{14}\) as shown in Fig. 1. M atoms are surrounded by octahedron of X atoms and these octahedrons form linear chains along the \(\hat{z}\)-axis by sharing common surfaces. Those chains are lined up and arranged into a trigonal lattice in the \(x–y\) plane with Ba atoms filling the space between the chains. As the inter-chain distance is much larger than the intra-chain distance, these materials are considered as quasi-one-dimensional crystals. Each unit cell contains two formula units of BaMX\(_3\) and thus has two M atoms, as labeled by A and B, respectively. Under the crystal field of the surrounding MX\(_3\) octahedra, the \(d\)-orbitals of the two M atoms are split into
two-fold $e_g$ orbital and three-fold $t_{2g}$ orbitals. The three-fold $t_{2g}$ orbitals is further split into a two-fold $e_g$ orbitals and a single $a_g$ orbital by the triangle-crystal field of the ionic chain array [see in Fig.1(b) for this evolution of $d$-orbitals]. The character of the wave-function mostly composed of $a_g$ manifold is $d_{3z^2-r^2}$ atomic orbital as shown in the inset of Fig.1(b). With this quasi-1D crystal structure, the first principles calculations of BaMX$_3$’s electronic structure are performed by using the Vienna ab initio simulation package (VASP)\cite{KV05} with generalized gradient approximation\cite{KV06} in the projector augmented-wave method\cite{KV07}. The Hubbard $U$ is simulated through Dudarev’s method\cite{KV08} by setting $(U-J)_V = 5.0$ eV and $(U-J)_{Ta} = 2.0$ eV. Slightly changing of $U-J$ value will not change the conclusion of this work. Tight-binding Hamiltonians are constructed based on the maximally localized Wannier functions (MLWFs)\cite{KV09}, and from these Hamiltonians surface band structures are calculated for slabs of BaMX$_3$.

III. ELECTRONIC STRUCTURES

A. Node-Surface in BaVS$_3$

Firstly, we investigate the electronic structure of BaVS$_3$ in which the effect of SOC can be safely ig-
symmetry $S_z = \{C_{2z}, T_z = c/2\}$, a nonsymmorphic symmetry combining a half-vector translation along the $\hat{c}$ axis and a two-fold rotation about the $\hat{z}$ axis. From these symmetries, two compound symmetries, $C = IT$ and $S = IS_z$ are constructed. $C$ is preserved at any $k$-point of BZ, while $S$ is respected at the $k_z = 0$ and $k_z = \pi/c$ planes. Applying $S$ twice on the lattice can bring the system back to its starting point, one has $S^2 = 1$ and the corresponding eigen-values of $S$ are $\pm 1$, which can be used to label the eigen-states of the Hamiltonian. Due to the anti-commutation of $C$ and $S$ on $k_z = \pi/c$ plane [see Appendix AI for the derivation], the action of $C$ switches each eigen-state to its degenerate partner of opposite $S$-label, ensuring the two-fold degeneracy of energy bands on the entire $k_z = \pi/c$ plane as found in Fig. 2(b). The details of the symmetry consideration and the derivation of the actions of the symmetry operators are summarized in Appendix AI.

### B. Symmetry Guaranteed Nodal-Lines in BaTaS$_3$

If SOC is included, the above discussion is not valid and the node-surface of $k_z = \pi/c$ plane will not persist. Luckily for BaVS$_3$, the effective SOC splitting in V’s $a_g$ bands is vanishingly small (about 1 $\sim$ 2 meV) and thus the conduction and valence bands can still be considered as degenerate at room temperature paramagnetic phase. However, for heavier $M = Nb$, and Ta, the SOC is large and its effect has to be taken into account. In Fig. 3(a), we show the band structure of BaTaS$_3$ with SOC turned on. The inclusion of SOC lifts the degeneracy of bands at a general $k$-point in the the node-surface $k_z = \pi/c$ plane, as seen from the splitting of energy bands along $L - H - A$ paths. Surprisingly, one can still find that along a special path $A - L$, the energy bands remain four-fold degenerate (counting both spin and orbital degrees of freedom), forming a so called node-line structure with Dirac nodes along it. In Fig. 3(b) we also plot a 3D band structure in $k_z = \pi/c$. Gradual colors are used to indicate the energy splitting in the conduction and valence bands. In this plot and its contour projection onto the $k_z = \pi/c$ plane, three node-lines related by $C_{3z}$ rotation symmetry are found along the high-symmetry paths $k_x = 0$ and $k_x = \pm \sqrt{3}k_y$.

The existence of node-lines also changes the Fermi surface around the $k_z = \pi/c$ plane as shown in Fig. 3(c). Due to the non-zero band dispersion of the node-lines, the Fermi level cuts these lines at six discrete points. In the 3D Fermi surface plot, it is readily found that the Fermi lines connecting two different colors in the spinless case [Fig. 2(c)] now evolve into six separated contacting points on the $A - L$ paths. Comparing with the Fermi-surface of BaVS$_3$ in Fig. 2(c), the additional ellipsoid-shaped Fermi surface surrounding the $\Gamma$ point is from the two $\epsilon'_y$ bands.
as clearly shown in the band structure in Fig. 3(a).

Now let us discuss about the symmetry protection of the four-fold degenerate node-lines in presence of SOC. The derivations of the actions of symmetry operators and their associated commutation relations are given in Appendix A. In the spinful case, time reversal operator is expressed as \( \mathcal{T} = is_y \mathcal{K} \) and thus \( \mathcal{T}^2 = -1 \). The skew axis \( S_z \) now also acts on the space spin, \( S_z \rightarrow (s_x, s_y, s_z) \rightarrow (-s_x, -s_y, s_z) \). Applying it twice rotates the spin by \( 2\pi \), giving a minus sign for a spin-1/2 system. Since acting \( S = IS_z \) twice on the real space brings the system back to its origin, one finds that the square of \( S \) becomes \( S^2 = -1 \) at its invariant plane \( k_z = \pi/c \). Notice that \( L \) does not act on spin space. Then the eigen-states of Bloch Hamiltonian can be labeled by the eigen-values \( \pm i \) of \( S \), \( S|\phi^\pm(k)\rangle = \pm i|\phi^\pm(k)\rangle \). Unlike the spinless case, applying \( C \) on \( |\phi^\pm(k)\rangle \) translates it to its Kramer partner with the same \( S \)-label. Thus, the two Kramer pairs with opposite \( S \)-label are not related and generally the bands should be two-fold degenerate. Therefore, extra symmetries are needed to provide the protection of the node-lines. We find the mirror symmetry \( M_x \) plays this role. \( M_x \) acts both on the real space and spin space. It takes an anti-commutation relation with \( S \) on the intersection line of its invariant plane \( k_x = 0 \) and the invariant plane of \( S \), \( k_z = \pi/c \). Because of \( \{M_x, S\} = 0 \), applying \( M_x \) on \( |\phi^\pm(k)\rangle \) will translate the state to a degenerate state with opposite \( S \)-label. Therefore, with the help of \( M_x \), the two Kramer pairs of opposite \( S \)-eigenvalues are now related by \( M_x \) at the high-symmetry path \( k_x = 0 \) on \( k_z = \pi/c \), proving the existence of the four-fold degenerate node-lines.

The node-lines bring about surface states on the surface of BaTaS\(_3\), which is another demonstration of the nontrivial topology of the node-line. In Fig. 4(a) we plot the surface electronic structure of a 20-unit-cell-thick BaTaS\(_3\) slab with \{-110\} facets. From the figure, one can see segments of thick (red) lines inside local “band gap” which are mainly contributed by the surface layers. When the surface bands immerse in bulk bands, the hybridization between the surface and the bulk bands will smear out the surface contribution. By using recursive Green’s function’s method, we calculated the surface Green’s function at the \{-110\} surface and the obtained density of states are plotted in Fig. 4(b) for Fermi energy \( E_F = 0.0, 0.18 \) and 0.27 eV. Bright lines highlighting the states’ contribution can be easily seen in these figures. On the other hand, drumhead-like flat surface bands observed in Graphene-network\(^{32}\) and Cu_{5}Pd_{3}\(^{33}\) however, is not found here due to the large dispersions of the node-lines.

The observation of surface states at the slab’s surface is unexpected because the symmetries that protect the node-lines are broken at the surfaces. This is understood from the nontrivial Berry phase \( \pi \) associated with each node-line\(^{14}\). In order to verify this point, we construct an effective four-band Hamiltonian for BaTaS\(_3\) in which the two \( a_g \) orbitals of Ta are considered [see in Appendix B for the construction of the Hamiltonian]. The low-energy Hamiltonian around a point on the node-line \( k_0 = (0, k_y, \pi/c) \) is written as,

\[
H_q = \epsilon(k) + q_y \tau_y s_x + q_z \tau_z + q_x \tau_y s_z,
\]

with \( q = (q_x, q_y, q_z) \) being small deviation from \( k_0 \). \( \tau \) denotes the orbital degree of freedom and the dependency of \( H_q \) on \( q_y \) is contained in \( \epsilon(k) \) based on the symmetry consideration. As \( \epsilon(k) \) is not important for the solutions of \( \epsilon(k) = 0 \), we omit it in the following discussion. The effective model \( \epsilon(k) \) has a symmetry \( \tau_x s_z \) whose eigenvectors build up a unitary matrix that block-diagonizes \( H_q \). By using an isospin-rotation and re-scaling of \( q_z \), one can finally rewrite the Hamiltonian in the nonzero sub-block into the form \( H_q = \begin{pmatrix} 0 & \tilde{q}_y + iq_x \\ \tilde{q}_y - iq_x & 0 \end{pmatrix} \). When \( \tilde{q} \) transverses along a closed loop circling the node-line, the wavefunction of the occupied state accumulates a nonzero Berry phase \( \pi \) (mod \( 2\pi \)), demonstrating the nontrivial topology of the node-line.

C. Parallel Ionic Chains: Material design for Node-surface and Node-line States

Our work provides a principle for novel materials design: creating TSMs through arrangement of ionic chains in parallel. Previously, Balents et al.\(^{15}\) and Phillips et al.\(^{16}\) have considered a layer-stacking approach to construct TSMs. In their scheme, the use of TI layers provides Dirac points from the TI layers’ surface states [see in Fig. 3(b)]. When the TI layers are stacked along the
IV. DISCUSSIONS AND CONCLUSIONS

We notice that the general physics of band-sticking in nonsymmorphic crystals has already been pointed out by Parameswaran et al.\cite{12} and some first principles calculations have been done on the family of BaMX$_3$\cite{13,14}. However, the topological features of such 2D degeneracy of conduction and valence bands are revealed for the first time, to the best of our knowledge. The node-lines induced by strong SOC from node-surface without SOC is quite different from those proposed previously\cite{11}, in which the node-lines are only stable in the absence of SOC. Some proposals claim the stability of node-lines with the inclusion of SOC, such as those in SrIrO$_3$\cite{13} and PbTaSe$_2$\cite{11}. These node-lines are off the high-symmetry paths and originate from accidental band touching and no guarantee of their existence. However, the node-lines in the present case are four-fold degenerate and guaranteed by happening at the high-symmetry paths.

We also notice that by decreasing the temperature, BaVS$_3$ experiences firstly a structure phase transition from the room temperature hexagonal phase to the low temperature orthogonal phase, and then a paramagnetic-anti-ferromagnetic phase transition under which the material becomes a gapped state. In BaTaS$_3$ and BaTaSe$_3$, semiconductor-metal transition are observed at low temperature, however, no clear signature of structure or magnetic transition is detected and the nature of semiconductor-metal transition is still under debate. Whether this phase-transition is topological in nature\cite{23} or not and what is the relation between the observed phase transitions and the node-surface and node-line discovered in the present work need further investigations.

In summary, we have found a 2D node-surface at the $k_z = \pi/c$ plane in the band structure of BaVS$_3$ with negligible SOC (about 1–2 meV). Such novel TSM is protected by the non-symmorphic symmetry $S_z$. In its family compound BaTaS$_3$ with strong SOC, node-surface evolves into node-lines along three high symmetry paths on the $k_z = \pi/c$ plane. The symmetries that protect the node-lines are the nonsymmorphic skew axial symmetries $S_z$, mirror symmetry $M_z$, inversion symmetry $I$ and time-reversal symmetry $T$. Two-orbital effective model are constructed to compute the nontrivial Berry phase associated with each node-line. The physics of the node-lines originated from the nonsymmorphic symmetry is analyzed. Surface states are observed in a slab of BaTaS$_3$ even though the large dispersions of node-lines and the breaking of crystal symmetries at the surface. Our work paves a way to design materials with peculiar energy band degeneracy through arrangement of ionic chains in parallel.

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V. APPENDIX

A. Symmetry Analysis

1. The spinless case

Let us prove that in a crystal preserving the time-reversal-symmetry $\mathcal{T}$, inversion symmetry $\mathcal{I}$ and a two-fold skew-axis along $\tilde{z}$, $\mathcal{S}_z : (x, y, z, t) \mapsto (-x, -y, z + \frac{\pi}{2}, t)$, the energy bands at $k_z = \pi/c$ plane will be two-fold degenerated if the spin effect is excluded. By using these three symmetries, one can compose two compound symmetries, $\mathcal{C} = \mathcal{IT}$ and $\mathcal{S} = \mathcal{IT} \mathcal{S}_z$. In the real space, $\mathcal{C}$ and $\mathcal{S}$ act as,

$$
\mathcal{C} : (x, y, z, t) \mapsto (-x, -y, -z, -t)
$$

$$
\mathcal{S} : (x, y, z, t) \mapsto (x, y, -z - \frac{1}{2}, t).
$$

(2)

In momentum space, one easily finds that all the $k$ points are invariant points under the action of $\mathcal{C}$. On the other hand, $\mathcal{S}$ translates $(k_x, k_y, k_z)$ to $(k_x, k_y, -k_z)$, which means $k_z = 0$ and $k_z = \pi/c$ are the two invarient planes of $\mathcal{S}$. Applying $\mathcal{S}$ twice, the coordinates in the real space return back and one finds $\mathcal{S}^2 = 1$, which means the eigen-values of $\mathcal{S}$ are $\pm 1$ and one can use them to label the Bloch states $|\psi(k)\rangle$ of the system’s Hamiltonian by $|\psi^{\pm}(k)\rangle = \pm |\psi^{\pm}(k)\rangle$.

We find that under the action of $\mathcal{C}$, each eigen-state $|\psi^{\pm}(k)\rangle$ is switched to a degenerate state of an opposite $\mathcal{S}$-label. Before showing this, we first prove that $\mathcal{C}$ and $\mathcal{S}$ take an anti-commutation relation at $k_z = \pi/c$. By using Eq.(2), one obtain,

$$
\mathcal{S}\mathcal{C} : (x, y, z, t) \mapsto (-x, -y, z - \frac{1}{2}, -t)
$$

$$
\mathcal{C}\mathcal{S} : (x, y, z, t) \mapsto (-x, -y, z + \frac{1}{2}, -t),
$$

(3)

from which one finds in $k$-space,

$$
\mathcal{C}\mathcal{S} = \mathcal{T}_e \mathcal{S}\mathcal{C} = e^{i k_z c} \mathcal{S}\mathcal{C},
$$

(4)

with $\mathcal{T}_e$ being the translation along the $\tilde{z}$ axis by one primary vector $c$. Therefore the anti-commutator of $\mathcal{C}$ and $\mathcal{S}$ becomes zero, $\{\mathcal{C}, \mathcal{S}\} = 0$ at $k_z = \pi/c$. With this anti-commutation relation, one can prove that $\mathcal{C}$ relates the eigenstates to their degenerate partners of opposite $\mathcal{S}$-label as follows,

$$
\mathcal{S}\mathcal{C}|\psi^{\pm}(k)\rangle = e^{-i \frac{\pi}{2} c} \mathcal{C}\mathcal{S}|\psi^{\pm}(k)\rangle = \mp \mathcal{C}|\psi^{\pm}(k)\rangle.
$$

(5)

Then on the $k_z = \pi/c$ plane, one proves that each band is two-fold degenerated. We should stress here that for the case of no spin, actually the inversion $\mathcal{I}$ is not necessary for the degeneracy at $k_z = \pi/c$. We can use an alternative compound symmetry $\Theta = \mathcal{IT} \mathcal{S}_z$ to protect the degeneracy. It is easy to check that it takes $\Theta^2 = -1$ at $k_z = \pi/c$ plane, which ensures a Krammer degeneracy with the two related states labeled by eigen-values $\pm i$ of $\Theta$. However, in the following spinful case, $\Theta$ is not enough to protect the node-lines. For the purpose of consistence with the spinful case below, we use the same compound symmetries $\mathcal{IT} \mathcal{S}_z$ and $\mathcal{IT}$ in the spinless case.

2. the effect of spin-orbit coupling

Including the spin degree of freedom and the effect of SOC generally splits the four-fold degeneracy (counting both spin and orbit degree of freedom) at $k_z = \pi/c$. In this spinful case, $\mathcal{S}_z$ also acts on the spin space, $\mathcal{S}_z : (s_x, s_y, s_z) \mapsto (-s_x, -s_y, s_z)$. The square of $\mathcal{S}_z$ then rotates the spins by $2\pi$, contributing a minus sign for the spin $-\frac{1}{2}$ system. Therefore the square of $\mathcal{S} = \mathcal{IT} \mathcal{S}_z$ becomes $\mathcal{S}^2 = -1$ and $\mathcal{S}$ now has eigen-values $\pm i$, which again can be used to label the eigen-states of Bloch Hamiltonian, $\mathcal{S}|\phi^{\pm}(k)\rangle = \pm i|\phi^{\pm}(k)\rangle$. Unlike the spinless case, the action of $\mathcal{C} = \mathcal{IT}$ on the eigen-states $|\phi^{\pm}(k)\rangle$ only switches it to a partner state of the same $\mathcal{S}$-label, even though the anti-commutation relation of $\mathcal{C}$ and $\mathcal{S}$ retains. This point is easily checked as,

$$
\mathcal{S}\mathcal{C}|\phi^{\pm}(k)\rangle = e^{-i k_z c} \mathcal{C}\mathcal{S}|\phi^{\pm}(k)\rangle
$$

$$
= -\mathcal{C}(\pm i|\phi^{\pm}(k)\rangle)
$$

$$
= \mp \mathcal{C}|\phi^{\pm}(k)\rangle.
$$

(6)

Eq.(6) is used in the first line of Eqs.(6) and the last equality in Eq.(6) is obtained based on that time reversal operator $\mathcal{T} = i\sigma_y K$ contained in $\mathcal{C}$ conjugates $i$ to $-i$.

As $\mathcal{C}$ only related the eigen-state to its partner with the same $\mathcal{S}$-label, we only obtain two Krammers pairs that can not be related by symmetry $\mathcal{S}$ and $\mathcal{C}$ only. To explain the four-degenerated node-lines of BaTaS$_3$, we need other symmetries. We find it is the mirror symmetry $\mathcal{M}_x : (x, y, z) \mapsto (-x, y, z)$ that provides the needed protection for these node-lines. The implication is that the high symmetry path $k_z = 0$ at $k_z = \pi/c$ is just the intersecting line of the invariant plane $k_z = 0$ of $\mathcal{M}_x$ and the invariant plane $k_z = \pi/c$ of $\mathcal{S}$. On this invariant line, action of $\mathcal{M}_x$ will transform the eigen-state $|\phi^{\pm}(k)\rangle$ to a partner of an opposite $\mathcal{S}$-label, which then related the two Krammer pairs and ensures a four-fold degenerate node-line. Before clarifying this point, we first prove that $\mathcal{M}_x$ anti-commutes with $\mathcal{S}$. It is easily checked that in the real space, action of $\mathcal{S}\mathcal{M}_x$ and $\mathcal{M}_x\mathcal{S}$ on the coordinate lead to the same result. The anti-commutation relation of $\mathcal{M}_x$ and $\mathcal{S}$ comes from their action on the spin space. In spin space, $\mathcal{S}$ reflects $s_x$ and $s_y$ but keeps $s_z$ invariant, from which one can express its action by
$\exp(i\pi/2\hat{s}_z) = i\hat{s}_z$. Similarly, the action of $M_z$ on the spin is expressed by $\exp(i\pi/2\hat{s}_z) = i\hat{s}_z$. It is the action of $M_x$ and $S$ on the space that ensure the anti-commutation relation, $\{S, M_x\} = 0$. By applying $M_x$ on the eigenstate $|\phi^{\pm}(k)\rangle$, one then finds,

$$SM_x|\phi^{\pm}(k)\rangle = -M_x S|\phi^{\pm}(k)\rangle = -M_x \{\pm i|\phi^{\pm}(k)\rangle\} = \mp iM_x|\phi^{\pm}(k)\rangle. \tag{7}$$

Eqs. (6) and (7) finally finish the proving that at $k_x = 0$ on the $k_z = \pi/c$ plane there must be a four-fold degenerated node-line guaranteed by symmetries $S = \mathcal{I}S_z$, $C = \mathcal{T}$ and $M_x$. The node-lines at $k_x = \pm \sqrt{3}k_y$ on the $k_z = \pi/c$ are then resulted from the $C_{3z}$ rotation.

### B. Effective Hamiltonian

There are two active $d$-$3z^2-r^2$ orbits hosted on Ta atom in the unit cell and they compose the electronic states around the fermi surface. When SOC is turned off, we can use these two orbits, denoted by $A$ and $B$, to construct a $2 \times 2$ Hamiltonian at each $k$-point in the momentum space,

$$\hat{H}_0(k) = \begin{bmatrix} H_{AA}(k) & H_{AB}(k) \\ H_{BA}^*(k) & H_{BB}(k) \end{bmatrix}. \tag{8}$$

Here $|\eta, k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik}\cdot r_{n\eta} \psi(r - r_{n\eta})$ are the two basis functions with $\eta = A, B$ denoting the orbits. $\psi(r - r_{n\eta})$ is the local $d3z^2-r^2$ wave function centered on atom site $r_{n\eta}$ in the $n^{th}$ unit cell. For the spinful Hamiltonian, we need to take the spin degree of freedom into consideration and thus define four basis functions, $|\eta, k, \sigma\rangle$ with $\sigma = \uparrow$ or $\downarrow$ denoting the spin direction. The Hamiltonian is then enlarged to a $4 \times 4$ size,

$$H(k) = \begin{bmatrix} H_{AA}(k) & H_{AB}(k) & H_{BA}^*(k) & H_{BB}(k) \\ H_{AB}^*(k) & H_{BB}(k) & H_{BA}^*(k) & H_{AA}(k) \\ H_{BA}^*(k) & H_{AB}(k) & H_{BB}(k) & H_{BA}^*(k) \\ H_{BB}(k) & H_{AB}(k) & H_{BA}^*(k) & H_{AA}(k) \end{bmatrix}. \tag{9}$$

The time-reversal operator $\mathcal{T}$ now becomes $\mathcal{T} = i\hat{s}_y \mathcal{K}$ with $\hat{s}_y = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}$ being the Pauli matrix acting on the spin space. It reads,

$$\mathcal{T}|\eta, k, \sigma\rangle = \text{sgn}(\sigma)|\eta, -k, \sigma\rangle \quad \mathcal{TH}(k) = H(-k)\mathcal{T}. \tag{10}$$

with the sign function $\text{sgn}(\sigma)$ being $+1$ ($-1$) for spin $\uparrow$ ($\downarrow$) and $H(k) = e^{-i\mathbf{k}\cdot\mathbf{r}}H(r)e^{i\mathbf{k}\cdot\mathbf{r}}$. For the entries of Hamiltonian [9], one finds,

$$H_{\eta_1\eta_2}^{\sigma_1\sigma_2}(k) = \langle \eta_1, k, \sigma_1|H(k)|\eta_2, k, \sigma_2\rangle = -\text{sgn}(\sigma_2)\langle \eta_1, k, \sigma_1|H(\mathcal{T})|\eta_2, -k, \sigma_2\rangle = -\text{sgn}(\sigma_2)\langle \eta_1, k, \sigma_1|\mathcal{T}[H(-k)]|\eta_2, -k, \sigma_2\rangle = \text{sgn}(\sigma_1)\text{sgn}(\sigma_2)\langle \eta_2, -k, \sigma_2|H(-k)|\eta_1, -k, \sigma_1\rangle = \text{sgn}(\sigma_1)\text{sgn}(\sigma_2)H_{\eta_2\eta_1}^{\sigma_2\sigma_1}(-k). \tag{11}$$

To obtain the second and forth lines of the above equation, we use the transformation [10] of wave function for the right and left ket, respectively. The transformation of Hamiltonian under $\mathcal{T}$ is used to obtain the third line. To get the fifth line, we use the property of time-reversal symmetry $\langle \mathcal{T}\phi|\mathcal{T}|\psi\rangle = \langle \psi|\phi\rangle$.

The $P6_3/mmc$ group also contains an inversion symmetry $\mathcal{I} = (x, y, z) \mapsto (-x, -y, -z)$. $\mathcal{I}$ does not flip the spin and orbit indices, and the wave functions and Hamiltonian are transformed as,

$$\mathcal{I}|\eta, k, \sigma\rangle = |\eta, -k, \sigma\rangle \quad \mathcal{I}H(k) = H(-k)\mathcal{I}. \tag{12}$$

Applying Eq. (12) one finds the consequence of applying $\mathcal{I}$ onto the elements of Hamiltonian [9],

$$H_{\eta_1\eta_2}^{\sigma_1\sigma_2}(k, k_y, k_z) = H_{\eta_1\eta_2}^{\sigma_1\sigma_2}(-k_x, -k_y, -k_z). \tag{13}$$

Applying Eqs. (11) and (13) successively one obtains

$$H_{\eta_1\eta_2}^{\sigma_1\sigma_2}(k, k_y, k_z) = \text{sgn}(\sigma_1)\text{sgn}(\sigma_2)H_{\eta_2\eta_1}^{\sigma_2\sigma_1}(k, k_y, k_z), \tag{14}$$

which reduces the Hamiltonian [9] to the below form,

$$H(k) = \begin{bmatrix} a(k) f(k) & 0 & 0 & g(k) \\ b(k) & -g(k) & 0 & 0 \\ 0 & a(k) & f^*(k) & 0 \\ 0 & b(k) & 0 & a(k) \end{bmatrix}, \tag{15}$$

where $a(k)$ and $b(k)$ are real functions, and $f(k)$ and $g(k)$ are complex functions.

Hamiltonian [15] is mathematically equivalent to a linear combination of five Dirac matrices $\Gamma_n$ together with the unit matrix $\Gamma_0$. The eigenvalues of Hamiltonian [15] become four-fold degenerate only if the five coefficients of the Dirac matrices become zero, that is to say $a(k) - b(k) = f(k) - g(k) = 0$, which, however, does not hold at a general $k$ point. Below we prove that this four-fold-degenerating condition readily fulfills at three high-symmetries paths, $k_x = 0$ and $k_x = \pm \sqrt{3}k_y$ on the $k_z = \pi/c$ plane with the help of $S_z$ and a mirror symmetry $M_z : (x, y, z) \mapsto (-x, -y, z)$.

In real space, the skew axial symmetries $S_z$ flips the orbit indices. While in spin space, it keeps the $s_z$ component invariant but reverse $s_x$ and $s_y$, indicating that its action can be represented by $i\hat{s}_z$. Therefore the wave function and Hamiltonian transform as,

$$S_z|\eta, k, \sigma\rangle = ie^{-i\hat{s}_z\cdot\mathbf{r}}\text{sgn}(\sigma)|\eta, -k_x, -k_y, k_z, \sigma\rangle \quad S_zH(k) = H(-k_x, -k_y, k_z)S_z. \tag{16}$$
With Eq. (16), one finds the below relation for Bloch Hamiltonian (15),

\[ H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k_z, k_y, k_z) = (\eta_1, k, \sigma_1 | H(k) | \eta_2, k, \sigma_2) \]

\[ = (\eta_1, k, \sigma_1) S_z^{-1} \hat{S}_z H(k) S_z^{-1} | \eta_2, k, \sigma_2 \]

\[ = (\eta_1, k, \sigma_1) S_z^{-1} H(k) | \eta_2, k, \sigma_2 \]

\[ = (\eta_1, k, \sigma_1) H(k) | \eta_2, k, \sigma_2 \]

\[ = \text{sgn}(\eta_1) \text{sgn}(\eta_2) H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (-k_z, k_y, k_z), \quad (17) \]

with \( \hat{k} = (-k_x, -k_y, k_z) \). Then a constraint for the spinful Hamiltonian (15) is obtained,

\[ H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k_x, k_y, k_z) = \text{sgn}(\eta_1) \text{sgn}(\eta_2) H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (-k_x, k_y, k_z). \]

Combining Eqs. (13) and (18), one arrives at the below important relation of Hamiltonian posed by symmetry \( S = IS_z \),

\[ H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k_x, k_y, k_z) = \text{sgn}(\eta_1) \text{sgn}(\eta_2) H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k_x, k_y, -k_z). \]

Applying the transformation \( H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k + G) = e^{iG \cdot \mathbf{r}_{\eta_1 \eta_2}} H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k) \) to Eq. (19) for \( k_z = \pi/c \), one finds

\[ H^{\tau^+}_{AB} (k_x, \eta_1 \eta_2, \pi/c) = \text{sgn}(\sigma_1) \text{sgn}(\sigma_2) H^{\tau^-}_{BA} (k_x, \eta_1 \eta_2, -\pi/c) \]

\[ = \text{sgn}(\sigma_1) \text{sgn}(\sigma_2) e^{i \pi \frac{z}{2} | \eta_1 \eta_2 \rangle \langle \eta_1 \eta_2 | H^{\tau^-}_{BA} (k_x, k_y, \eta_1 \eta_2, \pi/c), \quad (20) \]

so that

\[ H^{\tau^+}_{AB} (k_x, \eta_1 \eta_2, \pi/c) = H^{\tau^+}_{BA} (k_x, \eta_1 \eta_2, \pi/c) \]

\[ H^{\tau^+}_{AB} (k_x, \eta_1 \eta_2, \pi/c) = -H^{\tau^+}_{BA} (k_x, \eta_1 \eta_2, \pi/c), \quad (21) \]

proving in Hamiltonian (15) that

\[ g(k_x, \eta_1 \eta_2, \pi/c) = 0, \quad \text{Re} \left[ f(k_x, \eta_1 \eta_2, \pi/c) \right] = 0. \]

Applying Eq. (19) to \( H^{\tau^+}_{AA} (k) \), one similarly obtains

\[ H^{\tau^+}_{AA} (k_x, \eta_1 \eta_2, \pi/c) = H^{\tau^+}_{BB} (k_x, \eta_1 \eta_2, \pi/c), \quad (23) \]

which proves

\[ a(k_x, \eta_1 \eta_2, \pi/c) = b(k_x, \eta_1 \eta_2, \pi/c). \]

Therefore, in the presence of \( \mathcal{I}, \mathcal{T} \) and \( S_z \), most elements of Hamiltonian (15) vanishes at \( k_z = \pi/c \) plane except imaginary party of \( H^{\tau^+}_{AB} (k_x, \eta_1 \eta_2, \pi/c) \) and a diagonal element \( \epsilon(k) = [a(k_x, \eta_1 \eta_2, \pi/c) + b(k_x, \eta_1 \eta_2, \pi/c)]/2 \).

It is possible to prove that \( \text{Im} \left[ f(0, \eta_1 \eta_2, \pi/c) \right] = 0 \) at the high-symmetry path \( k_y = 0 \) on \( k_z = \pi/c \) plane. To do so, we need extra symmetries, which in the present case is a mirror symmetry \( \mathbf{M}_x \) with the mirror plane lying at the \( y \)-\( z \) plane. In real space the mirror symmetry \( \mathbf{M}_x \) keeps the orbit indices invariant and inverts the \( x \)-component of coordinates. While in spin space, it keeps the spin component \( s_z \) invariant but reverses \( s_y \) and \( s_z \), indicating its action on the spin space represented by \( i \hat{s}_z \). Therefore the wave function and Hamiltonian transform as,

\[ \mathbf{M}_x \eta_1 \eta_2 \frac{\mathbf{r}}{\sigma} = i \eta_1 \eta_2 \frac{\mathbf{r}}{\sigma} \]

\[ \mathbf{M}_x H(k) = H(-k_x, k_y, k_z) \mathbf{M}_x. \]

which indicates,

\[ H^{\sigma_1 \sigma_2}_{\eta_1 \eta_2} (k_x, \eta_1 \eta_2, \pi/c) = H^{\overline{\sigma_1} \overline{\sigma_2}}_{\eta_1 \eta_2} (-k_x, \eta_1 \eta_2, \pi/c). \]

With Eq. (26), one gets \( H^{\tau^+}_{AB} (0, k_y, k_z) = H^{\tau^+}_{AB} (0, k_y, k_z) \) and \( H^{\tau^+}_{AB} (0, k_y, k_z) = H^{\tau^+}_{AB} (0, k_y, k_z) \), which proves

\[ \text{Re} \left[ g(0, k_y, k_z) \right] = 0. \]

For entry \( H^{\tau^+}_{AA} \), \( \mathbf{M}_x \) also sets \( H^{\tau^+}_{AA} (0, k_y, k_z) = H^{\tau^+}_{AA} (0, k_y, k_z) \) which results into the constraint.

By summarizing the above discussion, we prove that there exists a node-line at the \( k_z = 0 \) path on \( k_z = \pi/c \) plane for BaMX\(_3\) when SOC is turned on. For other two node-lines at \( k_z = \pm \sqrt{3}k_y \) (see in Fig. [3 b]), they can be produced by using the \( \tilde{C}_3 \) symmetry of the system, which rotates the \( k_z = 0 \) node-line to the \( k_z = \pm \sqrt{3}k_y \) directions.

We then expand the Hamiltonian around a point on the node-line \( k = (0, k_y, \pi/c) + (q_x, q_y, q_z) \) with \( (q_x, q_y, q_z) \) being small deviations from the expanding point \( k_0 = (0, k_y, \pi/c) \). From the above Eqs. (22), (24) and (27) one finds,

\[ \frac{\partial g}{\partial q_x} |_{k_0} = 0, \quad \frac{\partial g}{\partial q_y} |_{k_0} = 0, \quad \text{Re} \left[ \frac{\partial f}{\partial q_z} \right] |_{k_0} = 0, \]

\[ \text{Re} \left[ \frac{\partial f}{\partial q_x} \right] |_{k_0} = 0, \quad \text{Re} \left[ \frac{\partial f}{\partial q_y} \right] |_{k_0} = 0, \quad \text{Im} \left[ \frac{\partial f}{\partial q_z} \right] |_{k_0} = 0 \]

from which the low energy Hamiltonian is obtained,

\[ H^0 = \epsilon(k) + \alpha q_x q_y s_x + q_z \tau_x + q_x \tau_y \]

As \( \epsilon(k) \) is not important for the solution of Hamiltonian (25), we omit it in the following discussions. The Hamiltonian (29) takes a symmetry \( \tau_x s_y \) and by using the unitary matrix \( U \) which diagonalizes \( \tau_x s_y \),

\[ U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & -i & 0 & i \\ -i & 0 & i & 0 \end{pmatrix}, \]

one can transform the Hamiltonian \( H^0 \) into a block-diagonalized matrix \( \tilde{H} \),

\[ \tilde{H} = \epsilon(k) + \frac{1}{\sqrt{2}} \begin{pmatrix} \alpha q_z & q_x + iq_x & 0 & 0 \\ q_x - iq_x & -\alpha q_z & 0 & 0 \\ 0 & 0 & -\alpha q_z & q_x + iq_x \\ 0 & 0 & q_x - iq_x & \alpha q_z \end{pmatrix}. \]

(31)
state has an eigen-value of \(-\sqrt{q_x^2 + q_y^2}\) with the corresponding eigen-vector being \(\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -\exp(-i\theta) \end{bmatrix}\). When \(\mathbf{q}\) transverses along a closed loop circling the node-line, the accumulated Berry phase is computed to \(\pi\) as follows,

\[
\Phi_B = -i \lim_{N \to \infty} \sum_{j=0}^{N-1} \log(j | j + 1)
\]

\[
= -i \lim_{N \to \infty} \sum_{j=0}^{N-1} \log \left(1 + \exp[i(\theta_{j+1} - \theta_j)]\right)
\]

\[
= -i \int_0^{2\pi} \frac{i \theta}{2} = \pi,
\]

where the loop is discretized into \(N\) successive points labeled by \(j (j = 0, 1, 2, \ldots, N - 1)\) with \(N = 0\). The Berry phase \(\Phi_B\) here is only meaningful for modulo \(2\pi\) as \(|N| = e^{i2m\pi} 0\) is also well defined for condition \(N = 0\), which will increase \(\Phi_B\) by \(2m\pi\).

### C. Tight-Binding Model

In this section we construct a tight-binding model that is fully consisted with the symmetry constraints discussed above. The active orbits are the two local \(dz^2\) states centered on the Ta atoms and they provide the four local basis states when spin degree of freedom is included. Four hopping parameters are given to describe the \(dz^2\) bands near the fermi surface and their definitions are presented in Fig. 6(a) schematically. The two types of Ta atoms are denoted by triangles pointing at different orientations. The hopping process along the TaS\(_3\) chains is denoted by \(t_z\). In the \(x - y\) plane, hopping process take places between the same Ta \(-\)sublattice is defined as \(t_{xy}\) while the hopping between different sublattice in the slant direction is defined as \(t_{xy}^{ab}\). There are also spin-dependent hoppings when the spin orbit coupling is taken into consideration.

With these hopping parameters we are able to construct a \(4 \times 4\) Hamiltonian \(H_{TB}(\mathbf{k})\) as,

\[
H_{TB}(\mathbf{k}) = \begin{bmatrix}
g(\mathbf{k}) & u(\mathbf{k}) + v(\mathbf{k}) & 0 & 0 \\
u(\mathbf{k}) & g(\mathbf{k}) & 0 & 0 \\
0 & 0 & g(\mathbf{k}) & u^*(\mathbf{k}) + v^*(\mathbf{k}) \\
0 & 0 & u^*(\mathbf{k}) + v^*(\mathbf{k}) & g(\mathbf{k})
\end{bmatrix},
\]

where

\[
g(\mathbf{k}) = 2t_{xy} [\cos k \cdot \mathbf{a} + \cos k \cdot \mathbf{b} + \cos k \cdot (\mathbf{a} + \mathbf{b})]
\]

\[
= 2t_{xy} \left[2 \cos \frac{k_x a_0}{2} \cos \frac{\sqrt{3} k_y a_0}{2} + \cos k_z a_0\right]
\]

\[
v(\mathbf{k}) = 2it_{soc} \sin \frac{k_x}{2} \left[\sin k \cdot \mathbf{a} + \sin k \cdot \mathbf{b} - \sin k \cdot (\mathbf{a} + \mathbf{b})\right]
\]

\[
= 2it_{soc} \sin \frac{k_x}{2} \left[2 \sin \frac{k_x a_0}{2} \cos \frac{\sqrt{3} k_y a_0}{2} - \sin k_z a_0\right]
\]

\[
u(\mathbf{k}) = t_{xy}^{ab} \cos \frac{k_z}{2} \left[\cos k \cdot \mathbf{a} + \cos k \cdot \mathbf{b} + \cos k \cdot (\mathbf{a} + \mathbf{b})\right]
\]

\[+ 2t_z \cos \frac{k_z}{2}
\]

\[
= 2t_{xy}^{ab} \cos \frac{k_z}{2} \left[2 \cos \frac{k_x a_0}{2} \cos \frac{\sqrt{3} k_y a_0}{2} + \cos k_z a_0\right]
\]

\[+ 2t_z \cos \frac{k_z}{2}
\]

(34)
with \( \hat{a} = (\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0) a_0 \) and \( \hat{b} = (\frac{1}{2}, \frac{\sqrt{3}}{2}, 0) a_0 \). Here \( a_0 \) is the lattice constant in the \( x - y \) plane. It is easily verified that at high symmetry paths \( k_z = 0 \) and \( k_z = \pm \sqrt{3} k_0 \) on the \( k_z = \pi/c \) plane, \( u(k) = v(k) = 0 \), indicating that there exist three node-lines.

We also fit the \textit{ab initio} band structure shown in the main text with this TB-model and the results are shown in Fig. 7. With suitable parameters, the \textit{ab initio} band structures are fitted qualitatively well. As the \textit{ab initio} band structures are strongly hybridized to the other valence bands, we are more focused on the bands along the path \( A - L - H - A \).
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