Chevrel phase materials form a family of ternary molybdenum chalcogenides with a general chemical formula $A_xMo_6X_8$ ($A$ = metal elements, $X =$ chalcogen). The variety of $A$ atoms makes a large number of family members and leads to many tunable physical properties, such as the superconductivity, thermoelectricity and the ionic conductivity. In this work, we have further found various nontrivial band topological states in these materials by using first-principle calculations. The compounds having time-reversal symmetry, such as $BaMo_6S_8$, $SrMo_6S_8$ and $Mo_6S_8$, are topological insulators in both of the $R\bar{3}$ and $P\bar{1}$ phases, whereas $EuMo_6S_8$ within ferromagnetic state is an axion insulator in the $R\bar{3}$ phase and a trivial one in the $P\bar{1}$ phase. This indicates that the change of $A$ ions can modify the chemical potential, lattice distortion, and magnetic orders, which offers a unique way to influence the topological states and other properties. We hope this work can stimulate further studies of Chevrel phase materials to find more intriguing phenomena, such as topological superconducting states and Majorana modes.

**INTRODUCTION**

The Chevrel phase (CP) is a ternary molybdenum chalcogenides compound family [1], which was first discovered in 1971 by Chevrel and Sergent [2]. The generic chemical formula of this family is $A_xMo_6X_8$. In its crystal structure, $Mo_6X_8$ can be looked as a cluster and forms a three-dimensional (3D) network. In each cluster, six Mo atoms construct a octahedron and chalcogen atoms ($X =$ S, Se) form a distorted pyramid ligand field around each Mo. $A$ fills in this cluster network with $x$ varying from 0 to 4 [1] and it can be monovalent, divalent, trivalent or rare-earth elements. This leads to many family members and large space to tune their physical properties. Therefore, there have been lots of research done on them, and many intriguing phenomena have been found and investigated. For example, $SnMo_6S_8$ and $PbMo_6S_8$ show superconductivity at low temperature with $T_c$ being about 14.2 and 15.2 K, respectively [3–5]. $BaMo_6S_8$ and $EuMo_6S_8$ have been found to be superconducting under pressure around several GPa [6–10]. $Ca_xMo_6S_8$ becomes superconducting when Ca vacancy is introduced with $x$ = 0.94 [11]. Moreover, many of them have upper critical fields $H_{c2}$ higher than 25 T and even up to 60 T [5, 8, 10], which violates the Pauli paramagnetic limit in the weak coupling Bardeen-Schrieffer-Copper superconductor [12, 13]. One of the possible reason is the strong spin-orbit coupling (SOC) of the electrons around the Fermi level, since Mo 4$d$ bands have been found to constitute the Fermi surface. In addition, we noticed that the resistance-temperature curve of $BaMo_6S_8$ shows an anomalous behavior like ZrTe$_5$ [14–17], which has sensitive topological phase transitions tuned by small external stimuli [18–21]. Thus, to understand these exotic physical properties, the extensive studies on their electronic structure and band topology are necessary and meaningful.

In this work, we calculated and analyzed the topological states of some sulfides in these CP materials. We have chosen four representative compounds, namely $Mo_6S_8$ with $A$ site un-
occupied, BaMo$_6$S$_8$ and SrMo$_6$S$_8$ with A site occupied by nonmagnetic divalent ions, and EuMo$_6$S$_8$ with A site occupied by magnetic rare-earth ions Eu. We found that some of them have nontrivial band topology and further studied their dependence on structural and magnetic phase transitions, as well as different occupation cases. On considering their unconventional superconductivity, the existence of nontrivial band topology will be very appealing, and their mutual coupling may induce topological superconductivity and Majorana modes, such as those proposed in FeTe$_{1-x}$Se$_x$ [22, 23], the HfRuP family [24], and YCoC$_2$ [25].

The rest of this paper is organized as follows: First, we introduced the computational methods and software packages as well as the parameters we set. Second, we discussed the topological states of nonmagnetic compounds with BaMo$_6$S$_8$ as the representative object. Third, we studied the magnetic compound EuMo$_6$S$_8$. Finally, we present a discussion and our conclusions.
FIG. 2: The band structures of $R\overline{3}$ phase BaMo$_6$S$_8$ calculated with non-SOC PBE (a), non-SOC HSE06 (b), SOC PBE (c), and SOC HSE06 (d). In Panels (c) and (d), “-” and “+” represent the parity eigenvalues of each Kramers degenerate pair at TRIMs and the red bands are the $N$ occupied ones, where $N$ represents the number of valence electrons of BaMo$_6$S$_8$. Here, the coordinates of these TRIMs are $\Gamma$ (0, 0, 0), L (0.5, 0, 0), F (0.5, 0.5, 0), and Z (0.5, 0.5, 0.5).

I. METHODOLOGY

We employed the Vienna ab initio simulation package (VASP) [26, 27] to perform the electronic structure calculations. The projector-augmented-wave (PAW) method [28, 29] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [30] was used. It is known that DFT calculation within local density approximation or generalized gradient approximation always underestimates the band gap and overestimates the band inversion. To amend this, hybrid functional HSE06 [31, 32] calculation is usually employed to check the band topology [33]. The plane-wave cutoff for kinetic energy was set as 500 eV, and a $7 \times 7 \times 7 \Gamma$-centered Monkhorst-Pack $k$-point mesh was used to sample the Brillouin zone (BZ) in the self-consistent charge convergence calculation. To investigate the topological states, we constructed the Wannier functional based effective Hamiltonian using the WANNIER90 package [34], and performed the calculations of surface states and flow spectra of Wannier charge centers (WCCs) of occupied bands within Wilson loop scheme [35] using the WANNIERTOOLS package [36]. This package is also used when we check the existence of the in-gap node points. We constructed the Wannier functions for the bands composed of Mo $d$ and S $p$ orbitals.
II. RESULT AND DISCUSSION

A. BaMo$_6$S$_8$

The crystal structures and the BZs of BaMo$_6$S$_8$ are shown in Fig. 1. As most of the CP materials, it is $R\bar{3}$ phase at room temperatures and takes a structural phase transition to $P\bar{1}$ phase around 175 K [37] when temperature drops down. $R\bar{3}$ phase can be assumed as a slightly distorted cubic structure, in which the MoS$_8$ cluster is centering the cubic lattice formed by Ba atoms. The 90° angle between the lattice vectors is reduced to 88.711° ($\alpha_{rh}$) to form the $R\bar{3}$ phase [37], as shown in Fig. 1(a). The point group symmetry of $R\bar{3}$ phase is $C_{3i}$, where the $C_3$ rotation axis is along $\langle 111 \rangle$ direction in the rhombohedral lattice. As temperature drops down, the $C_3$ rotation symmetry is broken, and the symmetry reduces to $P\bar{1}$. This structural phase transition can be seen in the changes of the Mo-S bond lengths indicated in Fig. 1(b), where the three Mo-S bond lengths are different. The size of ions at A sites will affect the amplitude of distortion from $C_3$ symmetry. This distortion of MoS$_8$ cluster is a kind of cooperative Jahn-Teller distortion [38] to form $P\bar{1}$ phase. All the crystal structures [37, 39–45] used in work are shown in the Supplementary Material [46].

Now, let us consider the electronic structures and the topological states of the $R\bar{3}$ phase. In Fig. 2, the bands around the Fermi level are mainly from Mo 4$d$ orbitals and they have been proposed to be understood in the basis set composed by molecular orbitals of Mo$_6$ octahedral cluster [47]. In the non-SOC case, as shown in Fig. 2(a), the two bands crossing the Fermi level are two-fold degenerated along the $\Gamma$–Z path, which is protected by the $C_3$ rotation symmetry, and their representation is $^1E \oplus ^2E$. These two irreducible representations $^1E$ and $^2E$ are complex conjugate to each other. By taking the time-reversal symmetry into account, they will combine together to form a two dimensional irreducible representation of the type II magnetic group [48]. After including SOC, as shown in Fig. 2(c), the splitting in these two bands is obvious, namely there are finite band gaps between these two bands (each has Kramers degeneracy) at any $k$ point in the BZ. For this reason, SOC is necessary for getting the possible band insulator state in $R\bar{3}$ phase BaMo$_6$S$_8$. Otherwise, it would be a filling-enforced metal [49, 50].

Now let us consider the topological states with SOC. For convenience, we denote $N$ to represent the number of valence electrons in the case of $A$ being a divalent ion with $x = 1$, such as BaMo$_6$S$_8$. There are $N-2$ valence electrons when $A$ site is empty. When SOC is considered, the Kramers degenerated ($N-1$)- and $N$-th bands are gapped from the ($N+1$)- and
FIG. 4: The (001) surface states of \( R\overline{3} \) phase BaMo\(_6\)S\(_8\) with SOC. (a) The surface states calculated with the original band structure. (b) The surface states calculated with the renormalized band structure, which has a global gap in the \( N \) occupation case. (c) The surface states calculated with the renormalized band structure, which has a global gap in the \( N - 2 \) occupation case.

\((N + 2)\)-th bands at each \( k \)-point as we mentioned before. According to the Fu-Kane formula [51], we can get the topological \( \mathbb{Z}_2 \) indices \((v_0, v_1, v_2, v_3)\) from the parity eigenvalues of all occupied Kramers degenerate pairs on time-reversal invariant momenta (TRIMs).

We found if all the lowest \( N + 2 \) bands were occupied, the \( \mathbb{Z}_2 \) indices are \((0; 0, 0, 0)\). If all the lowest \( N \) bands are occupied (i.e., the \( N \) occupation case), the \( \mathbb{Z}_2 \) indices are \((1; 0, 0, 0)\), which means the \( \mathbb{Z}_2 \) indices for Kramers degenerated \((N + 1)\)- and \((N + 2)\)-th bands are \((1; 0, 0, 0)\). If all the lowest \( N - 2 \) bands are occupied (i.e., the \( N - 2 \) occupation case, namely \( A \) is unoccupied), the \( \mathbb{Z}_2 \) indices are \((1; 1, 1, 1)\), which means the \( \mathbb{Z}_2 \) indices for the \((N - 1)\)- and \((N)\)-th bands are \((0; 1, 1, 1)\). From these \( \mathbb{Z}_2 \) indices, the gap between the group of the lowest \( N - 2 \) bands and that of \( N - 1 \) to \( N + 2 \) bands is topologically non-trivial. That means there is band inversion happening between these two groups, which indicates there must be nodal line(s) in this gap in the non-SOC case [52]. The detailed calculations including the parity distribution and WCCs are shown in the Supplementary Material [46].

The band structures with HSE06 functional are shown in Figs. 2(b) and 2(d). In the non-SOC + HSE06 case, the band structure is much more like a semimetal than the PBE case. But the degeneracy of the bands crossing the Fermi level along the \( \Gamma - Z \) path remains. In the SOC + HSE06 case, such degeneracy is broken, and the band gap between them is much more enlarged than PBE case with small electron and hole pockets left. Comparing the parities in both cases, the parity eigenvalues and their distribution of the \( N \)-th and the \((N + 2)\)-th bands are not changed as shown in Figs. 2(c) and 2(d). So the topological states from HSE06 functional are not changed.

For a better understanding of the topological states in both the \( N - 2 \) occupation and the \( N \) occupation cases, we investigated the band inversion mechanism, which provides an intuitive picture of topological phase transitions. Let us consider the non-SOC condition first. By scaling the lattice vectors by \( 128 \% \) and fixing the Mo\(_6\)S\(_8\) cluster as a rigid molecular centering on the \((0.5, 0.5, 0.5)\) inversion center, the hopping between the clusters have been reduced and we got topologically trivial flat bands as shown in Fig. 3(a). We labeled the flat bands as “B1,” “B2,” and so on. B1 and B2 can be represented as the elementary band representation \((\text{eBR})\) \( 1E^2_2E^2_9@3b \). B3 is from \( \text{eBR} \ A_u@3b \), and B4 and B5 are from \( \text{eBR} \ 1E^2_2E^2_9@3b \).

To clarify the topological states in both the
FIG. 5: The band structures of $\overline{P} \overline{1}$ phase BaMo$_6$S$_8$ without SOC (a) and with SOC (b). In panel (b), the red bands are the $N$ occupied bands, where $N$ represents the number of valence electrons of BaMo$_6$S$_8$.

$N$ occupation and the $N-2$ occupation cases, we only need to tell which bands (i.e., B3, B4, and B5) inverted with the B1 and B2 in the real crystal because the other lower bands are not entangled with B1 and B2 until the lattice constants reduce to the real values. Comparing the parity eigenvalues at TRIMs (i.e., $\Gamma$, $Z$, $L$, and $F$ points) in the flat bands and those in the real crystal, we can find the following:

1) At the $\Gamma$ point, B1, B2 (with “+” parity eigenvalues) and B4, B5 (with “-” parity eigenvalues) are inverted;

2) At the $L$ point, the parities of B1 and B2 change from two negative values to one negative and one positive, which means there is band inversion happens. Comparing Figs. 2(c) and 3(b), we can find that SOC can only lift the band degeneracy but not affect the parity distribution at TRIMs. The hopping between the molecular orbitals from Mo$_6$S$_8$ clusters is crucial to the band inversion.

We further calculated the (001) (rhombohedral basis) surface states of $R3$ phase BaMo$_6$S$_8$ with SOC as shown in Fig. 4(a). Because of the absence of global gap in both $N$ and $N-2$ occupation cases, the surface Dirac cone is mixed with the bulk states. Therefore, we artificially shifted all the ab initio bands at every $k$ point by a $k$-dependent energy value, which does not change the energy order of the bands and the band topology, but it results in a global band gap. The details of this method are described in the Supplementary Material [46]. For later convenience, we call this procedure “renormalization”. We constructed two renormalized band structures which have global gap in the $N$ and $N-2$ occupation cases, respectively. Based on these renormalized band structures, we calculated the corresponding surface states with 0.02 and 0.01 eV onsite energy correction to the atoms in the surface region for the $N$ occupation and $N-2$ occupation cases, respectively. As shown in Figs. 4(b) and 4(c), there is a global gap in bulk states and clear surface Dirac cones in both cases. In the $N$ occupation case, there is only one surface Dirac cone at $\overline{\Gamma}$ and there are three surface Dirac cones in $N-2$ occupation case at $X$, $\Gamma$ and $\overline{X}_1$. The number and the distribution of surface Dirac cones are consistent with the parity distribution.

Now let us consider $\overline{P} \overline{1}$ phase BaMo$_6$S$_8$. The electronic structure of $\overline{P} \overline{1}$ is quite similar to the $R3$ phase. The obvious difference is that there is no double degenerated band in the non-SOC case due to the breaking of $C_3$ rotation symmetry, as shown in Fig. 5(a). With the inversion symmetry retained, we can still get their topological states from Fu-Kane formula. Due to the tiny difference in both the crystal and electronic structures between $R3$ and $\overline{P} \overline{1}$ phases, the topological $\mathbb{Z}_2$ indices remain unchanged in both of the $N-2$ occupation and $N$ occupation cases. The detailed information (including the parity distribution, WCCs, and surface states)
is shown in the Supplementary Material [46].

**B. SrMo₆S₈ and Mo₆S₈**

In the $R3$ phase, the crystal structure and the band structure of SrMo₆S₈ are basically the same as $R3$ phase BaMo₆S₈, except for the larger bandwidth of SrMo₆S₈ due to the smaller lattice constants. The topological $Z_2$ indices of $R3$ phase SrMo₆S₈ are the same as $R3$ phase BaMo₆S₈ in both of the $N - 2$ occupation and the $N$ occupation cases. We do not repeat the discussion in the main text. The band structures and the information of the topological states of $R3$ phase SrMo₆S₈ are shown in the Supplementary Material [46].

As shown in Figs. 6(a) and 6(b) for $P1$ phase SrMo₆S₈, the gap between the $N$- and the $(N + 2)$-th bands at $\Gamma$ point is much larger than the one in $P1$ phase BaMo₆S₈, and there are only small electron- and hole- pockets near the Fermi level. This may be attributed to the subtle difference between the structures of BaMo₆S₈ and SrMo₆S₈ in the $P1$ phase, as shown in the Supplementary Material [46].

In the $N$ occupation case, the topological $Z_2$ indices with SOC are $(1; 0, 0, 0)$, which are the same as $P1$ phase BaMo₆S₈. The larger bulk band gap at $\Gamma$ leads to a clear surface Dirac cone as shown in Fig. 6(c), which is calculated normally without above renormalization procedure. But for the $N - 2$ occupation case, the topological $Z_2$ indices with SOC are $(0; 1, 1, 1)$. They are different from those of $P1$ phase BaMo₆S₈. The nearly closing band gap at the $\Gamma$ point indicates SrMo₆S₈ is close to the topological phase transition point from $(1, 1, 1)$ to $(0, 1, 1, 1)$ due to the crystal distortion induced by replacing Ba with smaller Sr ions.

Because the topological state of BaMo₆S₈ in the $N - 2$ occupation case is a strong topological insulator, it is natural to reduce two valence electrons by removing the divalent metal atoms (i.e., Ba) to get a topological insulator with a large gap near the Fermi level. This is exactly Mo₆S₈ with the $A$ site empty. In the $R3$ phase, Mo₆S₈ has a similar crystal structure to that of BaMo₆S₈. The lattice constant is 6.428 Å and $\alpha_{ch}$ is large then 90° (i.e., 91.250°) [41, 42]. Thus, the Brillouin zone is different from BaMo₆S₈ which have divalent metal atoms. The crystal structure and the Brillouin zone of $R3$ phase Mo₆S₈ are shown in Fig. 7.

But from the band structures shown in Fig. 8, the gap is not as large as we expected before. The $Z_2$ indices with SOC are $(1, 1, 1, 1)$, which are the same as those of BaMo₆S₈ in the $N - 2$ occupation case. The detailed information can be found in the Supplementary Material [46].

For the $P1$ phase, Mo₆S₈ has quite different crystal structure from BaMo₆S₈ and SrMo₆S₈ and the electronic structure is also quite different from them, as shown in Fig. 9. The $Z_2$ indices with SOC are $(1; 0, 0, 1)$, which are dif-
different from BaMo$_6$S$_8$ and SrMo$_6$S$_8$ in the $P\bar{1}$ phase and the $N - 2$ occupation case. The parity distribution is shown in the Supplementary Material [46].

C. EuMo$_6$S$_8$

EuMo$_6$S$_8$ has magnetic order at low temperatures (less than 0.4 K), but it seems not to be the simple ferromagnetic order [53]. The seven $4f$ electrons on Eu$^{2+}$ ions are fully spin polarized and completely localized. In this sense, EuMo$_6$S$_8$ and BaMo$_6$S$_8$ are very similar, except for the breaking of the time-reversal symmetry and the Kramers degeneracy. Thus, we expect that the $\mathbb{Z}_2$ topological insulator in BaMo$_6$S$_8$ can be driven to axion insulator [54–58], Weyl semimetal [59–63] or trivial magnetic insulator in EuMo$_6$S$_8$. We assumed an artificial ferromagnetic order for both the $R\bar{3}$ and $P\bar{1}$ phases to investigate their topological states.

Now let us consider the $R\bar{3}$ phase firstly. Figure 10 shows the LDA+U band structures of EuMo$_6$S$_8$ in the ferromagnetic order. The on-site Hubbard $U = 5$ eV on the $f$ orbitals of Eu is considered. The difference between EuMo$_6$S$_8$ and BaMo$_6$S$_8$ is the spin splitting in the band structure. The spin splitting is quite small and it does not introduce any band inversion. Therefore, the topological states of EuMo$_6$S$_8$ in both the $N$ and $N-2$ occupation cases are axion...
FIG. 9: The band structures of $P\bar{1}$ phase Mo$_6$S$_8$ without SOC (a) and with SOC (b). In panel (b), the red bands are the $N-2$ occupied ones, where $N$ represents the number of valence electrons of BaMo$_6$S$_8$.

insulators as indicated by $z_4 = 2$, which is calculated with SOC according to the formula [64–67]

$$z_4 = \sum_K n_K^{-} \mod 4,$$

where $n_K^{-}$ is the number of occupied bands with odd parity eigenvalues at inversion-invariant momentum $K$. We also checked our results with increasing $U$ to 6, 7 and 8 eV, and they are not changed.

For the $P\bar{1}$ phase, the band structures are shown in Figs. 11(a) and 11(b). In the $P\bar{1}$ phase, the $z_4$ indices with SOC are 0 in both of the $N-2$ and $N$ occupation cases. This difference comes from the additional band inversion caused by structural phase transition from $R\bar{3}$ to $P\bar{1}$ phase. For the $N$ occupation case, at $Y (0.0, 0.5, 0.0)$, the $(N-1)$- and $N$-th bands are inverted with the $(N+1)$- and $(N+2)$-th bands referring to the $R\bar{3}$ case. The $(N-1)$- and $N$-th bands and the $(N+1)$- and $(N+2)$-th bands have different parity eigenvalues, leading to the topological trivial state. For the $N-2$ occupation case, the number of occupied bands with odd parities is reduced by two at $V (0.5, 0.5, 0.0)$, and this results in the topological triv-
FIG. 11: The band structures of $P\bar{1}$ phase EuMo$_6$S$_8$ without SOC (a) and with SOC (b) in ferromagnetic order. In panel (a), the red and blue colors represent the spin up and spin down, respectively. In panel (b), the red bands are the $N$ occupied ones, where $N$ represents the number of valence electrons of BaMo$_6$S$_8$. Here, the seven 4$f$ electrons of Eu$^{2+}$ are localized and not counted into the valence electrons.

III. CONCLUSION AND DISCUSSION

We systematically studied the topological states of CP materials. For BaMo$_6$S$_8$ in both of the $R3$ and $P\bar{1}$ phases, the topological $Z_2$ indices are (1; 0, 0, 0) in the $N$ occupation and (1; 1, 1, 1) in the $N-2$ occupation cases. For $R3$ phase SrMo$_6$S$_8$, the topological states are the same as $R3$ phase BaMo$_6$S$_8$. For $P\bar{1}$ phase SrMo$_6$S$_8$, it is a strong topological insulator in the $N$ occupation case, with $Z_2 = (1; 0, 0, 0)$. For the $N-2$ occupation case, it is close to a topological phase transition point between the strong and weak topological states. For Mo$_6$S$_8$ without the divalent metal atoms, it is a topological insulator and the topological invariants are the same as $R3$ phase BaMo$_6$S$_8$ in the $N-2$ occupation case. But in the $P\bar{1}$ phase, the topological indices are (1; 0, 0, 1), which are different from the previous compounds because of the further crystal distortion without cation ions $A$. For EuMo$_6$S$_8$ with ferromagnetic order, it is an axion insulator with $z_A = 2$ in both the $N$ and $N-2$ occupation cases in the $R3$ phase, whereas it is a trivial magnetic insulator in the $P\bar{1}$ phase because of the additional band inversion. The information of topological states of the compounds with time-reversal symmetry can also be seen in the results of the high-throughput searching of topological materials [68–72]. However, some of the results are different from ours because of the difference in detail of calculations, such as the crystal structures and the exchange-correlation functionals. Combining the intriguing physical properties of CP materials, such as high transition temperature and high upper critical field superconductivity, the nontrivial band topology revealed in this work may open another dimension in their research and provide a platform to construct topological superconductivity and Majorana modes.

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Supplementary Materials: Topological States in Chevrel Phase
Materials from First-principle Calculations

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I. THE PROCEDURE OF BAND RENORMALIZATION

Suppose our aim is to get a global gap between the $N$ lowest bands and the $(N+1)$-th band (i.e., a global gap in the $N$ occupation case) at the reference energy $\varepsilon_0$. We define $m_k = (E_{N+1,k} + E_{N,k})/2$ as the middle point of the $N$- and the $(N+1)$-th bands at $k$, where $E_{N,k}$ is the energy of the $N$-th band. Then, we define $\delta_k = \varepsilon_0 - m_k$. After shifting the energy of all the bands at $k$ with $\delta_k$, we can get a global gap at the reference energy $\varepsilon_0$. For convenience, we call this procedure “renormalization”. There is no band inversion at each $k$ point during this procedure. Thus, this kind of renormalization does not affect the band topology.

II. THE PARITY DISTRIBUTION, WCCS AND SURFACE STATES OF BaMo$_6$S$_8$

In Fig. S1, we show the parity distribution and WCCs of $R\bar{3}$ phase BaMo$_6$S$_8$ with SOC in the $N-2$ occupation, $N$ occupation and $N+2$ occupation cases, respectively. These results indicate that the $\mathbb{Z}_2$ indices of $R\bar{3}$ phase BaMo$_6$S$_8$ are $(1; 0, 0, 0)$ in the $N$ occupation case and $(1; 1, 1, 1)$ in the $N-2$ occupation case. Fig. S1c, S1f, S1i and S1l demonstrate that the the lowest $N+2$ bands are topologically trivial, as we mentioned in the main text.

In Fig. S2, we show the parity distribution and WCCs of $P\bar{1}$ phase BaMo$_6$S$_8$ with SOC in the $N-2$ occupation, $N$ occupation and $N+2$ occupation cases, respectively. These results indicate that the $\mathbb{Z}_2$ indices of $P\bar{1}$ phase BaMo$_6$S$_8$ are the same as the ones of $R\bar{3}$ phase BaMo$_6$S$_8$ in both of the $N-2$ and $N$ occupation cases. Fig. S2c, S2f, S2i and S2l demonstrate that the the lowest $N+2$ bands are topologically trivial.

The (001) surface states of $P\bar{1}$ phase BaMo$_6$S$_8$ with SOC are shown in Fig. S3a. Because of the absence of global gap in both of the $N$ and $N-2$ occupation cases, the surface Dirac cone is mixed with the bulk states. We calculated the renormalized band structures and the corresponding surface states with 0.02 eV and 0.01 eV onsite energy correction to the atoms in the surface region for the $N$ occupation and $N-2$ occupation cases, respectively. As shown in Fig. S3b and S3c, there is a global gap in bulk states and clear surface Dirac cones in both cases. There is only one surface Dirac cone at $\bar{\Gamma}$ in the $N$ occupation case and three surface Dirac cones at $X$, $\bar{\Gamma}$ and $X_1$ in the $N-2$ occupation case. The number and the distribution of surface Dirac cones are consistent with the parity distribution.
FIG. S1: The band structures, parities, WCCs of $R\bar{3}$ phase BaMo$_6$S$_8$ in different occupation cases with SOC. Here, each column belongs to the same occupation case. In (a), (b) and (c), the red bands represent the occupied ones, which show the $N - 2$ occupation, $N$ occupation, and $N + 2$ occupation cases intuitively. In (d), (e) and (f), “-” represents the product of parity eigenvalues of all occupied Kramers degenerate pairs at this TRIM to be odd, and “+” represents even. (g), (h), (i) show the evolution of WCCs on the $k_3 = \pi$ plane, and Fig. (j), (k), (l) show the evolution of WCCs on the $k_3 = 0$ plane. Here, the WCCs integral direction is $k_1$ and WCCs evolve along $k_2$. 
FIG. S2: The band structures, parities, WCCs of $P\bar{1}$ phase BaMo$_6$S$_8$ in different occupation cases with SOC. Here, each column belongs to the same occupation case. In (a), (b) and (c), the red bands represent the occupied ones, which show the $N-2$ occupation, $N$ occupation, and $N+2$ occupation cases intuitively. In (d), (e) and (f), “−” represents the product of parity eigenvalues of all occupied Kramers degenerate pairs at this TRIM to be odd, and “+” represents even. (g), (h), (i) show the evolution of WCCs on the $k_3 = \pi$ plane, and (j), (k), (l) show the evolution of WCCs on the $k_3 = 0$ plane. Here, the WCCs integral direction is $k_1$ and WCCs evolves along $k_2$. 
FIG. S3: The (001) surface states of \( P\bar{1} \) phase \( \text{BaMo}_6\text{S}_8 \) with SOC. (a) The surface states calculated with the original band structure. (b) The surface states calculated with the renormalized band structure, which has a global gap in the \( N \) occupation case. (c) The surface states calculated with the renormalized band structure, which has a global gap in the \( N - 2 \) occupation case.

III. THE BAND STRUCTURE, PARITY DISTRIBUTION, WCCS AND SURFACE STATES OF \( \text{SrMo}_6\text{S}_8 \)

Fig. S4 shows the band structures of \( R\bar{3} \) phase \( \text{SrMo}_6\text{S}_8 \), which are basically the same as the ones of \( R\bar{3} \) phase \( \text{BaMo}_6\text{S}_8 \).

In Fig. S5, we show the parity distribution and WCCs of \( R\bar{3} \) phase \( \text{SrMo}_6\text{S}_8 \) with SOC in the \( N - 2 \) occupation, \( N \) occupation and \( N + 2 \) occupation cases, respectively. These results indicate that the \( \mathbb{Z}_2 \) indices of \( R\bar{3} \) phase \( \text{SrMo}_6\text{S}_8 \) are \((1; 0, 0, 0)\) in the \( N \) occupation case and \((1; 1, 1, 1)\) in the \( N - 2 \) occupation case. Fig. S5c, S5f, S5i and S5l demonstrate that the the lowest \( N + 2 \) bands are topologically trivial.

The (001) surface states of \( R\bar{3} \) phase \( \text{SrMo}_6\text{S}_8 \) with SOC are shown in Fig. S6a. Because of the absence of global gap in both of the \( N \) and \( N - 2 \) occupation cases, the surface Dirac cone is mixed with the bulk states. We calculated the renormalized band structures and the corresponding surface states with 0.02 eV onsite energy correction to the atoms in the surface region for the \( N \) occupation and \( N - 2 \) occupation cases, respectively. As shown in Fig. S6b and S6c, there is a global gap in bulk states and clear surface Dirac cones in both cases. There is only one surface Dirac cone at \( \bar{\Gamma} \) in the \( N \) occupation case and three surface Dirac cones at \( \bar{X} \), \( \bar{\Gamma} \) and \( \bar{X}_1 \) in the \( N - 2 \) occupation case. The number and the distribution of surface Dirac cones are consistent with the parity distribution.

The parity distribution and WCCs of \( P\bar{1} \) phase \( \text{SrMo}_6\text{S}_8 \) with SOC in the \( N \) occupation case are shown in Fig. S7. These results show that the \( \mathbb{Z}_2 \) indices of \( P\bar{1} \) phase \( \text{SrMo}_6\text{S}_8 \) are \((1; 0, 0, 0)\) in the \( N \) occupation case.

The three Mo-S bond lengths in \( P\bar{1} \) phase \( \text{BaMo}_6\text{S}_8 \) and \( \text{SrMo}_6\text{S}_8 \) are shown in Fig. S8 to compare the difference in their crystal structures.
FIG. S4: The band structures of $R\bar{3}$ phase SrMo$_6$S$_8$ without SOC (a) and with SOC (b). In (b), the red bands are the $N$ occupied ones, where $N$ represents the number of valence electrons of BaMo$_6$S$_8$. 
FIG. S5: The band structures, parities, WCC of $R\bar{3}$ SrMo$_6$S$_8$ in different occupation cases with SOC. Here, each column belongs to the same occupation case. In (a), (b) and (c), the red bands represent the occupied ones, which show the $N - 2$ occupation, $N$ occupation, and $N + 2$ occupation cases intuitively. In (d), (e) and (f), “-” represents the product of parity eigenvalues of all occupied Kramers degenerate pairs at this TRIM to be odd, and “+” represents even. (g), (h), (i) show the evolution of WCCs on the $k_3 = \pi$ plane, and (j), (k), (l) show the evolution of WCC on the $k_3 = 0$ plane. Here, the WCCs integral direction is $k_1$ and WCCs evolve along $k_2$. 
FIG. S6: The (001) surface states of $R\bar{3}$ phase SrMo$_6$S$_8$ with SOC. (a) The surface states calculated with the original band structure. (b) The surface states calculated with the renormalized band structure, which has a global gap in the $N$ occupation case. (c) The surface states calculated with the renormalized band structure, which has a global gap in the $N - 2$ occupation case.

FIG. S7: The information of the topological state of $P\bar{1}$ phase SrMo$_6$S$_8$ with SOC. (a) The parity distribution, where the “+” represents even and the “-” represents odd. (b) and (c) show the evolution of WCCs on the $k_3 = \pi$ plane and the $k_3 = 0$ plane, respectively. Here, the WCCs integral direction is $k_1$ and WCCs evolve along $k_2$. 
FIG. S8: The Mo$_6$S$_8$ clusters of BaMo$_6$S$_8$ (a) and SrMo$_6$S$_8$ (b) in the $P\bar{1}$ phase and the three bond lengths (in unit Å) is labeled. Here we omitted the Ba (Sr) atoms for clearness.

IV. THE PARITY DISTRIBUTION, WCCS AND SURFACE STATES OF Mo$_6$S$_8$

In Fig. S9, we show the parity distribution and WCCs of $R\bar{3}$ phase Mo$_6$S$_8$ with SOC. These results show that the $Z_2$ indices of $R\bar{3}$ phase Mo$_6$S$_8$ are $(1; 0, 0, 0)$, which are the same as the ones of $R\bar{3}$ phase BaMo$_6$S$_8$ in the $N - 2$ occupation case.

The (001) surface states of $R\bar{3}$ phase Mo$_6$S$_8$ are shown in Fig. S10a. Because of the absence of global gap, the surface Dirac cone is mixed with the bulk states. We calculated the renormalized band structure, which has a global gap, and the corresponding surface states, as shown in Fig. S10b. There are three surface Dirac cones at $X$, $\Gamma$ and $X_1$. The number and the distribution of surface Dirac cones are consistent with the parity distribution.

The parity distribution with SOC of $P\bar{1}$ phase Mo$_6$S$_8$ is shown in Fig. S11, which indicates the $Z_2$ indices of $P\bar{1}$ phase Mo$_6$S$_8$ are $(1; 0, 0, 1)$. 
FIG. S9: The information of the topological states of \( R3 \) phase \( \text{Mo}_6\text{S}_8 \) with SOC. (a) The parity distribution, where “+” represents even and “-” represents odd. (b) and (c) show the evolution of WCCs on the \( k_3 = \pi \) plane and the \( k_3 = 0 \) plane, respectively. Here, the WCCs integral direction is \( k_1 \) and WCCs evolve along \( k_2 \).
FIG. S11: The parity distribution of $P\bar{1}$ phase Mo$_6$S$_8$ with SOC, where “+” represents even, and “-” represents odd.

V. THE CRYSTAL STRUCTURES OF BaMo$_6$S$_8$, SrMo$_6$S$_8$, Mo$_6$S$_8$ AND EuMo$_6$S$_8$

We list the crystal structures used in calculations in Tab. I-IV.
TABLE I: The crystal structures of \( \text{BaMo}_6\text{S}_8 \) in the \( R\bar{3} \) phase (ICDD PDF: 01-088-1169) [1] and the \( P\bar{1} \) phase (ICDD PDF: 01-088-1170) [1].

| Lattice vectors (Å) | \( R\bar{3} \) | \( P\bar{1} \) |
|---------------------|----------------|----------------|
| a                   | 4.64870 2.68393 3.92447 | -6.56850 0.00000 0.00000 |
| b                   | -4.64870 2.68393 3.92447 | -0.11946 -0.12586 -6.69535 |
| c                   | 0.00000 -5.36786 3.92447 | -0.24048 -6.65015 0.00000 |

| Atom positions (fraction) | \( R\bar{3} \) | \( P\bar{1} \) |
|---------------------------|----------------|----------------|
| Ba                        | 0.00000 0.00000 0.00000 | 0.00000 0.00000 0.00000 |
| Mo                        | 0.76541 0.43444 0.58245 | -0.58084 -0.76250 -0.43557 |
| Mo                        | 0.23459 0.56556 0.41755 | -0.41916 -0.23750 -0.56443 |
| Mo                        | 0.56556 0.41755 0.23459 | -0.43472 -0.58235 -0.76695 |
| Mo                        | 0.58245 0.76541 0.43444 | -0.56528 -0.41765 -0.23305 |
| Mo                        | 0.41755 0.23459 0.56556 | -0.76736 -0.43322 -0.58331 |
| Mo                        | 0.43444 0.58245 0.76541 | -0.23264 -0.56678 -0.41669 |
| S                         | 0.60969 0.26402 0.87703 | -0.26310 -0.87600 -0.60760 |
| S                         | 0.39031 0.73598 0.12297 | -0.73690 -0.12400 -0.39240 |
| S                         | 0.73598 0.12297 0.39031 | -0.74760 -0.74440 -0.75310 |
| S                         | 0.87703 0.60969 0.26402 | -0.25240 -0.25560 -0.24690 |
| S                         | 0.12297 0.39031 0.73598 | -0.87530 -0.60850 -0.26410 |
| S                         | 0.26402 0.87703 0.60969 | -0.12470 -0.39150 -0.73590 |
| S                         | 0.74850 0.74850 0.74850 | -0.61220 -0.26240 -0.87760 |
| S                         | 0.25150 0.25150 0.25150 | -0.38780 -0.73760 -0.12240 |
TABLE II: The crystal structures of SrMo$_6$S$_8$ in the $R\bar{3}$ phase (ICDD PDF: 01-085-9202) [2] and the $P\bar{1}$ phase (ICDD PDF: 04-001-6572) [3].

| SrMo$_6$S$_8$ | R$\bar{3}$ | P$\bar{1}$ |
|--------------|------------|-----------|
| Lattice vectors (Å) | | |
| a | 4.59480 | 2.65281 | 3.84773 | -6.48100 | 0.00000 | 0.00000 |
| b | -4.59480 | 2.65281 | 3.84773 | -0.08030 | -0.08447 | -6.60997 |
| c | 0.00000 | -5.30562 | 3.84773 | -0.20999 | -6.56864 | 0.00000 |
| Atom positions (fraction) | | |
| Sr | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Mo | 0.22900 | 0.41799 | 0.56300 | -0.23100 | -0.41700 | -0.56400 |
| Mo | 0.77100 | 0.58201 | 0.43700 | -0.76900 | -0.58300 | -0.43600 |
| Mo | 0.56300 | 0.22900 | 0.41799 | -0.41800 | -0.56800 | -0.23200 |
| Mo | 0.43700 | 0.77100 | 0.58201 | -0.58200 | -0.43200 | -0.76800 |
| Mo | 0.41799 | 0.56300 | 0.22900 | -0.56700 | -0.22600 | -0.41800 |
| Mo | 0.58201 | 0.43700 | 0.77100 | -0.43300 | -0.77400 | -0.58200 |
| S | 0.38400 | 0.12801 | 0.74100 | -0.12600 | -0.76500 | -0.38500 |
| S | 0.61600 | 0.87199 | 0.25900 | -0.87400 | -0.23500 | -0.61500 |
| S | 0.74100 | 0.38400 | 0.12801 | -0.23200 | -0.22500 | -0.25500 |
| S | 0.25900 | 0.61600 | 0.87199 | -0.76800 | -0.77500 | -0.74500 |
| S | 0.12801 | 0.74100 | 0.38400 | -0.37300 | -0.12300 | -0.71800 |
| S | 0.87199 | 0.25900 | 0.61600 | -0.62700 | -0.87700 | -0.28200 |
| S | 0.24700 | 0.24700 | 0.24700 | -0.74800 | -0.35900 | -0.14400 |
| S | 0.75300 | 0.75300 | 0.75300 | -0.25200 | -0.64100 | -0.85600 |
TABLE III: Information of the crystal structures of Mo$_6$S$_8$ in the $R\bar{3}$ phase (SpringerMaterials Dataset ID: sd_0312550) [4, 5] and the $P\bar{1}$ phase (ICDD PDF: 04-020-4062) [6].

| Mo$_6$S$_8$ | $R\bar{3}$ | $P\bar{1}$ |
|------------|-----------|-----------|
| Lattice vectors (Å) | | |
| a | 4.59460 | 2.65269 | 3.62933 | 1.59392 | -6.41288 | 0.00000 |
| b | -4.59460 | 2.65269 | 3.62933 | 6.36400 | 0.00000 | 0.00000 |
| c | 0.00000 | -5.30539 | 3.62933 | 3.19332 | -2.47343 | 5.49467 |
| Atom positions (fraction) | | | |
| Mo | 0.77696 | 0.58703 | 0.45392 | -0.00147 | -0.22401 | 0.50321 |
| Mo | 0.22304 | 0.41297 | 0.54608 | -0.99853 | 0.22401 | 0.49679 |
| Mo | 0.45392 | 0.77696 | 0.58703 | -0.48276 | 0.27235 | 0.18129 |
| Mo | 0.54608 | 0.22304 | 0.41297 | -0.51724 | -0.27235 | 0.81871 |
| Mo | 0.58703 | 0.45392 | 0.77696 | -0.48563 | 0.78343 | 0.19147 |
| Mo | 0.41297 | 0.54608 | 0.22304 | -0.51437 | -0.78343 | 0.80853 |
| S | 0.62083 | 0.87260 | 0.25530 | -0.21270 | -0.41750 | 0.94820 |
| S | 0.37917 | 0.12740 | 0.74470 | -0.78730 | 0.41750 | 0.05180 |
| S | 0.25530 | 0.62083 | 0.87260 | -0.26930 | -0.41800 | 0.47220 |
| S | 0.74470 | 0.37917 | 0.12740 | -0.73070 | 0.41800 | 0.52780 |
| S | 0.87260 | 0.25530 | 0.62083 | -0.79460 | 0.92020 | 0.06350 |
| S | 0.12740 | 0.74470 | 0.37917 | -0.20540 | -0.92020 | 0.93650 |
| S | 0.78627 | 0.78627 | 0.78627 | -0.71490 | 0.92020 | 0.53200 |
| S | 0.21373 | 0.21373 | 0.21373 | -0.28510 | 0.08660 | 0.46800 |
TABLE IV: Information of the crystal structures of EuMo$_6$S$_8$ in the $R\bar{3}$ phase (ICDD PDF: 00-048-1791) [7] and the $P\bar{1}$ phase (ICDD PDF: 01-079-0877) [8].

| EuMo$_6$S$_8$       | $R\bar{3}$ | $P\bar{1}$ |
|---------------------|------------|------------|
| **Lattice vectors (Å)** |            |            |
| a                   | 4.58870    | -0.08492   |
| b                   | 2.64929    | -0.08293   |
| c                   | 3.85410    | -6.59193   |
|                     | -0.21025   | -6.56263   |
|                     | 0.00000    | 0.00000    |
|                     | -6.48200   | 0.00000    |
|                     | -0.76400   | 0.00000    |
|                     | -0.14600   | -0.56150   |
|                      |            |            |
| **Atom positions (fraction)** |            |            |
| Eu                  | 0.00000 0.00000 0.00000 | 0.00000 0.00000 0.00000 |
| Mo                  | 0.43803 0.77274 0.58377 | -0.43890 -0.58160 -0.76700 |
| Mo                  | 0.56197 0.22726 0.41623 | -0.56110 -0.41840 -0.23300 |
| Mo                  | 0.22726 0.41623 0.56197 | -0.76950 -0.44380 -0.58360 |
| Mo                  | 0.58377 0.43803 0.77274 | -0.23050 -0.55620 -0.41640 |
| Mo                  | 0.41623 0.56197 0.22726 | -0.58550 -0.58700 -0.43850 |
| Mo                  | 0.77274 0.58377 0.43803 | -0.41450 -0.21930 -0.56150 |
| S                   | 0.87471 0.25789 0.61699 | -0.60200 -0.23600 -0.85400 |
| S                   | 0.12529 0.74211 0.38301 | -0.39800 -0.14600 |
| S                   | 0.74211 0.38301 0.12529 | -0.75400 -0.75200 |
| S                   | 0.61699 0.87471 0.25789 | -0.24600 -0.24800 |
| S                   | 0.38301 0.12529 0.74211 | -0.26200 -0.62000 |
| S                   | 0.25789 0.61699 0.87471 | -0.73800 -0.38000 |
| S                   | 0.75637 0.75637 0.75637 | -0.88900 -0.26000 |
| S                   | 0.24363 0.24363 0.24363 | -0.11100 -0.74000 |

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