

## 1 Accidental persistent spin textures in the proustite mineral family

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5 Persistent spin textures (PSTs) in momentum space have the potential to enable spintronic devices which are  
6 currently limited by spin lifetimes in nonmagnetic spin-orbit coupled materials. We perform a first-principles  
7 study on the proustite mineral family,  $\text{Ag}_3\text{BQ}_3$  ( $\text{B} = \text{As, Sb}$ ;  $\text{Q} = \text{S, Se}$ ), and show these chalcogenides exhibit  
8 nonsymmetry-protected PSTs, which we refer to as symmetry-assisted PSTs. Chemical substitution can be used  
9 to tune the PST quality and properties, e.g., spin lifetime, and we find that a Rashba anisotropy criterion correlates  
10 with the PST area and spin lifetime for two of the three proustites examined. Last, we show that a first-order  
11 effective SOC Hamiltonian, often used in two-dimensional systems, is insufficient to describe the PST state in  
12 all proustites, suggesting that higher order models are necessary to fully describe PSTs in bulk three-dimensional  
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## 15 I. INTRODUCTION

16 Nonmagnetic materials with unidirectional spin-  
17 momentum locking, or a persistent spin texture (PST),  
18 exhibit electrical transport properties useful for spintronic  
19 applications [1,2]. In particular, a PST at the Fermi level  
20 of a conducting system enables the persistent spin helix  
21 (PSH) transport mode in which an electron's spin precesses  
22 around a fixed axis as it moves through the material. This  
23 mode is immune to decoherence from some low-temperature  
24 scattering mechanisms. PST formation requires the presence  
25 of strong spin-orbit coupling (SOC) combined with inversion  
26 symmetry breaking. This combination produces SOC-derived  
27 band splitting and is responsible for the well-known  
28 Rashba and Dresselhaus splittings and spin textures. In  
29 contrast to the aforementioned spin textures, a PST consists  
30 of unidirectionally aligned spins which are momentum  
31 independent. This feature has been reported theoretically  
32 and observed experimentally in quantum well structures,  
33 2D materials, and at interfaces [3–5]. PSTs were recently  
34 theorized to exist in bulk three-dimensional (3D) systems  
35 exhibiting nonsymmorphic symmetries [6] along with strong  
36 SOC and broken inversion symmetry, and several bulk  
37 materials, primarily ferroelectric oxides, have since been  
38 predicted to host a PST [7–9].39 The 3D PST materials predicted thus far all exhibit a  
40 symmetry-protected PST (SP-PST), also known as a type-I  
41 PST [10,11], which is enforced through crystalline symme-  
42 tries. Recently, mirror symmetries were shown to be the key  
43 ingredient for forming a SP-PST [9]. The symmetry protec-  
44 tion, however, is a sufficient but not necessary component  
45 to form a PST in bulk materials—it is possible to tune  
46 the strength of SOC parameters to produce an “accidental”  
47 or type-II PST that is not enforced by symmetry [11]. In48 this paper, we perform electronic structure simulations and  
49 model Hamiltonian calculations to show that the proustites  
50 ( $\text{Ag}_3\text{BQ}_3$ ), a family of silver chalcogenide minerals, exhibit  
51 type-II PSTs. By looking beyond symmetry-constrained PSTs  
52 and examining a family with high chemical tunability, we  
53 uncover symmetry-assisted PSTs in the proustite family. Our  
54 study expands the number of polar compounds that can exhibit  
55 high-quality PSTs and spin helices.

## 56 II. MATERIALS AND METHODS

## 57 A. Proustite family

58 The proustite family consists of three compounds in space  
59 group  $R\bar{3}c$ : The namesake mineral  $\text{Ag}_3\text{AsS}_3$ , as well as  
60  $\text{Ag}_3\text{SbS}_3$  and  $\text{Ag}_3\text{AsSe}_3$ . The former two are naturally oc-  
61 ccurring minerals and all three have been experimentally  
62 synthesized as bulk single crystals [12–14]. The crystal  
63 structure of  $\text{Ag}_3\text{AsS}_3$  [Fig. 1(a)] consists of  $\text{AsS}_3$  pyramids  
64 connected along the  $c$  axis by Ag-S chains [Fig. 1(b)] which  
65 are generated by a  $3_1$  screw axis. Owing to the  $c$ -glide plane,  
66 two sublattices of the  $\text{AsS}_3$  pyramids and chains exist, where  
67 each sublattice is chiral but of opposite handedness from the  
68 other, resulting in an achiral crystal. The isostructural variants  
69 are similar (see Table I and Ref. [15]).

## 70 B. Computational details

71 Density functional theory (DFT) calculations were per-  
72 formed using the VIENNA *AB INITIO* SIMULATION PACKAGE  
73 [16–18] with a plane-wave cutoff of 350 eV and projector-  
74 augmented wave (PAW) pseudopotential [19,20] with Ag 5s  
75 and 4d, As 4s and 4p, Sb 5s and 5p, S 3s and 3p, and Se  
76 4s and 4p electrons as valence states. We utilized the PBEsol  
77 exchange-correlation functional with SOC included, unless  
78 specified otherwise [21,22]. The Brillouin zone is sampled  
79 with a  $4 \times 4 \times 4$   $k$ -point mesh and integrations are performed  
80 with the tetrahedron method [23].

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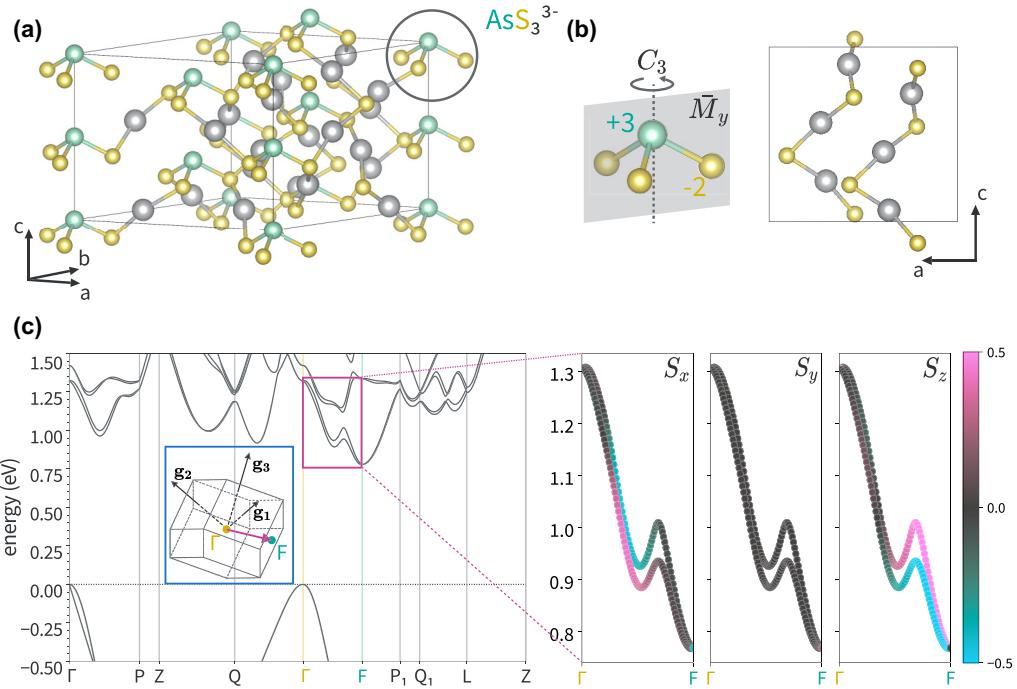


FIG. 1. (a) Crystal structure of  $\text{Ag}_3\text{AsS}_3$  in the hexagonal setting (b) comprises two building blocks:  $\text{AsS}_3$  pyramids linked together by Ag-S chains. (c) The band structure of  $\text{Ag}_3\text{AsS}_3$  showing the valence band minimum (VBM) and conduction band maximum (CBM) at  $\Gamma$  and  $F$ , respectively. Inset: The Brillouin zone of the material with special points of interest. Zoomed: Lowest two conduction bands in the  $F \rightarrow \Gamma$  path with projected spin character (color mapped).

Structures were relaxed until forces were below  $1 \times 10^{-4} \text{ eV}\text{\AA}^{-1}$ . Electric polarizations were calculated using the Berry phase method [24]. The HSE06 hybrid functional [25] was used for accurate band-gap calculations and dense  $k$ -point meshes were constructed for non-self-consistent field band dispersion and spin-texture calculations. The Atomic Simulation Environment was used to aid calculations and post-processing [26]. The LOBSTER code was used for parsing density of states calculations [27–30] and VESTA [31] was used for structure visualization.

### C. Spin lifetime calculations

To compute the spin lifetime, we follow previous analysis of bulk PST systems [9] and the Keldysh formulation of the nonequilibrium Green's function for the spin transport equation (using units of  $\hbar = 1$ ) [32]. The following derivation follows closely that in Ref. [32]:

$$\partial_t \hat{g} + \nabla_{\mathbf{R}} \cdot \left\{ \frac{1}{2} \hat{\mathbf{V}}, \hat{g} \right\} + i[\mathbf{B}(\mathbf{k}) \cdot \hat{\sigma}, \hat{g}] + \frac{\hat{g}}{\tau} = \frac{\hat{\rho}}{\tau}, \quad (1)$$

where  $\hat{g}(\theta, \mathbf{R})$  is the distribution function;  $\hat{\rho}(\mathbf{R})$  is the density operator (which is the distribution function integrated over  $\theta$ ),

TABLE I. Computed lattice parameters ( $\text{\AA}$ ) and  $c/a$  ratios of the proustite family members in their hexagonal setting.

Compound	$a$	$c$	$c/a$ ratio
$\text{Ag}_3\text{AsS}_3$	10.6	8.74	0.825
$\text{Ag}_3\text{SbS}_3$	10.6	9.10	0.858
$\text{Ag}_3\text{AsSe}_3$	11.3	8.35	0.739

$\hat{\mathbf{V}}$  is the velocity operator  $\partial_k \mathcal{H}$ ,  $\mathbf{B}$  is the effective SOC field,  $\hat{\sigma}$  is the vector of Pauli matrices, and  $\tau$  is the scattering time of the dominant scattering mechanism.

We note that Eq. (1) relies on several assumptions, one of which is that the relevant low-energy electronic structure is two-dimensional. We apply this equation to our material as a point of comparison to previous studies which use the same formalism; however, we acknowledge that the result is only physical if the material is synthesized in a thin film geometry or such that the carrier density is confined effectively to two dimensions through, for example, electrostatic gating or  $\delta$ -doping approaches. We also neglect the temperature-dependent effects, assuming transport at 0 K and take  $\tau = 1 \text{ ps}$  as per Ref. [9] to allow for direct comparison with prior results.

We solve Eq. (1) by performing a Fourier transform of  $\partial_t \rightarrow -i\omega$  and  $\partial_{x,y,z} \rightarrow i\mathbf{q}_{x,y,z}$ . By arranging the terms into a matrix equation in the Pauli matrix basis where  $\hat{g} = g_c \sigma_0 + g_x \sigma_x + g_y \sigma_y + g_z \sigma_z$  and letting  $\tilde{\Omega} = 1 - i\omega\tau + i\mathbf{q} \cdot \mathbf{v}\tau$ , we arrive at  $\hat{D} = D\hat{g}$ , where

$$D = \int \frac{d\theta}{2\pi} \begin{bmatrix} \tilde{\Omega} & i\alpha_{yx}q_y\tau & i\alpha_{xy}q_x\tau & i\alpha_{yz}q_y\tau \\ i\alpha_{yx}q_y\tau & \tilde{\Omega} & 2\alpha_{yz}k_y\tau & -2\alpha_{xy}k_x\tau \\ i\alpha_{xy}q_x\tau & -2\alpha_{yz}k_y\tau & \tilde{\Omega} & 2\alpha_{yx}k_y\tau \\ i\alpha_{yz}q_y\tau & 2\alpha_{xy}k_x\tau & -2\alpha_{yx}k_y\tau & \tilde{\Omega} \end{bmatrix}^{-1}, \quad (2)$$

and we have substituted the allowed first-order  $\alpha_{ij}$  SOC terms for our proustites.

TABLE II. Experimental (Exp.) and DFT band gaps ( $E_g$ ) of the proustite-structured compounds in units of eV.

Material	$E_g$ (Exp.)	$E_g$ (DFT)		
		PBEsol	+SOC	+SOC+HSE06
$\text{Ag}_3\text{AsS}_3$	1.99 [33]	0.782	0.767	1.57
$\text{Ag}_3\text{SbS}_3$		0.372	0.361	1.07
$\text{Ag}_3\text{AsSe}_3$		0.446	0.413	1.14

For the dynamical equation to have nontrivial solutions, the determinant of  $(I - D)$  must be zero. Solving the determinant equation thus gives the eigenfrequencies of the dynamical equation  $\omega$ , which leads to the characteristic timescale or spin lifetime  $\tau_s = 1/i\omega$  for the damped PSH. A more useful quantity than  $\tau_s$  for relative comparison is  $\tau_s/T_{\text{PSH}}$ , the ratio of the spin lifetime to the PSH period. The PSH period was computed with  $T_{\text{PSH}} = \pi/(k_F \alpha_{\text{eff}})$ , using the Fermi velocity  $k_F/m$  and the PSH length  $\pi/(m \alpha_{\text{eff}})$  from our DFT calculations. The Fermi wave vector  $k_F$  was determined by integrating the density of states to a carrier density of  $n = 1 \times 10^{19} \text{ cm}^{-3}$  and taking the  $k_F$  value along the PST direction. Equation (2) was implemented in MATHEMATICA and the Wolfram Script code is available at Ref. [15].

### III. RESULTS AND DISCUSSION

#### A. Electronic structure

$\text{Ag}_3\text{AsS}_3$  is a semiconductor with an experimental band gap of  $E_g = 1.99 \text{ eV}$  [33]. Its computed band gap at the

DFT-PBEsol level is significantly smaller than the experimental value (Table II). The inclusion of SOC reduces the computed band gap further; however, the HSE06 functional with SOC predicts a value of  $E_g = 1.57 \text{ eV}$ , which is closer to the experimental value. Thus, PBEsol underestimates the band gap by approximately 61%, while the hybrid functional underestimates it by 21%. Although experimental band gaps are not available for the other proustite variants, their computed band gaps follow similar trends with respect to functional choice.

The DFT-computed band structure with SOC [Fig. 1(c)] reveals an indirect band gap with its valence band maximum (VBM) at  $\Gamma$  and its CBM at  $F(\frac{1}{2}, -\frac{1}{2}, 0)$ . This is consistent with prior experimental reports of an indirect band gap [33]. The lowest conduction band in the  $F \rightarrow \Gamma$  path shows strong spin polarization near the  $F$  point with  $s_y \approx 0$  [Fig. 1(c)]. This suggests that an interesting spin texture may exist near the  $F$  point; we show later that this is a PST.

The orbital-projected density of states shows that the valence band is made up of primarily hybridized Ag 4d and S 3p orbitals [Fig. 2(a)], while the conduction band consists of hybridized As 4p and S 3p with Ag 5s orbitals. The band edges are dominated by S and As  $p$  orbitals. To elucidate the nature of the frontier orbitals forming these bands, we construct a molecular orbital (MO) diagram of the  $\text{AsS}_3$  molecular units with their  $p$  orbitals as basis functions [Fig. 2(a), inset]. Since the  $\text{AsS}_3$  unit has  $C_{3v}$  symmetry, the  $\sigma$  interactions form pairs of bonding and antibonding  $a_1$  and  $e$  orbitals as deduced from the character table [Fig. 2(b)]. The remaining S  $p$  orbitals remain nonbonding with the As orbitals and form the valence band through interactions with the Ag  $d$  orbitals. The MO description accurately predicts the orbital characters at the

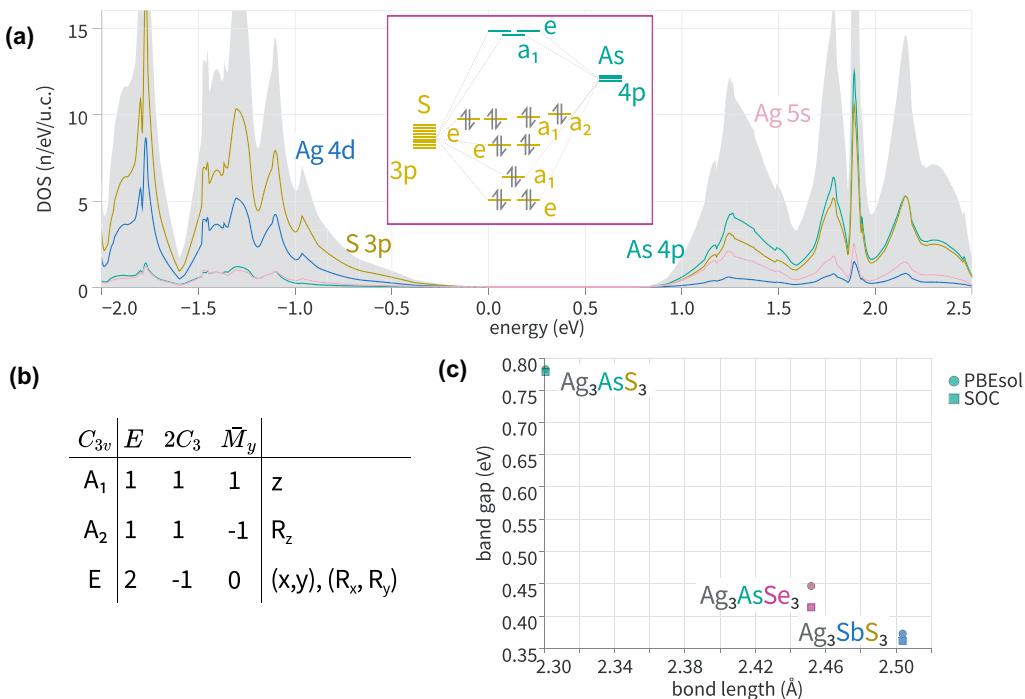


FIG. 2. (a) Orbital projected density of states (DOS) near the Fermi level. The inset shows the molecular orbital diagram of the  $\text{AsS}_3^{3-}$  unit in  $\text{Ag}_3\text{AsS}_3$  which explains the origin of the As and S orbital characters at the band edges. (b) Character table of the  $C_{3v}$  point group of  $\text{AsS}_3^{3-}$ . (c) Band-gap dependence on As-S bond length in the proustite family showing that shorter bond lengths (stronger As-S interactions) are linearly correlated with larger band gaps.

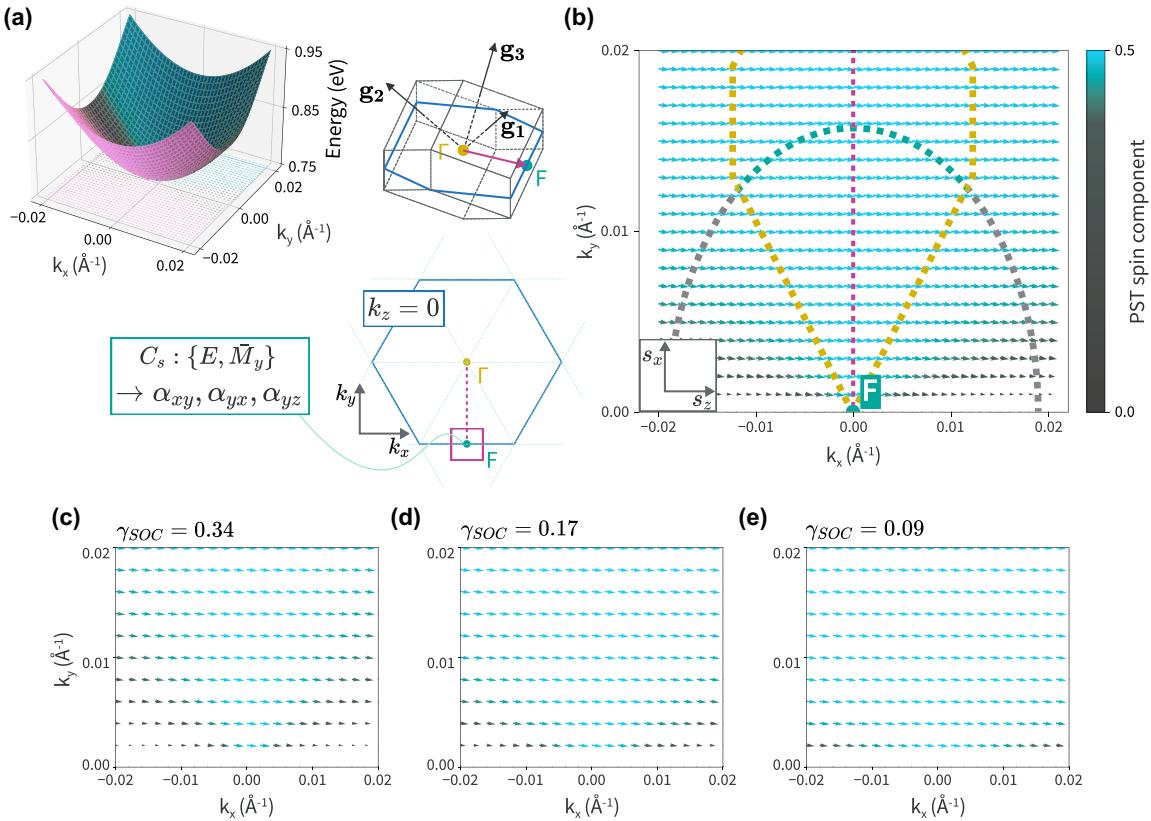


FIG. 3. (a) The lowest conduction band of  $\text{Ag}_3\text{AsS}_3$  in the  $k_z = 0$  plane in the Brillouin zone. The full Brillouin zone and the  $k_z = 0$  plane are shown to the right with the  $F \rightarrow \Gamma$  path highlighted. First-order SOC Hamiltonian terms in Eq. (3) are derived from the little group symmetries at the high-symmetry point of interest. (b) The spin texture of  $\text{Ag}_3\text{AsS}_3$  showing a PST extending in the  $k_y$  direction along the  $F \rightarrow \Gamma$  path. The spins are shown projected onto the  $s_z - s_x$  plane. The color map indicates the spin component along the PST direction. The yellow-bordered region shows where the spin deviation is  $<10^\circ$  from the PST direction and the elliptical region is the Fermi arc at a doping level of  $n = 1 \times 10^{19} \text{ cm}^{-3}$ . (c)–(e) The spin texture modeled with a two-band model [Eq. (3)] with varying values of Rashba anisotropy  $\gamma_{SOC}$ . Larger  $\gamma_{SOC}$  leads to a smaller PST region. (d) The model spin texture obtained using parameters fitted to the DFT data for  $\text{Ag}_3\text{AsS}_3$ .

highest occupied energy level (the VBM) and the lowest unoccupied energy level [the conduction band minimum (CBM)].

The MO diagram grants us insight into the chemical origin of the band gap: The interaction between the As and S atoms. If the orbital overlap is increased (decreased) between the  $p$  orbitals of the two species, we would expect the band gap to increase (decrease) due to further destabilization (stabilization) of the antibonding orbitals. Since the proustite variants are isoelectronic and isostructural, the frontier orbitals are the same and we should expect the same mechanism to control the band gap. Figure 2(c) shows this linear dependence of the band gap on the As-S (or equivalent) bond length for each of the proustite variants, verifying this mechanism of band-gap control.

## B. Spin texture

Figure 3(a) shows the spin character of the lowest conduction band projected onto the  $k_z = 0$  plane of the first Brillouin zone. We then use this projection to plot the spin texture of the conduction band near the  $F$  point in Fig. 3(b). We note that a mirror plane perpendicular to the  $F \rightarrow \Gamma$  path intersects the  $F$  point, meaning the little group of the  $k$  vector at  $F$  is  $C_s$ . Based on Ref. [9], we expect a PST to occur

along the mirror plane ( $\hat{M}_y$ ) with spin locking along  $s_y$ . We find, however, a PST forming near the  $F$  point with spins aligned orthogonal to  $s_y$  centered along the  $F \rightarrow \Gamma$  path and extending in the  $\pm k_x$  directions. This PST is not symmetry protected and has another origin, which we explain below is accidental owing to anisotropy in the SOC strengths. We refer to the  $F \rightarrow \Gamma$  path as the PST path and the orthogonal path along the mirror plane as the  $F + k_x$  path. In addition to the unexpected direction of the PST path, we observe a small region on either side of the  $F + k_x$  path where the spin deviates from the dominant PST direction (see color scale). The dominant PST spin orientation has normalized spin components  $(-0.069, 0.495)$ , given as an ordered pair  $(s_x, s_z)$ ; this oblique PST direction relative to the reciprocal lattice vectors is also unusual compared to previously reported bulk PST materials.

## C. Two-band model

We now perform a symmetry analysis of the band structure of proustite near the  $F$  point to describe the SOC characteristics and attain a better understanding of the origin of the PST. Proustite exhibits  $R3c$  symmetry and the little group of the  $F$  point is  $C_s$ , i.e., the only symmetry operators are the identity

TABLE III. Polarization ( $P$ ), SOC parameters ( $\alpha_{ij}$ ,  $\gamma_{\text{SOC}}$ ), and PSH properties (length  $l_{\text{PSH}}$  and period  $T_{\text{PSH}}$ ) for proustite and its variants. The Rashba anisotropy  $\gamma_{\text{SOC}}$  is the ratio of the coupling strength along  $x$  to that along  $y$ . A smaller (more pronounced) Rashba anisotropy is favorable to PST formation and larger spin lifetime.  $\text{Ag}_3\text{AsSe}_3$  has no computed spin lifetime ( $\tau_s$ ), indicated by N/A, because its conduction band minimum lies outside the PST region, making it practically inaccessible.

Material	$P$ ( $\mu\text{C cm}^{-2}$ )	$\alpha_{xy}$ (eV Å)	$\alpha_{yx}$ (eV Å)	$\alpha_{yz}$ (eV Å)	$\gamma_{\text{SOC}}$	$l_{\text{PSH}}$ (nm)	$\tau_s$ (ps)	$\tau_s/T_{\text{PSH}}$
$\text{Ag}_3\text{AsS}_3$	71.9	0.195	0.155	-1.12	0.173	231	2.00	3.18
$\text{Ag}_3\text{AsSe}_3$	109	0.210	1.192	1.81	0.0972	N/A	N/A	N/A
$\text{Ag}_3\text{SbS}_3$	65.1	0.166	0.539	-1.92	0.0833	148	3.69	21.7

and mirror plane:  $\{E, \hat{M}_y\}$ . Following previous symmetry analyses [6,7], we construct a two-band model by applying symmetry constraints to obtain a first-order SOC Hamiltonian, with the  $F$  point as the origin:

$$\mathcal{H}_{\text{SOC}} = \alpha_{xy}k_x\sigma_y + \alpha_{yx}k_y\sigma_x + \alpha_{yz}k_y\sigma_z. \quad (3)$$

Equation (3) allows us to immediately discern how the observed spin-momentum locking results along the  $F \rightarrow \Gamma$  and  $F + k_x$  paths. Along the  $F + k_x$  path,  $k_y = 0$  and the only relevant term couples  $k_x$  with  $\sigma_y$ , which explains the locking of the spin direction along the  $s_y$  axis on this path. Along the  $F \rightarrow \Gamma$  path,  $k_x = 0$  and the relevant terms couple  $k_y$  to both  $\sigma_x$  and  $\sigma_z$ , explaining the oblique spin texture along this path.

We assume that the full Hamiltonian describing the system near the CBM takes the form  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{SOC}}$ , with  $\mathcal{H}_{\text{SOC}}$  given by Eq. (3) and  $\mathcal{H}_0$  being the free electron Hamiltonian,  $\mathcal{H}_0 = \hbar^2 k^2 / 2m^*$ . Although  $\mathcal{H}_0$  is a poor approximation of the real system as a whole, the approximation holds utility as an analytic tool to understand the mechanisms of the PST in proustite since the CBM can be locally approximated as parabolic. Since the Hamiltonian is quadratic in  $k$  and is otherwise only dependent on system-specific parameters, the Schrödinger equation can be solved analytically to give the following eigenvalues:

$$E_{\pm}(k) = \mathcal{H}_0 \pm \sqrt{(\alpha_{xy}k_x)^2 + (\alpha_{yx}k_y)^2 + (\alpha_{yz}k_y)^2}. \quad (4)$$

Along each  $F \rightarrow \Gamma$  and  $F + k_x$  path, one of the momentum components  $k_i$  is zero and the energy dispersion takes the form of a simple parabola with a linear coupling term. We can also solve for the eigenstates and their corresponding spin expectation values; by doing so, we are able to fit the computed DFT data to extract the  $\alpha_{ij}$  coupling coefficients. With these values, we plot the resulting spin textures to assess whether the model reproduces the DFT-simulated PST [15]. Table III presents the  $\alpha_{ij}$  values obtained by fitting to the DFT data about the  $F$  point. We define an effective  $\alpha_{y,\text{eff}} = (\alpha_{yx}^2 + \alpha_{yz}^2)^{1/2}$  to describe the net SOC band shift along  $k_y$  and note that there is an order of magnitude difference between the SOC coupling strengths along  $k_x$  and along  $k_y$ . This variation explains the dominance of the spin texture along  $k_y$  and the accidental origin of the PST. Because the SOC is much larger along the  $F \rightarrow \Gamma$  path, the associated spin texture dominates the larger 2D region of the Brillouin zone.

We show the spin texture resulting from the two-band model with the fitted parameters in Fig. 3(d). We see that the first-order approximation fits the computed spin texture well in the region close to the  $F$  point. In Figs. 3(c)–3(e), we vary the SOC parameters in the two-band model to show how the

parameters affect the PST. We find that the PST is controlled by the ratio  $\gamma_{\text{SOC}} = \alpha_{xy}/\alpha_{y,\text{eff}}$ ; this ratio is equivalent to the Rashba anisotropy identified in Ref. [9] as a predictor of PST quality in type-I PSTs. A high degree of Rashba anisotropy (small  $\gamma_{\text{SOC}}$ ) leads to the suppression of the weakly coupled spin component which results in a large PST area. As  $\gamma_{\text{SOC}} \rightarrow 0$ , we approach a perfect PST.  $\gamma_{\text{SOC}} = 1$  corresponds to a case with no anisotropy between the SOC parameters, and the model reproduces a Rashba or Dresselhaus type spin texture, which has no inherent PST character. We note that the scalar  $\gamma_{\text{SOC}}$  is not dependent on the PST direction and can be used to characterize SOC in any material. Thus, we have identified and further confirmed the first-order Rashba anisotropy as one of the key indicators of PST quality for non-symmetry-protected PSTs.

It is of particular interest that the Rashba anisotropy is an effective predictor of PST areas in both type-I symmetry-protected PSTs, such as in Ref. [9], and type-II accidental PSTs, as in this paper. This finding blurs the lines between the current field of type-I and type-II PSTs, especially because if  $\alpha_{xy}$  were to dominate the SOC Hamiltonian in Eq. (3), the resulting PST would be along a mirror plane and thus potentially be categorized as a type-I SP-PST. Consequently, the particular symmetries do not appear to dictate the quality of the PST, and instead the chemical interactions of the system and their interplay with the momentum-space physics determines the PST quality. This has been noted for some quasi-2D layered perovskite PSTs where the structural characteristics combine with the crystalline symmetries to constrain the relevant SOC terms to one in-plane direction, producing a PST which is occasionally labeled as symmetry protected. However, this type of symmetry protection is distinct from that of Ref. [6], in which symmetry constraints alone guarantee the existence of a PST near certain high-symmetry points. This strict symmetry requirement for defining SP-PSTs has been disputed [9] and is evidently too stringent for searching for new PST materials, as a multitude of materials without the strict symmetry protection have been shown to host a PST.

For these reasons, we propose a distinction between symmetry-protected PSTs in which symmetry guarantees a PST to first order and  $\gamma_{\text{SOC}} = 0$  exactly (e.g.,  $\text{BiInO}_3$  [6]) and symmetry-assisted PSTs in which symmetry reduces the number of first-order SOC terms such that structural or chemical features may force the system into a PST where  $\gamma_{\text{SOC}} \approx 0$  (e.g., layered perovskites [9,34]). The proustite PSTs presented here fit into the latter category, although there is a significant distinction in the PST formation mechanism in quasi-2D perovskites (see Ref. [34]) and the materials presented here. The layered perovskites exhibit PSTs due to

structural constraints—since the polarization is in-plane and the structure is quasi-2D, spin splitting occurs largely along one in-plane direction, producing a PST. In the 3D proustites, there is no intrinsic structural constraint. The large Rashba anisotropy forms exclusively through orbital interactions. Both cases, however, are notably distinct from true symmetry-protected PSTs by the fact that symmetry only plays a partial role in producing a symmetry-assisted PST.

Additionally, the result of our model is in contrast to the analysis presented in Ref. [7] for the layered perovskite  $\text{CsBiNb}_2\text{O}_7$ , where the *cubic* SOC splitting terms dominate and the anisotropy between those terms determines the PST quality. The difference in results can be explained by the difference in band dispersions. Since the PST in proustite is observed near the  $F$  point, the first-order expansion is sufficient to describe the PST near it. In  $\text{CsBiNb}_2\text{O}_7$ , the band extremum and associated PST is seen at large momentum, where higher order terms dominate and are thus necessary as part of the analysis.

#### D. Proustite variants

We now examine the two isostructural and isoelectronic proustite variants:  $\text{Ag}_3\text{SbS}_3$  and  $\text{Ag}_3\text{AsSe}_3$ . Although they are chemically similar, there are significant changes in the SOC strengths. In addition, the location of the CBM changes drastically in  $\text{Ag}_3\text{AsSe}_3$ . Figure 4 shows the SOC band dispersions and PSTs of the conduction band of these variants; the corresponding SOC parameters are tabulated in Table III. The Rashba anisotropy is greatest in  $\text{Ag}_3\text{SbS}_3$  followed by  $\text{Ag}_3\text{AsSe}_3$ . The PST areas outlined in yellow indicate regions within which the spin direction does not deviate from the PST beyond  $10^\circ$ ; the larger the area with small spin deviation, the closer the PST is to ideal. We see that immediate to the  $F$  point ( $k_y < 0.01 \text{ \AA}^{-1}$ ),  $\gamma_{\text{SOC}}$  is a good predictor of PST area—smaller  $\gamma_{\text{SOC}}$  leads to a larger area. In  $\text{Ag}_3\text{AsSe}_3$ ,  $\gamma_{\text{SOC}}$  fails as a predictor of PST area, although the fraction of the Fermi arc in the PST region is still large. This failure of  $\gamma_{\text{SOC}}$  in predicting the PST area is likely due to large cubic contributions to the SOC Hamiltonian as in  $\text{CsBiNb}_2\text{O}_7$  [7]. This again suggests that first-order terms are insufficient to fully describe the PST in all materials, particularly those where the band minimum lies far from a high-symmetry point.

An important note is the location of the CBM. The PST states must lie at the CBM since they are transport states which need to be electron doped to access. While the band structure shown suggests that the CBM of  $\text{Ag}_3\text{AsSe}_3$  lies within the  $F \rightarrow \Gamma$  path, it is rather located in the  $\Gamma \rightarrow M$  ( $\frac{1}{3}, -\frac{2}{3}, \frac{1}{3}$ ) path, which is along a mirror plane (Fig. 5). Along this  $\Gamma \rightarrow M$  path, however, there is no PST. The CBM seen in the  $F \rightarrow \Gamma$  path is nearly degenerate with the true CBM. While these PST states are accessible through doping, most of the states within the donut-shaped Fermi surface are not PST states (Fig. 6). Thus,  $\text{Ag}_3\text{AsSe}_3$  does not have a practically accessible PST.

The PSTs of the proustite variants confirm that the first-order Rashba anisotropy is a predictor of PST quality in materials where the CBM lies near the high-symmetry point. We further confirm this by computing the spin lifetime  $\tau_s$  of the resulting PSH and the ratio of spin lifetime to the PSH

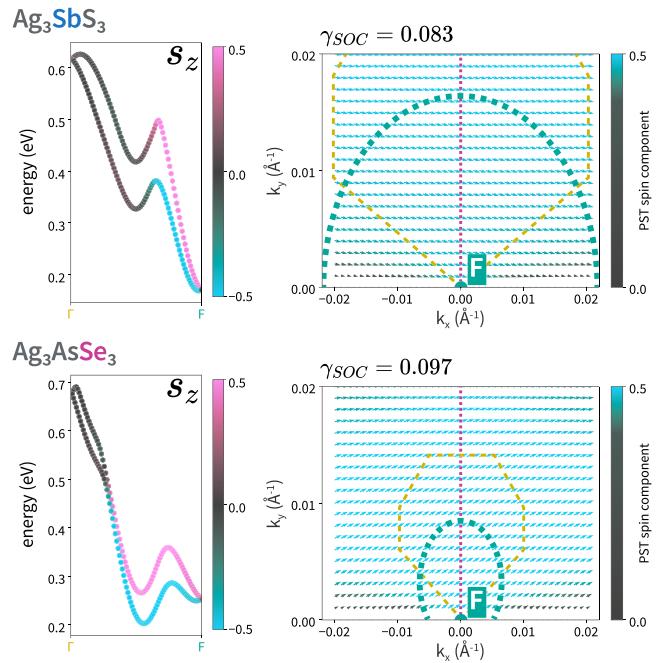


FIG. 4. The (left)  $s_z$ -projected conduction band and (right) spin textures of  $\text{Ag}_3\text{SbS}_3$  and  $\text{Ag}_3\text{AsSe}_3$  near the  $F$  point. The spins are shown projected onto the  $s_z - s_x$  plane, and the color map indicates the spin component along the PST direction. The yellow-bordered region shows where the spin deviation is  $< 10^\circ$  from the PST direction and the green-bordered region is the Fermi arc at a doping level of  $n = 1 \times 10^{19} \text{ cm}^{-3}$ . Both variants display PSTs with  $\text{Ag}_3\text{SbS}_3$  possessing a significantly greater PST area compared to  $\text{Ag}_3\text{AsSe}_3$ . In the case of  $\text{Ag}_3\text{AsSe}_3$ , the CBM shifts due to bands shifting to lower energy along both the  $F \rightarrow \Gamma$  path and the  $\Gamma \rightarrow M$  ( $1/3, -2/3, 1/3$ ) paths (Fig. 5); these two-band minima are nearly degenerate within  $\sim 10 \text{ meV}$  of each other. Consequently, the PST is inaccessible in  $\text{Ag}_3\text{AsSe}_3$ .

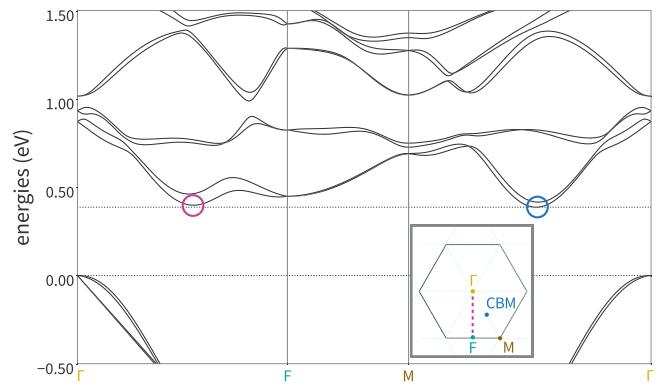


FIG. 5. Band structure of  $\text{Ag}_3\text{AsSe}_3$  showing the  $F \rightarrow \Gamma$  path as well as the true conduction band minimum (CBM) in the  $\Gamma \rightarrow M$  path, circled in blue. The local CBM in the  $F \rightarrow \Gamma$  path is circled in pink and the PST near this point is shown in Fig. 6. Inset:  $k_z = 0$  slice of the Brillouin zone of  $\text{Ag}_3\text{AsSe}_3$  showing the high-symmetry points of the band path. The  $M$  point, which is not part of standardized  $k$ -point paths for the  $R3c$  space group, has  $C_{3v}$  point-group symmetry.

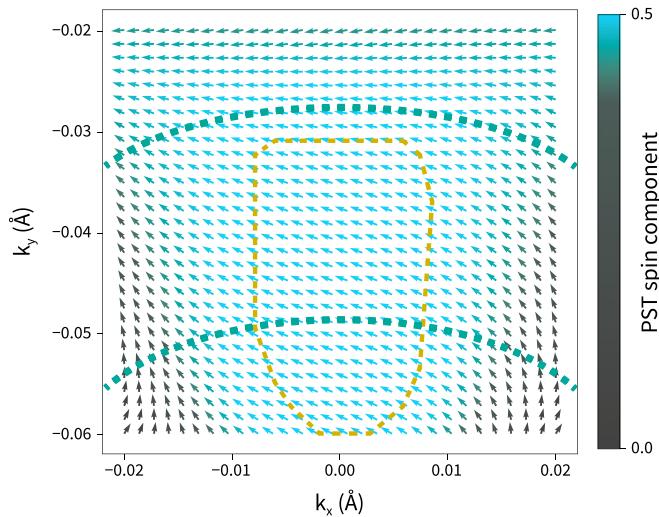


FIG. 6. PST of  $\text{Ag}_3\text{AsSe}_3$  near the local CBM in the  $F \rightarrow \Gamma$  path, circled in pink in Fig. 5. The spins are shown projected onto the  $s_z - s_x$  plane, and the color map indicates the spin component along the PST direction. The yellow-bordered region shows where the spin deviation is  $<10^\circ$  from the PST direction and the green-bordered region is the Fermi arc at a doping level of  $n = 1 \times 10^{19} \text{ cm}^{-3}$ .

period, which is a limiting factor in the material's device application potential (see Ref. [32] for details). We see that in the proustite family,  $\text{Ag}_3\text{SbS}_3$  has the longest spin lifetime (3.69 ps) and  $\tau_s/T_{\text{PSH}}$  ratio (21.7). However, compared to recently predicted bulk PST materials, these quantities are 1–3 orders of magnitude smaller and may require further engineering to find practical use [9]. For  $\text{Ag}_3\text{AsSe}_3$ , the location of the band minimum prevents the two-band model from fully describing the PST and therefore we do not compute the spin lifetime using the first-order model.

We also recognize the necessity of finding appropriate dopants to access the PST states. The PST states lie in the conduction band, so  $n$ -type doping is needed to access the PSH transport mode. One possible route to doping could be through vacancies on the chalcogenide site as in  $\text{MoS}_2$  [35]. Photodoping could also be used to probe the PST states by utilizing circularly polarized light to excite electrons into the spin-polarized bands [34]. Finally, a two-dimensional electron gas (2DEG) may be achieved via interfacial doping or modulation doping [36], which would allow for direct verification of the 2DEG model we used to compute the spin lifetime.

#### IV. CONCLUSION

Although recent research into 3D bulk PST compounds has focused on PSTs formed by specific crystalline symmetries, such as the  $C_{2v}$  point group, we showed that such symmetries are unnecessary constraints in the search for new PST materials. We showed that the proustite mineral family offers a flexible platform to design structural and electronic properties, including tuning the low-symmetry PST in the conduction band. We also distinguished symmetry-assisted PSTs from symmetry-protected PSTs, categorizing the majority of previously identified PST materials along with the proustites as symmetry-assisted PSTs. We propose that the Rashba anisotropy  $\gamma_{\text{SOC}}$  is a useful parameter in evaluating PSTs near a high-symmetry  $k$  vector and that this concept may be extended to higher orders. We conjecture that high Rashba anisotropy at multiple orders could result in an ideal PST that spans a significant portion of the Brillouin zone. We propose that this Rashba anisotropy criterion could be used in high-throughput screening of materials for future bulk PST identification in a manner similar to searches for novel Rashba materials [37]. Since symmetry does not present a strong constraint on the existence of bulk PSTs, there may be several unexplored material classes in which PSTs are hidden. In addition, future work into studying the fundamental mechanisms of PSTs should focus on the chemical and structural origins of the Rashba anisotropy, as this is still unclear. Understanding how to control this Rashba anisotropy may be the key to unlocking full design and performance optimization of PST materials.

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