Persistent spin textures (PSTs) in momentum space have the potential to enable spintronic devices which are currently limited by low spin lifetimes in nonmagnetic spin-orbit coupled materials. We perform a first-principles study on the proustite mineral family, Ag$_3$BQ$_4$ (B=As, Sb; Q=S, Se), and show these chalcogenides exhibit a non-symmetry protected PST, which we refer to as symmetry-assisted PSTs. Chemical substitution can be used to tune the PST quality and properties, e.g., spin lifetime, and we find that a Rashba anisotropy criterion correlates with the PST area and spin lifetime for two of the three proustites examined. Last, we show that a first-order effective SOC Hamiltonian, often used in two-dimensional systems, is insufficient to describe the PST state in all proustites, suggesting that higher order models are necessary to fully describe PSTs in bulk three-dimensional materials.

Nonmagnetic materials with unidirectional spin-momentum locking, or a persistent spin texture (PST), exhibit electrical transport properties useful for spintronic applications [1, 2]. In particular, a PST at the Fermi level of a conducting system enables the persistent spin helix (PSH) transport mode in which an electron’s spin precesses around a fixed axis as it moves through the material. This mode is immune to decoherence from some low-temperature scattering mechanisms. PST formation requires the presence of strong spin-orbit coupling (SOC) combined with inversion symmetry breaking. This combination produces SOC-derived band splitting and is responsible for the well-known Rashba and Dresselhaus splittings and spin textures. In contrast to the aforementioned spin textures, a PST consists of unidirectionally aligned spins which are momentum-independent. This feature has been reported theoretically and observed experimentally in quantum well structures, 2D materials, and at interfaces [3–5]. PSTs were recently theorized to exist in bulk three-dimensional (3D) systems exhibiting nonsymmetric symmetries [6] along with strong SOC and broken inversion symmetry, and several bulk materials, primarily ferroelectric oxides, have since been predicted to host a PST [7–9].

The 3D PST materials predicted thus far all exhibit a symmetry-protected PST (SP-PST), also known as a Type-I PST [10, 11], which is enforced through crystalline symmetries. Recently, mirror symmetries were shown to be the key ingredient for forming a SP-PST [9]. The symmetry protection, however, is a sufficient but not a necessary component to form a PST in bulk materials – it is possible to tune the strength of spin-orbit coupling parameters to produce an “accidental” or Type-II PST that is not enforced by symmetry [11]. In this work, we perform electronic structure simulations and model Hamiltonian calculations to show that the proustites (Ag$_3$BQ$_4$)$_3$, a family of silver chalcogenide minerals, exhibit Type-II PSTs. By looking beyond symmetry-constrained PSTs and examining a family with high chemical tunability, our study expands the number of polar compounds that can exhibit high quality PSTs and spin helices.

The proustite family consists of three compounds in space group R3c: the namesake mineral Ag$_3$AsS$_3$, as well as Ag$_3$SbS$_3$ and Ag$_3$AsSe$_3$. The former two are naturally occurring materials and all three have been experimentally synthesized as bulk single crystals [12–14]. The crystal structure of Ag$_3$AsS$_3$ (Fig. 1a) consists of AsS$_3$ pyramids connected along the c axis by Ag–S chains (Fig. 1b) which are generated by a 3$_1$ screw axis. Owing to the c-glide plane, two sublattices of the AsS$_3$ pyramids and chains exist, where each sublattice is chiral but of opposite handedness from the other, resulting in an achiral crystal. The isostructural variants are similar (see Table S1 of the Supporting Information [15] and Ref. 16).

Ag$_3$AsS$_3$ is a semiconductor with an experimental bandgap of $E_g = 1.99$ eV [17]. Its computed bandgap at the DFT-PBEsol level (see [18] for computational details) is significantly smaller than the experimental value Table S2. The inclusion of spin-orbit coupling (SOC) reduces the computed bandgap further; however, the HSE06 functional with SOC predicts a value of $E_g = 1.57$ eV, which is closer to the experimental value. Thus, PBEsol underestimates the bandgap by approximately 61%, while the hybrid functional underestimates it by 21%. Although experimental bandgaps are not available for the other proustite variants, their computed bandgaps follow similar trends with respect to functional choice.

The DFT-computed band structure with SOC (Fig. 1c) reveals an indirect bandgap with its valence band maximum at $\Gamma$ and its conduction band minimum at $F$ ($\frac{1}{2}, -\frac{1}{2}, 0$). This is consistent with prior experimental reports of an indirect bandgap [17]. The lowest conduction band in the $F \rightarrow \Gamma$ path shows strong spin polarization near the F point with $s_F = 0$ (Fig. 1c). 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 (DOS) shows that the valence band is made up of primarily hybridized Ag 4$d$ and S 3$p$ orbitals (Fig. 2a), while the conduction band consists of hybridized As 4$p$ and S 3$p$ with Ag 5$s$...
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 AsS$_3$ molecular units with their p orbitals as basis functions (Fig. 2a, inset). Since the AsS$_3$ unit has C$_{3v}$ symmetry, the σ interactions form pairs of bonding and antibonding a$_1$ and e orbitals as deduced from the character table (Fig. 2b). The remaining S p orbitals remain non-bonding 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 highest occupied energy level (the valence band maximum, 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 bandgap to increase (decrease) due to further destabilization (stabilization) of the anti-bonding 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 bandgap. Fig. 2c 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 bandgap control.

Fig. 3a 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. 3b. We note that a mirror plane perpendicular to the F $\rightarrow$ Γ 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 (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 $\rightarrow$ Γ path and extending in the $\pm k_x$ directions. We refer to the F $\rightarrow$ Γ path as the PST path and the orthogonal path along the mirror plane as the F $\rightarrow$ k$_x$ path. In addition to the unexpected direction of the PST path, we observe a small region on either side of the F $\rightarrow$ 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 ($k_x$, $k_z$); this oblique PST direction relative to the reciprocal lattice vectors is also unusual compared to previously reported bulk PST materials.

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 and mirror plane: \{E, 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:

$$\mathcal{H}_{SOC} = \alpha_{xy} k_x \sigma_y + \alpha_{xz} k_y \sigma_x + \alpha_{yz} k_y \sigma_z.$$  \hspace{1cm} (1)

Eq. 1 allows us to immediately discern how the observed spin-momentum locking results along the F $\rightarrow$ Γ and F $\rightarrow$ k$_x$ paths. Along the F $\rightarrow$ k$_x$ path, $k_y = 0$ and the only relevant term couples $k_z$ with $\sigma_z$, 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 conduction band minimum takes the form $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{SOC}$, with $\mathcal{H}_{SOC}$ given by Eq. 1 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:

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

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 $\alpha_{ij}$ coupling coefficients and plot the resulting spin textures to assess whether the model reproduces the DFT-simulated PST. Table I presents the $\alpha_{ij}$ values obtained by fitting to the DFT data about the F point. We define an effective $\alpha_{y,eff} = (\alpha_{yx}^2 + \alpha_{yz}^2)^{1/2}$ 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 $k_y$. 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. 3d. We see that the first-order approximation fits the computed spin texture well in the region close to the F point. In Fig. 3c-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 $\gamma_{SOC} = \alpha_{xy}/\alpha_{y,eff}$; 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 $\gamma_{SOC}$) leads

FIG. 3. (a) The lowest conduction band of Ag$_3$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. 1 are derived from the little group symmetries at the high-symmetry point of interest. (b) The spin texture of Ag$_3$AsS$_3$ showing a PST extending in the $k_y$ direction along the $F \rightarrow \Gamma$ path. The colormap indicates the spin-deviation angle from the PST direction. The yellow-bordered region shows where the spin deviation is $< 10^\circ$ and the elliptical region is the Fermi arc at a doping level of $n = 1 \times 10^{19}$ cm$^{-3}$. Panels (c), (d), and (e) show the spin texture modeled with a two-band model (Eq. 1) with varying values of Rashba anisotropy $\gamma_{SOC}$. Larger $\gamma_{SOC}$ leads to a smaller PST region. Panel (d) shows the model spin texture obtained using parameters fitted to the DFT data for Ag$_3$AsS$_3$.
to the suppression of the weakly coupled spin component which results in a large PST area. As $\gamma_{SOC} \to 0$, we approach a perfect PST. $\gamma_{SOC} = 1$ 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. Thus, we have identified and further confirmed the first-order Rashba anisotropy as one of the key indicators of PST quality for symmetry-protected PSTs.

It is of particular interest that the Rashba anisotropy is an effective predictor of PST area in both Type-I symmetry-protected PSTs, such as in Ref. 9, and Type-II accidental PSTs, as in this work. 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. 1, 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. Thus we propose a distinction between symmetry-protected PSTs in which symmetry guarantees a PST to first order (e.g., 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 (e.g., layered perovskites [9, 19]). 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. 19) 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 CsBiNb$_2$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 CsBiNb$_2$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.

We now examine the two isostructural and isoelectronic proustite variants: Ag$_3$SbS$_3$ and Ag$_3$AsSe$_3$. Although they are chemically similar, there are significant changes in the spin-orbit coupling strengths. In addition, the location of the CBM changes drastically in Ag$_3$AsSe$_3$. Fig. 4 shows the SOC band dispersions and PSTs of the conduction band of these variants; the corresponding SOC parameters are tabulated in Table I. The Rashba anisotropy is greatest in Ag$_3$SbS$_3$ followed by Ag$_3$AsSe$_3$. The PST areas outlined in yellow indicate regions within which the spin direction does not deviate from the PST beyond 10°; the larger the area with small spin deviation, the closer the PST is to ideal. We see that immediate to the F point ($|k_y| < 0.01$ Å$^{-1}$), $\gamma_{SOC}$ is a good predictor of PST area – smaller $\gamma_{SOC}$ leads to a larger area. In Ag$_3$AsSe$_3$, $\gamma_{SOC}$ fails as a predictor of PST area, although the fraction of the Fermi arc in the PST region is still large. This failure of $\gamma_{SOC}$ in predicting PST area is likely due to large cubic contributions to the SOC Hamiltonian as in CsBiNb$_2$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 conduction band minimum. 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 conduction band minimum of Ag$_3$AsS$_3$ lies within the F → Γ path, it is rather located in the Γ → M(1/3, −2/3, 1/3) path (Figure S2 of Ref. 15). The CBM seen in the F → Γ path is nearly degenerate with the true CBM. This path lies outside of the useful PST region, making the PST in Ag$_3$AsS$_3$ practically inaccessible.

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 persistent spin helix and the ratio of spin lifetime to the PSH period, which is a limiting factor in the material’s device application potential (see Refs. 15 and 20 for details). We see that in the proustite family, Ag$_3$SbS$_3$ has the longest spin lifetime (3.69 ps) and $\tau_s/\tau_{PSH}$ 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 Ag$_3$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 MoS$_2$ [21]. Photodoping could also be used to probe the PST states by utilizing circularly polarized light to excite electrons into the spin-polarized bands [19].

Although the 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 $\gamma_{SOC}$ 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 searchers for novel Rashba materials [22]. 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 unlock full design control of PST materials.

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