Spin splitting of energy bands can be induced by relativistic spin-orbit interactions in materials without inversion symmetry. Whereas polar space-group symmetries permit Rashba (R-1) spin splitting with helical spin textures in momentum space, which could be reversed upon switching a ferroelectric polarization via applied electric fields, the ordinary Dresselhaus effect (D-1A) is active in materials exhibiting nonpolar noncentrosymmetric crystal classes with atoms occupying exclusively nonpolar lattice sites. Consequently, the spin-momentum locking induced by D-1A is not electric field switchable. Here we find a type of ferri-chiral materials with an alternative type of Dresselhaus symmetry, referred to as D-1B, exhibiting crystal class constraints similar to D-1A (all dipoles add up to zero), but unlike D-1A, at least one polar site is occupied. The spin splitting is associated with the crystalline chirality, which in principle could be reversed upon a change in chirality. Focusing on alkali metal chalcogenides, we identify NaCu₅S₃ in the nonenantiomorphic ferri-chiral structure, which exhibits CuS₃ chiral units differing in the magnitude of their Cu displacements. We then synthesize NaCu₅S₃ (space group P6₃22) and confirm its ferri-chiral structure with powder x-ray diffraction. Our electronic structure calculations demonstrate it exhibits D-1B spin splitting as well as a ferri-chiral phase transition, revealing spin splitting interdependent on chirality. Our electronic structure calculations show that a few percent biaxial tensile strain can reduce (or nearly quench) the switching barrier separating the monodomain ferri-chiral P6₃22 states. We compute the circular dichroism absorption spectrum of the two ferri-chiral orientations and discuss what type of external stimuli might switch the chirality so as to reverse the (nonhelical) Dresselhaus D-1B spin texture. Our study suggests the design of ferri-chiral crystals as potential spintronic and optoelectronic materials.

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I. INTRODUCTION

Spin splitting in nonmagnetic materials arises fundamentally from a few symmetry rules [1] in the presence of spin-orbit coupling (SOC), combining to produce an internal magnetic field that can split energy bands just as an external magnetic field would do. The various forms of spin splitting in noncentrosymmetric (Non-CS) compounds [1] is generally classified into Rashba [2] (R-1) and Dresselhaus [3] (D-1) effects, whereas hidden spin splitting in centrosymmetric compounds [1] corresponds to R-2 and D-2. The allure of such effects lies in the hope that the relevant spin splitting can be switched by an external operation, to the benefit of spintronic devices. This generally requires some spatial directionality of the underlying effect—such as vector dipolar polarization—that can be manipulated in a device structure. Such directionality is supplied by the R-1 Rashba effect, but not by the conventional D-1 Dresselhaus effect, since atoms occupy nonpolar sites in D-1 crystals. Indeed, the R-1 effect is enabled in Non-CS compounds that have a polar point group due to a nonzero sum of local dipoles from atoms occupying polar sites. Thus, the R-1 effect is associated with a net directional electric dipolar polarization [1,2,4]; once the ferroelectric polarization is switched, e.g., by an electric field, the Rashba spin splitting can be reversed [5]. On the other hand, the traditional Dresselhaus effect [1,3,4] (hereby denoted D-1A) is enabled in Non-CS compounds where each occupied Wyckoff orbit has nonpolar site symmetry and dipoles add up to zero, as in tetrahedral GaAs. As this D-1A effect is created by a nondirectional inversion asymmetry, external electric fields cannot reverse the spin texture.

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splitting is interlocked with its ferri-chirality. We show that application of modest strain significantly reduces the barrier between the two orientations of ferri-chiral NaCu$_3$S$_3$. We discuss features of various external stimuli that might switch the chirality and reverse the (nonhelical) Dresselhaus D-1B spin texture, offering an alternative to the traditional reversal of the (helical) Rashba spin texture.

II. THEORETICAL SEARCH FOR FERRI-CHIRAL COMPOUNDS OF TYPE D-1$_B$

We search for compounds that satisfy the basic design principles for ferri-chiral D-1$_B$ Dresselhaus spin splitting. These design constraints include: (i) the material is chiral with nonpolar and noncentrosymmetric space groups; (ii) at least one atomic site in the unit cell of the crystal has polar site symmetry; (iii) the transition barrier between the two chiral phases is sufficiently low (e.g., does not require bond breaking); and (iv) the material is thermodynamically stable (i.e., does not phase separate).

Regarding the last condition, we previously advanced an approach to search for materials that are stable and likely synthesizable by constructing the chemical potential polygon [7–9] in the relevant elemental chemical potential space. This process relies on finding whether there is a region (“green zone”) where none of the possible competing phases will render the targeted phase unstable. Details of the density functional theory used are given in Appendix A. Application to the equiatomic ($p = q = r = 1$) ternary $A_pB_qX_r$ 18-electron phases has previously shown numerous [7,10], never before made compounds that were subjected to the search of target functionalities and selective synthesis [Figs. 2(a)–2(c)]. Here we extend the search of stable new phases to general, i.e., nonequiatomic, stoichiometries ($p$, $q$, $r$) of the ternary ($A$, $B$, $X$) family with $A^I$, $B^I$, and $X^{VI}$, filtering compounds that fulfill the conditions for ferri-chiral D-1$_B$ Dresselhaus spin splitting.

To find the lowest energy crystal structure of a missing compound (e.g., NaCu$_5$), we construct a set of candidate crystal structures for its composition from those that are known for existing compounds in ICSD [11], such as AgMgAs-type ($F$-43m), LiGaGe-type ($P6_3/mmc$), and ZrBeSi-type ($P6_3/mmc$) structures for 1:1:1 composition, and compute the total energy of each missing material in each structure subject to local relaxations, and then select from this list the lowest energy structure [12]. For the reported compounds, we use the experimentally determined crystal structures. To determine the thermodynamic stability of a target ternary compound $A_pB_qX_r$, we consider all of its possible disproportionation channels to competing phases (elemental phases, binaries and ternaries) with neighboring compositions. This is done by solving a set of inequalities in a three-dimensional space of chemical potentials $\Delta\mu_A$, $\Delta\mu_B$, and $\Delta\mu_X$. For all competing elemental phases, we used inequalities of the form $I=0$, $A_pB_qX_r < 0$. For all competing binary phases $A_pB_q$, we used the inequalities $p\Delta\mu_A + q\Delta\mu_B < \Delta H_f(A_pB_qX_r)$. For all competing ternary phases $A_pB_qX_r$, we used $p\Delta\mu_A + q\Delta\mu_B + r\Delta\mu_X < \Delta H_f(A_pB_qX_r)$. This three-dimensional space of chemical potentials was reduced to two dimensions by the $l\Delta\mu_A + m\Delta\mu_B + n\Delta\mu_X = \Delta H_f(A_pB_qX_r)$ equation. The values of $\Delta\mu_A$ and $\Delta\mu_B$, where all inequalities were used to remove the Kramer’s degeneracy in crystals with chiral spin texture, offering an alternative to the traditional reversal of the (helical) Rashba spin texture.
FIG. 2. Stability assessment of alkali metal copper chalcogenides. (a) Predicted (+ signs) and previously reported (check marks) I-I-VI compounds. (b), (c) Stability regions (green zones) of NaCuS and NaCu5S3 in the space of elemental chemical potentials. Each blue line indicates a binary or ternary competing phase. The areal size of the stability regions (in units of eV^2) for NaCuS and NaCu5S3 are 0.080 and 0.287, respectively, compared to the other ternary compounds in the Na-Cu-S system: Na4Cu2S3 (0.175), Na3Cu4S4 (0.083), Na7Cu12S10 (0.052), NaCu4S4 (0.037), and Na2Cu4S3 (0.003).

are satisfied, define the stability area of the \( A_i B_{m} X_{n} \) compound.

Our analysis of sodium thiocuprates in the Na-Cu-S system shows several previously made I-I-VI compounds indicated by checkmarks in Fig. 2(a), and previously unknown compounds predicted here are stable (denoted by + sign; subsequently realized in experiments [13,14] except NaCuS). Appendix B lists the predicted as well as previously known alkali metal copper chalcogenides. According to structural symmetry analysis, we identify one compound (NaCu3Te2) with a polar space group permitting R-1 spin splitting, three materials (NaCuS, KCuSe, and KCuTe) with hidden spin polarization (D-2) effect [1], and 26 compounds (e.g., KCu3Te2) with the R-2 and D-2 effects [1]. We identify among alkali metal copper chalcogenides one candidate compound NaCu5S3 that possesses the structural symmetries required for the D-1B effect.

We evaluated the thermodynamic stability of the candidate material NaCu5S3 against disproportionation into its competing phases, as well as those of the other ternaries in the Na-Cu-S system, to examine the synthetic feasibility. Our results show that NaCu5S3 exhibits the largest stability (green) zone [0.287 eV^2, Fig. 2(c)]; it is a few times larger than those of NaCuS [0.08 eV^2, Fig. 2(b)] and the other ternaries.

FIG. 3. Experimentally synthesized NaCu5S3. (a) Rietveld fit to PXRD data. (b) Typical SEM image of as-prepared NaCu5S3 microcrystals. (c) SEM image of bulk NaCu5S3 obtained by the SPS sintering at 500 °C with high relative density of 96%. (d) Crystal structure of NaCu5S3 (P6\(_3\)22) with two unique Cu atoms (Cu-1 and Cu-2). One Cu-1 (Cu-2) atom becomes another under the \( C_3 \) (\( C_2 \)) symmetry operation with the rotation axis coinciding with the Cu-2 (Cu-1) sites.
Our first-principles thermodynamic data agree well with the previous synthesis [15–20] of Na-Cu-S compounds, and the calculated sizes of stability zones suggest that the synthetic feasibility of NaCu₅S₃ is the highest among all Na-Cu-S compounds.

III. SYNTHESIS AND CRYSTALLOGRAPHIC ANALYSIS

A. Synthesis

Six sodium thiocuprates in the Na-Cu-S system, including NaCu₅S₃, NaCu₄S₄, Na₂Cu₄S₃, Na₃Cu₃S₄, Na₄Cu₂S₃, and Na₇Cu₁₂S₁₀ [15–20], were generally prepared by melting mixtures of the following three products in different ratios of sodium metal (sodium sulfide, Na₂S), copper (copper sulfide, Cu₂S), and sulfur powder. Reagent chemicals were used as received: NaOH flake (98%, Alfa Aesar), thiourea (99%+, Sigma-Aldrich), and ethanediamine (≥99%, Sigma-Aldrich).

We prepared NaCu₅S₃ microcrystals by using the solvothermal method and ethanediamine as the solvent. NaCu₅S₃ was first reported by Effenberger and Pertlik [15] in 1985 via the hydrothermal synthesis from the starting materials of Cu powder and Na₂S in H₂O. Here we prepared the NaCu₅S₃ microcrystals by a facile solvothermal method. In our typical procedure, 3.125 mmol Cu₂S, 0.625 mmol thiourea, 12.5 mmol NaOH (tenfold excessive stoichiometry), and 6 mL ethanediamine were added in a 3 × 1.75 in. rectangle Teflon pouch. Then six Teflon pouches were placed in a 100-mL Teflon-lined Parr pressure vessel filled with 50 mL of deionized H₂O as backfill. Pressure vessels were heated to 200 °C for 24 h and cooled to room temperature naturally. Pouches were opened in air, and the microcrystal products were recovered via vacuum filtration and the following drying in a vacuum furnace at 60 °C for 12 h.

B. Characterization

The phase purity of the products was assessed by powder XRD (PXRD). The products were finely ground and mounted on a flat-plate sample holder. Diffraction data were collected on a Rigaku MiniFlex 600 diffractometer with the Cu Kα source, operating at 40 kV and 15 mA under a continuous scanning method in the 2θ range 5°–120°. PXRD data were analyzed with the Rietveld method using the TOPAS 4.2 program. The morphologies of the typical as-prepared NaCu₅S₃ microcrystal product and the cracked section of the NaCu₅S₃ pellet were performed with a Hitachi S-4700-II scanning electron microscope.

Electrical conductivity measurements were performed on as-prepared NaCu₅S₃, and microcrystal products were first densified by the spark plasma sintering (SPS) method (SPS-211LX, Fuji Electronic Industrial Co., Ltd.), which was treated at 723 K for 5 min in a 12.7-mm-diameter graphite die under an axial compressive stress of 40 MPa in vacuum. Highly dense (>95% of theoretical density) disk-shaped
pellets with dimensions of 12.7-mm diameter and 8-mm thickness were obtained.

C. Crystallographic analyses

Figure 3(a) presents the results of our powder x-ray diffraction measurements. All diffraction peaks were indexed using a hexagonal cell (P6_322) with parameters close to previously reported NaCu_5S_3 and the refined lattice constants, \(a = 7.0102(1) \text{ Å}, c = 7.2395(1) \text{ Å},\) and volume \(V = 308.09(1) \text{ Å}^3\). Our Rietveld refinements yielded excellent refinement statistics, \(R_w = 3.03\%\), \(R_p = 1.88\%\), \(R_{exp} = 1.03\%\), and \(\chi^2 = 2.96\), which indicate that the sample was prepared with high phase purity. Well-defined NaCu_5S_3 crystals varying in size from 30 to 50 \(\mu\text{m}\) with rod- and platelike morphologies are observed [see the scanning electron microscopy (SEM) image in Fig. 3(b)], which are consistent with the crystalline habit of the hexagonal crystal system. Exposed to SPS sintering at 500 °C, the NaCu_5S_3 microcrystals are fractured into smaller uniform ones with 2–3-\(\mu\text{m}\) diameters in size [Fig. 3(c)]. We observe compact packing after the SPS process, which supports the high relative density of 96% calculated by volume and weight.

NaCu_5S_3 belongs to the class of chiral materials with a nonpolar nonenantiomorphic space group (P6_322, No. 182), meaning that the same space group can permit structures in two equivalent orientations rather than forming enantiomeric pairs (e.g., P6_322 and P6_1/mcm). The crystal structure for the experimentally synthesized phase is shown in Fig. 3(d), and the occupied Wyckoff sites are presented in Table I, Appendix C. The important feature emphasized herein, following Zhang et al. [1], is that the point-group polarities of individual Wyckoff positions matter: the Na sublattice in NaCu_5S_3 has the Non-CS and nonpolar point group D_3; the two Cu sublattices host C_3 (polar and chiral) and C_2 (polar and chiral) site symmetries, respectively, and the sum of dipoles on the Cu sublattices is zero. Although the Cu sublattices are individually polar, they cannot contribute to a net polarization because the axis of rotation for the site symmetry is orthogonal to the direction of the displacements permitted by the free parameter in the Wyckoff orbits. This is the key local crystallographic feature that enables the D-1B Dresselhaus subclass without unlocking a Rashba-like interaction. Finally, the S sublattice has the polar chiral site symmetry C_2, which also prohibits a net dipole.

We next use these refined experimental structures with additional symmetry analysis to further understand the atomistic origin of the chirality in NaCu_5S_3, which we show is best referred to as a ferri-chiral (FEC) configuration. NaCu_5S_3 can exist in two forms: the higher-energy symmetric CS achiral P6_3/mcm structure [Figs. 4(a) and 4(b)], which can transform into one of the two lower-energy FEC-1 and FEC-2 orientations of space group P6_322 [Figs. 4(c) and 4(d)]. The atomistic displacements that enable the ferri-chirality involve...
FIG. 8. (a) Partial density of states (PDOS) for NaCu₅S₃ with \( P_6_{3}22 \) (FEC-1/2) and \( P_6_{3}mcm \) (AC) symmetries from DFT + \( U \) (\( U = 6 \) eV) without SOC. (b) Charge densities (\( \rho = 0.02 \) e Å\(^{-3} \)) of the FEC-1/2 and AC phases.

displacements of Cu-1 in the CuS\(_2\) chain [Fig. 3(d)] and Cu-2 (in the CuS\(_3\) triangle) that transform as the irreducible representation \( \Gamma^{-1}_1 \). Although CuS\(_2\) linear chains have been found in copper chalcogenides [11], CuS\(_3\) planar triangles are an uncommon coordination for copper, which provides a driving force for bond distortion to a nonplanar structure as follows: Cu-1 displaces within the \( ab \) plane, which removes one mirror plane, whereas Cu-2 displaces along the \( c \) axis, eliminating the reflection operation perpendicular to the sixfold axis. Chirality arises in this structure because of a perceptual rotation sense due to the antisymmetric displacements on the copper planes, as illustrated for the ferri-chiral phase of NaCu₅S₃ with red/blue arrows in Fig. 4(c), which together remove the glide operation. Indeed, these local 3-in-2-out (or 3-out-2-in) displacements exhibit dihedral symmetry; however, their combination results in partial instead of full compensation of the \( \sigma^+ \) and \( \sigma^- \) chiralities to produce the ferri-chiral structures with \( P_6_{3}22 \) symmetry. The chiral motifs and the mechanism of ferri-chirality of NaCu₅S₃ are described as follows:

(a) The chiral copper sulfide structural motifs are linearly arranged along the \( c \) axis in NaCu₅S₃ [Fig. 4(b)], with alternating left-handed chirality (\( \sigma^+ \)) and right-handed chirality (\( \sigma^- \)). The smallest chiral unit consists of two CuS\(_3\) triangles arranged one above the other with a relative rotation of 60° and the CuS\(_2\) chains connecting their vertices. This chiral unit can be deduced from a triangular prism by a right-handed (left-handed) “twist,” hinting at its chirality.

(b) The Non-CS chiral phase of NaCu₅S₃ possesses \( P_6_{3}22 \) symmetry and an enantiomorphic point group \( 622 \) (\( D_{6h} \)). Owing to the sense of the net atomic displacements within the lattice, two chiral configurations (orientations) with \( P_6_{3}22 \) symmetry are possible in the same space group [Fig. 4(c)]: the left (right) structure exhibits the \( \sigma^- (\sigma^+) \) chiral structural units shrinking and the \( \sigma^+ (\sigma^-) \) chiral structural units expanding, leading to a net ferri-chirality with partially compensated opposite handedness.

(c) The CS achiral phase of NaCu₅S₃ as shown in Fig. 4(a) belongs to the \( P_6_{3}mcm \) space group (see Table I for its Wyckoff positions). Since the CuS\(_3\) triangles in the chiral units become ideally planar and the CuS\(_2\) chains evolve into ideally linear geometries, the \( \sigma^+ \) and \( \sigma^- \) units exactly compensate, leading to an achiral CS phase.

Thus the intensity of the crystalline chirality is determined by the magnitude of the structural unit distortion. This is evidenced by the calculated circular dichroism (CD) absorption spectrum of pristine and strained (±3%) NaCu₅S₃ in Fig. 5. The FEC-1 and FEC-2 structures exhibit opposite strong CD absorption intensities. As the compressive strain is applied on the structure, the discrepancy between the shrunk and expanded units enlarges with less compensated opposite handedness, leading to the increased net ferri-chirality and enhanced CD intensity. In contrast, the compensation for the \( \sigma^+ (\sigma^-) \) chiral structural units increases prominently when the tensile strain is induced due to the weakened Cu-S bonding distortion deviated from linearity. The evaluated CD behaviors of the FEC-1/2 structures are consistent with our above analysis for the origin of the chirality in NaCu₅S₃ and further demonstrate the correlation between the crystalline chirality and the chiral structural unit distortions.

IV. BAND DISPERSIONS AND SPIN TEXTURES INCLUDING SOC

We next evaluate the spin splitting and spin texture of the ferri-chiral phases of NaCu₅S₃ by density functional theory DFT + \( U \) [21,22] with SOC and \( U = 6 \) eV. The Non-CS \( P_6_{3}22 \) ferri-chiral phase shows strong spin splitting at the top valence bands along the \( \Gamma - A \) direction, in contrast to the CS \( P_6_{3}mcm \) achiral phase with no
spin splitting (Fig. 6). Band structures and electronic densities of states (along with charge densities) obtained without SOC are shown in Figs. 7 and 8, respectively, of Appendix C. Figure 9 compares the band dispersions without SOC obtained using a screened hybrid functional (HSE06 [23,24]) against our DFT + U results, showing good agreement between the two levels of theory. Figure 10 shows that the partial charge densities at the Γ point of the valence-band maximum (VBM) evaluated with DFT + U and HSE06 approaches are also in good agreement.

Detailed band structures near the VBM in Figs. 6(c)–6(e) show the lifting of the Kramer’s degeneracy and the appearance of spin splitting in the ferri-chiral phases, as compared to the CS achiral phase. The overall dependencies of the orbital energy levels in Fig. 6(a) are similar to the electronic structure without SOC (Fig. 7) because of the broken inversion; however, the Kramer’s degeneracies are only fully removed in the former case with SOC, which results in spin splitting that is clearly discernable at the VBM along the Γ − A direction in Fig. 6(a) [see Fig. 6(c) for the spin notation]. Figure 12 and Appendix C, Fig. 8 show that the following atomic orbitals are hybridized and mainly contribute to the valence bands along the Γ − A direction: S \(p_x, p_y\), Cu-2 \(d_{z^2}, d_{xy}\), Cu-1 \(d_{xz}, d_{yz}\), and \(d_{z^2}\). The contribution of these orbitals in the spin splitting leads to a rather complicated spin texture for the valence band around the Γ point, as shown in Fig. 13.

Although the two ferri-chiral structures possess the same crystalline symmetry, the spin splitting and spin textures are distinct. For the FEC-1 orientation of NaCu5S3, the top two valence bands along the Γ − A k path split into four singly degenerate bands with spin polarization along the \(z\) direction and individual spin components, showing large linear Dresselhaus spin splitting [Fig. 6(c)] with linear spin-splitting coefficients of \(\frac{\partial E}{\partial k} \approx 275\) meV Å. The derived spin-splitting energy for the top valence bands near the A point is \(\sim 208\) meV, which is remarkably large for the low-atOMIC-Mass elements in NaCu5S3. The large spin splitting of the valence band in NaCu5S3 originates from the distorted Cu-S unit, which eliminates the inversion center of the undistorted antichiral phase (\(P6_3/mcm\)) and enhances the spin splitting beyond that expected from atomic interactions alone. As a comparison, zinc-blende CuF exhibits modest spin splitting (Fig. 14). Whereas in the FEC-2 phase orientation, the spin splitting is reversed compared to FEC-1, producing completely opposite spin components [Fig. 6(e)]. In other words, the spin splitting switches between the two ferri-chiral phases of NaCu5S3, suggesting that the ferri-chirality is associated with the Dresselhaus spin splitting (D-1B type), analogous
FIG. 12. Atomic and orbital projected band structures (a)–(h) of NaCu$_5$S$_3$ with $P6_322$ symmetry calculated at the DFT + $U$ + SOC level.

to the association between dipolar polarization and R-1 spin splitting. Similarly, Fig. 15 shows the spin-split bands in the $k_y$-$k_z$ plane ($k_x = 0$) with annotated spin polarization directions for the FEC-1 phase, demonstrating the Dresselhaus-like nonhelical spin textures. The spin textures of the top valence bands around the $\Gamma$ point for a wide $k$ range is shown in Fig. 13, which further demonstrate the Dresselhaus effect and reveal a nearly unidirectional spin texture along $k_y$ for small $k$. (The corresponding spin texture of FEC-2 phase is opposite to that of FEC-1). Figure 16 shows the spin components of the spin-split bands in the full $k$ range along a $k$ path for FEC-1.

FIG. 13. Spin texture of the FEC-1 structure of NaCu$_5$S$_3$ in a wide $k$ range around the $\Gamma$ point for VB1 and VB2 (in comparison to Fig. 15(a) in a narrow $k$ range).
V. PROSPECTS FOR SWITCHABILITY OF FERRI-CHIRAL SPIN TEXTURE

The ferri-chiral phases in NaCu₅S₃ differ only by the chiral unit contracting or expanding without breaking bonds [Figs. 4(c) and 4(d)]. The conversion between the two ferri-chiral phases [indicated by the red/blue arrows in Fig. 4(c)] involves only small atomic displacements but not breaking of chemical bonds, as in a reconstructive transformation. Thus the transition barrier between the two orientations could be rather low for the monodomain state transformation. We assess computationally the transition barrier from FEC-1 to FEC-2. The calculated transition barrier between FEC-1 and FEC-2 is as low as ~12 meV/f.u., as indicated by the black dashed curve (unstrained case) in Fig. 17(a).

Yet, unlike the case in R-1 compounds, here a static and conventional electric field alone cannot switch the polarization. Another switching agent needs to be identified. At this time we note that switching of chirality in molecular materials has been realized in experiments using external stimuli such as photoexcitation [25–27], electron tunneling [28], and electric fields [29]. On the other hand, chirality-selective synthesis, i.e., chiral induction, was applied to both molecular materials [30–32] and inorganic crystals [33] by using circular polarized light. Furthermore, circularly polarized x-rays [34] and light [35–37], as well as an optical vortex [38], were widely used to probe/manipulate material chirality. Recently, circularly polarized light-induced chirality switching has been realized in metal-inorganic plasmonic nanostructures [39]. Whether these approaches can be used or new avenues advanced for switching NaCu₅S₃ is a challenge area for future research.

The ferri-chiral transition barrier can be tuned to zero by a few percent biaxial tensile strain or increased significantly by compressive strain [Fig. 17(a)], indicating thin-film, device-relevant geometries of NaCu₅S₃, probed with electrical measurements or optical spectroscopies are a promising strategy to demonstrate the ferri-chiral dependent spin splitting but not necessarily switch it. Table II in Appendix C lists a potential substrate material for imposing tensile strain on NaCu₅S₃, which may be grown using pulse-laser deposition from ceramic targets produced using our synthesis strategy. For large enough biaxial tensile strain (~3%), the atomic...
displacements that break the full compensation of $\sigma^+$ and $\sigma^-$ chiralities can be restored [see the variation of the crystallographic parameters in Fig. 17(b)] and the CS antichiral phase ($P6_3/mcm$) is stabilized as the ferri-chiral transition barrier is quenched. Figure 5 also shows that the CD absorption intensity can be significantly decreased (increased) by applying biaxial tensile (compressive) strain.

The ferri-chirality and D-1B Dresselhaus spin splitting in NaCu$_5$S$_3$ are inherently interlocked. Figures 6(c) and 6(e) demonstrate the switch of the spin splitting once the chirality is reversed. Furthermore, the D-1B effect is due to a convergent effect of the atomic-site dipolar polarizations (that sum to zero in the ferri-chiral structure) and thus depends on their relative positions and magnitudes. For that reason, the D-1B spin splitting could be much more sensitive to crystallographic parameters than the D-1A effect—this sensitivity could offer new knobs to manipulate the electron’s spin. Figures 17(c) and 17(d) show that the spin-splitting energy near the A point of NaCu$_5$S$_3$ can be tuned from 16 meV under 3% tensile strain along the c lattice direction to 435 meV under 3% compressive strain. As to the biaxial strain in the $ab$ plane, along with the significant modulation of the chirality-enabling atomic displacements [Fig. 17(b)], a range of spin-splitting energies from zero spin splitting to $\sim$200% relative to the unstrained case near the A point can be obtained. Figure 18 shows the variation in the electronic structures of NaCu$_5$S$_3$ under biaxial/uniaxial strains along $a/b$ lattice directions. The calculated strong strain modulation effect of D-1B spin splitting further demonstrates the interlocking of ferri-chirality and the Dresselhaus effect in ferri-chiral materials, which could offer chirality-related modalities to manipulate/detect spin splitting or vice versa.
FIG. 17. Tunable ferri-chiral phase transition and spin splitting in NaCu$_5$S$_3$. (a) Transition barrier between the two ferri-chiral phases of NaCu$_5$S$_3$. The black dashed curve corresponds to the unstrained case, and other curves correspond to different strain values. (b) Detailed crystallographic information including the movement of Cu-2 away from the center of the CuS$_3$ planar triangle along [001] lattice direction ($\Delta d$), the movement of Cu-1 away from the center of the CuS$_2$ linear chain as represented by the S-Cu-S angle ($\theta$), and along the transition between FEC-1/2 and AC states under external biaxial strain in the ab plane. The +/- signs represent tensile and compressive strain. (c), (d) Low-energy valence bands in the $\Gamma$-A direction for the FEC-1 ferri-chiral phase of NaCu$_5$S$_3$ under uniaxial strain along the c lattice direction. Red/blue colors indicate the spin projection, with the spin polarization axis along the z direction. The gray background indicates the magnitude of the spin-splitting energy. Similar tunability of spin-splitting energy under a/b/c uniaxial/biaxial strains is demonstrated in Fig. 18, in the Appendixes.

VI. CONCLUSION

In summary, we designed a type of ferri-chiral material with potentially switchable Dresselhaus spin splitting via a combined theoretical and experimental study. The unconventional Dresselhaus effect D-1B found in the experimentally synthesized candidate NaCu$_5$S$_3$ is interlocked with its ferri-chirality, analogous to the association of the Rashba effect with dipolar polarization. The ferri-chiral transition barrier can be significantly lowered or quenched by external strain, facilitating the potential transition between monodomain ferri-chiral states as well as their associated spin splitting by external stimuli, analogous to the chirality switching of metal-inorganic nanostructures by circular polarized light [39]. This study initiates the design of novel ferri-chiral materials with potential applications in spintronics and optoelectronics: the Non-CS ferri-chiral phases are active for piezoelectric, nonlinear optics, as well as circularly polarized light that interacts with spin splitting, offering a natural platform to combine mechanical, optical, and spintronic effects.

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The electronic structure of NaCu₅S₃ is evaluated by density functional theory (DFT) [40] using the projector-augmented wave (PAW) pseudopotentials [41] with the exchange-correlation of Perdew-Burke-Ernzerhof (PBE) form [42] as implemented in the Vienna Ab-initio Simulation Package (VASP [41,43]). The electronic wave functions were expanded using a plane-wave basis set with an energy cutoff of 520 eV. The Brillouin zone was sampled on 8 x 8 x 8 Monkhorst-Pack [44] k-point meshes. For the Cu element, we introduced the on-site Coulomb interactions in the localized d orbitals by using the DFT/GGA+U method [21]. The initial crystal structure is taken from experiment, and the lattice constants and atomic positions are fully relaxed under the energy and force tolerance of 10⁻⁶ eV and 5 x 10⁻³ eV Å⁻¹ per unit cell using a conjugate-gradient (CG) algorithm. Spin-orbit coupling (SOC) effects are taken into account by a perturbation \( \sum_{i,m} V^{SO} \cdot \Sigma \cdot \Phi_{i,m} \), where \( \Phi_{i,m} \) is the angular momentum eigenstate of the ith atomic site [22], the Wigner-Seitz radii for constructing the Fermi sphere, as conducted by using the PWMAT code [47,48]. A plane-wave basis set is employed at a cutoff energy of 80 Ry, and a dense plane-wave basis set is employed at a cutoff energy of 6 eV on Cu predicts almost the same band-gap value as HSE06. Crystal structures and charge densities were drawn using the VESTA software [46].

The experimental lattice constants of NaCu₅S₃ and NaCu₅Se₃ are a = b = 5.67 Å, c = 12.3 Å, and a = b = 5.80 Å, c = 13.8 Å, respectively [11,15]. The theoretical values are a = b = 5.76 Å, c = 12.38 Å for NaCu₅S₃, and a = b = 5.90 Å, c = 13.80 Å for NaCu₅Se₃, which are well consistent with the experimental data. The crystallographic information of the chiral alkali metal copper chalcogenide compounds, NaCu₅S₃ (P6₃22), is given in Table I, along with the corresponding AC structure in space group P6₃/mcm. The chiral structure (P6₃22) given in Table I corresponds to the FEC-1 structure in the main text, which is the experimental phase. Table II lists the lattice constants of the potential substrate InN for applying tensile strain on NaCu₅S₃.

Figure 7 shows the evaluated band structure for NaCu₅S₃ from DFT + U (\( U = 6 \) eV) without SOC for comparison with the band structure with SOC in Figs. 6(a) and 6(b), and 8 shows the partial density of states and charge densities of the FEC-1/2 and AC phases in NaCu₅S₃ from DFT + U without SOC. The top valence bands of the three phases are mainly from DFT + U = 6 eV on Cu predicts almost the same band-gap value as HSE06. Crystal structures and charge densities were drawn using the VESTA software [46].

The band-gap values of the three phases are mainly from DFT + U = 6 eV on Cu predicts almost the same band-gap value as HSE06. Crystal structures and charge densities were drawn using the VESTA software [46].

| Space group | Site | Wyckoff Position | X  | Y  | Z  |
|-------------|------|------------------|----|----|----|
| P6₃22       | Na   | 2b               | 0  | 0  | 1/4|
|             | Cu   | 6h               | -0.4854 | 0.4854 | 1/4|
|             | S    | 6g               | 0.6699 | 0.6699 | 1/2|
|             | Na   | 2b               | 0  | 0  | 1/2|
| P6₃/mcm     | Cu   | 6f               | 1/2 | 1/2 | 1/2|
|             | Cu   | 4c               | 2/3 | 1/3 | 1/4|
|             | S    | 6g               | 0.672 | 0.672 | 3/4|

TABLE II. Comparison of lattice constants of potential substrate InN with NaCu₅S₃, where \( a_{sub} \) and \( a_{opt} \) represent the primitive and minimal coincident lattice constants of the specified crystal plane.

| wz-InN (001) | \( a_{sub} \) (Å) | \( a_{opt} \) (Å) | \( |a_{opt} - a_{NaCu₅S₃}|/a_{NaCu₅S₃} \) |
|-------------|-----------------|-----------------|----------------------------------|
| 3.584 7.168 (2 x 2) | +2.3 | Tensile |

APPENDIX A: DETAILS OF DENSITY FUNCTIONAL CALCULATIONS

The crystallographic information of the chiral alkali metal copper chalcogenide compound, NaCu₅S₃ (P6₃22), is given in Table I, along with the corresponding AC structure in space group P6₃/mcm. The chiral structure (P6₃22) given in Table I corresponds to the FEC-1 structure in the main text, which is the experimental phase. Table II lists the lattice constants of the potential substrate InN for applying tensile strain on NaCu₅S₃.

APPENDIX B: PREDICTED AND PREVIOUSLY KNOWN ACHIRAL ALKALI METAL COPPER CHALCOGENIDES

The crystallographic information of the chiral alkali metal copper chalcogenide compound, NaCu₅S₃ (P6₃22), is given in Table I, along with the corresponding AC structure in space group P6₃/mcm. The chiral structure (P6₃22) given in Table I corresponds to the FEC-1 structure in the main text, which is the experimental phase. Table II lists the lattice constants of the potential substrate InN for applying tensile strain on NaCu₅S₃.

Figure 7 shows the evaluated band structure for NaCu₅S₃ from DFT + U (\( U = 6 \) eV) without SOC for comparison with the band structure with SOC in Figs. 6(a) and 6(b), and 8 shows the partial density of states and charge densities of the FEC-1/2 and AC phases in NaCu₅S₃ from DFT + U without SOC. The top valence bands of the three phases are mainly from DFT + U = 6 eV on Cu predicts almost the same band-gap value as HSE06. Crystal structures and charge densities were drawn using the VESTA software [46].

The band-gap values of the three phases are mainly from DFT + U = 6 eV on Cu predicts almost the same band-gap value as HSE06. Crystal structures and charge densities were drawn using the VESTA software [46].

| wz-InN (001) | \( a_{sub} \) (Å) | \( a_{opt} \) (Å) | \( |a_{opt} - a_{NaCu₅S₃}|/a_{NaCu₅S₃} \) |
|-------------|-----------------|-----------------|----------------------------------|
| 3.584 7.168 (2 x 2) | +2.3 | Tensile |

TABLE II. Comparison of lattice constants of potential substrate InN with NaCu₅S₃, where \( a_{sub} \) and \( a_{opt} \) represent the primitive and minimal coincident lattice constants of the specified crystal plane.
the other half decrease [Fig. 8(b)]. This small change of atomic coordination as well as charge distribution lead to the ferri-chirality. The calculated band gap of NaCu$_2$S$_3$ from DFT + $U = 6$ eV is almost the same as the band gap from HSE06 ($\sim$0.12 eV). Figure 9 compares the band structures obtained with the two different functionals. The band splitting of the top valence bands is weakly dependent on the $U$ parameter (Fig. 11).

[1] X. Zhang, Q. Liu, J. W. Luo, A. J. Freeman, and A. Zunger, Nat. Phys. 10, 387 (2014).
[2] D. Di Sante, P. Barone, R. Bertacco, and S. Piccozzi, Adv. Mater. 25, 509 (2013).
[3] G. Dresselhaus, Phys. Rev. 100, 580 (1955).
[4] J.-W. Luo, G. Bester, and A. Zunger, Phys. Rev. Lett. 102, 056405 (2009).
[5] H. Mirhosseini, I. V. Maznichenko, S. Abdelouahed, S. Ostanin, A. Ernst, I. Mertig, and J. Henk, Phys. Rev. B 81, 073406 (2010).
[6] P. S. Halasyamani and K. R. Poeppelmeier, Chem. Mater. 10, 2753 (1998).
[7] R. Gautier, X. Zhang, L. Hu, L. Yu, Y. Lin, T. O. L. Sunde, D. Chon, K. R. Poeppelmeier, and A. Zunger, Nat. Commun. 7, 308 (2015).
[8] X. Zhang, V. Stevanović, M. d’Avezac, S. Lany, and A. Zunger, Phys. Rev. B 86, 014109 (2012).
[9] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. 78, 4059 (1997).
[10] F. Yan, X. Zhang, Y. G. Yu, L. Yu, A. Nagaraja, T. O. Mason, and A. Zunger, Nat. Commun. 6, 7308 (2015).
[11] G. Bergerhoff, I. D. Brown, and F. Allen, Crystallographic Databases (International Union of Crystallography, Chester, 1987).
[12] X. Zhang, L. Yu, A. Zakutayev, and A. Zunger, Adv. Funct. Mater. 22, 1425 (2012).
[13] M. J. DeVries Vermeer, X. Zhang, G. Trimarchi, M. D. Donakowski, P. J. Chupas, K. R. Poeppelmeier, and A. Zunger, J. Am. Chem. Soc. 137, 11383 (2015).
[14] G. Trimarchi, X. Zhang, M. J. D. Vermeer, J. Cantwell, K. R. Poeppelmeier, and A. Zunger, Phys. Rev. B 92, 165103 (2015).
[15] H. Effenerberger and F. Pertlik, Monatsh. Chem. 116, 921 (1985).
[16] X. Zhang, M. G. Kanatzidis, T. Hogan, and C. R. Kannewurf, J. Am. Chem. Soc. 118, 693 (1996).
[17] G. Savelsberg and H. Schäfer, Mater. Res. Bull. 16, 1291 (1981).
[18] Z. Pelpinski, D. B. Brown, T. Watt, W. E. Hatfield, and P. Day, Inorg. Chem. 21, 1752 (1982).
[19] K. O. Klepp, M. Sing, and H. Boller, J. Alloy. Compd. 184, 265 (1992).
[20] K. O. Klepp, M. Sing, and H. Boller, J. Alloy. Compd. 198, 25 (1993).
[21] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
[22] P. Blöfuss and J. Hafner, Phys. Rev. B 79, 224418 (2009).
[23] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 124, 219906 (2006).
[24] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).
[25] K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, and S. Shinkai, J. Am. Chem. Soc. 116, 6664 (1994).
[26] J. J. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, and B. L. Feringa, Science 304, 278 (2004).
[27] N. P. M. Huck, W. F. Jager, B. de Lange, and B. L. Feringa, Science 304, 6664 (1994).
[28] K. Morisawa, T. Ishida, and T. Tatsuma, ACS Nano 5, 9180 (2011).