Large band splitting with tunable spin polarization in
two-dimensional ferroelectric GaXY ($X = \text{Se, Te; } Y = \text{Cl, Br, I}$)
family

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Abstract

It has been generally accepted that the spin-orbit coupling effect in noncentrosymmetric materials leads to the band splitting and non-trivial spin polarization in the momentum space. However, in some cases, zero net spin polarization in the split bands may occurs, dubbed as the band splitting with vanishing spin polarization (BSVSP) effect, protected by non-pseudo-polar point group symmetry of the wave vector in the first Brillouin zone [Nat. Commun. 10, 5144 (2019)]. In this paper, by using first-principles calculations, we show that the BSVSP effect emerges in two-dimensional (2D) nonsymmorphic GaXY ($X = \text{Se, Te; } Y = \text{Cl, Br, I}$) family, a new class of 2D materials having in-plane ferroelectricity. Taking the GaTeCl monolayer as a representative example, we observe the BSVSP effect in the split bands along the $X - M$ line located in the proximity of the conduction band minimum. By using $\vec{k} \cdot \vec{p}$ Hamiltonian derived based on the symmetry analysis, we clarify that such effect is originated from the cancellation of the local spin polarization, enforced by non-pseudo-polar $C_{2v}$ point group symmetry of the wave vector along the $X - M$ line. Importantly, we find that the spin polarization can be effectively induced by applying an external out-of-plane electric field, indicating that an electrically tunable spin polarization for spintronic applications is plausible.
I. INTRODUCTION

The next generation of spintronics relies on the new pathway for manipulating electron’s spin without additional external magnetic field, which is achievable by utilizing the effect of spin-orbit coupling (SOC)\textsuperscript{[1]}. In noncentrosymmetric crystalline systems, the SOC leads to an effective magnetic field, $\vec{B} \propto [\nabla V(\vec{r}) \times \vec{p}]$, where $V(\vec{r})$ and $\vec{p}$ denote the crystal potential and electron momentum, respectively, that induces the band splitting and non-trivial spin polarization in the momentum space as usually referred as the Rashba\textsuperscript{[2]} and Dresselhaus\textsuperscript{[3]} effects. While the Dresselhauss effect occurs on a system hold bulk inversion asymmetry such as bulk zincblend\textsuperscript{[4]} and wurtzite semiconductors\textsuperscript{[4]}, the Rashba effect has been widely observed on a system having structural inversion asymmetry as previously reported on semiconductor quantum well\textsuperscript{[5],[6]}, surface heavy metal\textsuperscript{[7],[8]}, and several two-dimensional (2D) layered compounds\textsuperscript{[9–13]}. Interestingly, it is possible to manipulate the Rashba spin polarization by using an external electric field, offering an opportunity for the realization of spintronic devices such as spin-field effect transistor\textsuperscript{[14],[15]}.

From fundamental point of view, the SOC is a relativistic effect, which strongly depends on the particular atomic-orbital character\textsuperscript{[16]}, thereby predominantly sensitives to the local individual atomic sites (called as local real space sectors) in the crystal. Therefore, both the Rashba and Dresselhaus effects can also arise from the local point-group inversion asymmetry of the local real space sectors\textsuperscript{[17],[18]}. In contrast to the conventional Rashba (Dresselhauss) effect, the local Rashba (Dresselhaus) effect is induced by the local dipole fields (site inversion asymmetry), leading to the local spin polarization. Therefore, the superposition of such polarization leads to the total crystalline spin polarization. In centrosymmetric systems, the global inversion symmetry arises but the local real space sectors is an inversion asymmetric. As a result, the compensated spin polarization with opposite orientation are degenerate in energy, but is spatially locked to different local sectors of the unit cell called as inversion partners, leading to a trivial (empty) spin polarization of the entire crystal. Such a concept is known as hidden spin polarization effect\textsuperscript{[17],[18]}, as recently observed in various centrosymmetric layered compounds\textsuperscript{[17],[22]}.

Analogous to the hidden spin polarization effect in the centrosymmetric systems\textsuperscript{[17],[18]}, a phenomenon dubbed as the band splitting with vanishing spin polarization (BSVSP), i.e., band splitting induced by the global inversion symmetry breaking but with zero net spin...
polarization, has recently been predicted\textsuperscript{23}. Such a phenomenon, which is occurred in non-
centrosymmetric system having both the symmorphic and nonsymmorphic symmetries, is
strongly different from the conventional Rashba and Dresselhaus effect, where the vanishing
spin polarization is protected by non-pseudo-polar symmetry of the little point group. Compared with the conventional Rashba and Dresselhaus effects, the BSVSP effect may
have advantages for electrically tunable spintronic devices since the spin polarization can
be easily induced by applying an external electric field\textsuperscript{23}. Therefore, finding novel materials
supporting the BSVSP effect for spintronics is very important.

In this paper, by performing first-principles density-functional theory calculations, we
predict the emergence of the BSVSP effect in 2D nonsymmorphic GaXY (X = Se, Te; Y =
Cl, Br, I) family, a new class of 2D materials having in-plane ferroelectricity. By using the
GaTeCl monolayer as a representative example, we find that the BSVSP effect is observed in
the split bands along the $X-M$ line, which is located in the proximity of the conduction band
minimum. By using $\vec{k} \cdot \vec{p}$ Hamiltonian obtained from the symmetry analysis, we confirm that
such effect is due to the cancellation of the local spin polarization, enforced by non-pseudo-
polar $C_{2v}$ point group symmetry of the wave vector along the $X-M$ line. Interestingly, we
find that significant spin polarization can be induced when an external out-of-plane electric
field is applied, indicating that an electrically controllable spin polarization for spintronic
applications is plausible.

II. COMPUTATIONAL DETAILS

Our first-principles DFT calculations are performed using the generalized gradient
approximation (GGA)\textsuperscript{24} implemented in the OpenMX code\textsuperscript{25}. Here, we adopted norm-
conserving pseudopotentials\textsuperscript{26} with an energy cutoff of 350 Ry for charge density. The
$12 \times 10 \times 1$ $k$-point mesh was used. The wave functions were expanded by linear combina-
tion of multiple pseudoatomic orbitals generated using a confinement scheme\textsuperscript{27,28}, where two
$s$-, two $p$-, two $d$-character numerical pseudo-atomic orbitals were used. The SOC interaction
was included self consistently in all calculations by using $j$-dependent pseudopotentials\textsuperscript{29}.

We deduced the spin vector component $(S_x, S_y, S_z)$ of the spin polarization in the recip-
rocral lattice vector $\vec{k}$ from the spin density matrix\textsuperscript{30}. The spin density matrix, $P_{\sigma\sigma'}(k, \mu)$,
are calculated using the following relation,

\[ P_{\sigma\sigma'}(\vec{k}, \mu) = \int \Psi_\sigma^{\mu}(\vec{r}, \vec{k}) \Psi_{\sigma'}^{\mu}(\vec{r}, \vec{k}) \, d\vec{r} \]

\[ = \sum_n \sum_{i,j} [c_{\sigma\mu_i} c_{\sigma'\mu_j} S_{i,j}] e^{i\vec{R}_n \cdot \vec{k}}, \]

where \( S_{ij} \) is the overlap integral of the \( i \)-th and \( j \)-th localized orbitals, \( c_{\sigma\mu(i)} \) is expansion coefficient, \( \sigma \) (\( \sigma' \)) is the spin index (\( \uparrow \) or \( \downarrow \)), \( \mu \) is the band index, and \( \vec{R}_n \) is the \( n \)-th lattice vector. Here, \( \Psi_\sigma^{\mu}(\vec{r}, \vec{k}) \) is the spinor Bloch wave function, which is obtained from the OpenMX calculations after self-consistent is achieved.

We used a periodic slab to model the GaXY ML, where a sufficiently large vacuum layer (20 Å) is applied in order to avoid interaction between adjacent layers. We used the axes system where the layer is chosen to sit on the \( x - y \) plane. During the structural relaxation, the energy convergence criterion was set to \( 10^{-9} \) eV. The lattice and positions of the atoms were optimized until the Hellmann-Feynman force components acting on each atom was less than 1 meV/Å. The phonon spectrum was obtained by using ALAMODE code\(^{31}\) based on the force constants obtained from the OpenMX code calculations. We used the modern theory of polarization based on the Berry phase method\(^{32}\) implemented in the OpenMX code to calculate the spontaneous electric polarization.

### III. RESULTS AND DISCUSSION

#### A. Structural symmetry and stability

First, we analyze the structural symmetry and stability of the GaXY ML compounds. As shown in Figs. 1(a)-(b) that the crystal structure of the GaXY ML compounds is noncentrosymmetric having black-phosphorus type structure, where its symmetry is isomorphic to the nonsymmorphic \( Pmn2_1 \) space group\(^{33-36}\). The first Brillouin zone (FBZ) corresponding to this structure is shown in Fig. 1(c). The \( Pmn2_1 \) symmetry in the GaXY ML is generated by the following symmetry operations: (i) identity operation \( E \), (ii) the glide reflection \( \bar{M}_{xy} \) which consists of reflection about \( z = 0 \) plane followed by \( a/2 \) translation along the \( x \) axis and \( b/2 \) translation along the \( y \) axis:

\[ \bar{M}_{xy} : (x, y, z) \rightarrow (x + \frac{a}{2}, y + \frac{b}{2}, -z), \]
FIG. 1. (a) (b) Atomic structure of the GaXY ML corresponding to its symmetry operations viewed in the $x − y$ and $y − z$ planes, respectively. The unit cell of the crystal is indicated by black lines and characterized by $a$ and $b$ lattice parameters in the $x$ and $y$ directions. Six atoms in the unit cell are shown for GaTeCl ML as representative example, namely Ga-1, Ga-2, Te-1, Te-2, Cl-1, and Cl-2, where number 1(2) represents the location of the selected atoms in the upper (lower) sub layer. $P$ represents the ferroelectric polarization oriented along the in-plane $y$ direction as indicated by the red arrows. (c) First Brillouin zone of the GaXY ML crystal characterized by the high symmetry $\vec{k}$ points ($\Gamma$, Y, M, and X). (d) Phonon spectrum of the monolayer GaTeCl as a representative of the monolayer GaXY compounds calculated in the FBZ.

(iii) the twofold screw rotation $\bar{C}_{2y}$ which consists of $\pi/2$ rotation around $y = b/2$ line followed by $a/2$ translation along the $x$ axis:

$$\bar{C}_{2y} : (x, y, z) \rightarrow (-x + \frac{a}{2}, y + \frac{b}{2}, -z),$$

(3)
and (iv) the mirror reflection \( M_{yz} \), which is reflection around the \( x = 0 \) plane:

\[
M_{yz} : (x, y, z) \to (-x, y, z),
\]

(4)

Here, \( a \) and \( b \) is the lattice parameters of the crystal as indicated in Fig. 1(a).

The nonsymmorphic \( Pmn2_1 \) space group symmetry in the GaXY ML plays an important role for generating the in-plane ferroelectricity\(^{35,36} \). Here, the orientation of the ferroelectric polarization is enforced by the \( C_{2v} \) point group related to the \( Pmn2_1 \) space group, similar to that observed on various group IV monochalcogenide monolayers\(^{37,38} \). Since the \( C_{2v} \) point group contains mirror \( xz \) and \( yz \) planes, this implies that the net ferroelectric polarization vanishes along the \( x \)- and \( z \)-directions, while it is substantial along the \( y \)-direction. This in-plane ferroelectric polarization is originated from the polar displacements between Ga and X atoms along the \( y \)-direction. In addition, the existence of the Ga-Y bond in the GaXY ML contributes to extra dipole moments in the \( y \)-direction, leading to the large magnitude of the in-plane ferroelectric polarization.

In this work, we will focus on the GaTeCl ML as a representative example of the GaXY ML family since the layered GaTeCl bulk material has been experimentally synthesized\(^{34} \). Here, the calculated-optimized lattice parameters, \( a \) and \( b \), are 4.17 Å and 5.93 Å respectively, which is in a good agreement with previous calculation\(^ {35,36} \). Our Berry phase calculation find that the in-plane ferroelectric polarization is 5.97 \( \mu \)C/cm\(^2 \), which is comparable to that observed on various 2D in-plane ferroelectric materials\(^{37,39} \). To confirm the structural stability of the GaTeCl ML, we show in Fig. 1(d) the calculated phonon dispersion bands. We can see clearly that there is no imaginary frequencies found in the phonon dispersion bands, indicating that the optimized GaTeCl ML is a dynamically stable.

### B. Band splitting and spin polarization

Figure 2 shows the electronic band structure of the GaTeCl ML along the selected \( \vec{k} \) paths in the FBZ corresponding to the density of states (DOS) projected to the atomic orbitals. One finds that the material is an indirect band-gap semiconductor with the valence band maximum (VBM) is located at the \( \Gamma \) point and the conduction band minimum (CBM) is located at the \( \vec{k} \) point along the \( \Gamma - Y \) line [Fig. 2(a)]. Without including the SOC, the calculated band-gap is 2.17 eV under GGA level, which is in a good agreement with previous
FIG. 2. (a) Electronic band structures of the GaTeCl ML calculated with (blue lines) and without (black lines) including the effect SOC. Partial density of states projected to the atomic orbital for (b) Ga, (c) Te, and (d) Cl atoms. The black, red, blue, and green lines indicate the $s$, $p_x$, $p_y$, and $p_z$ orbitals, respectively.

calculations. Since there is no magnetic ordering found in the GaTeCl ML, so the time reversal symmetry (TRS) is also preserved. Our calculated DOS projected to the atomic orbitals confirmed that the VBM is mostly dominated by contribution of the Te-$p$ orbital with a small admixture of the Ga-$p$ and Cl-$p$ orbitals, while the CBM is mainly originated from the Ga-$s$ orbital with small contribution of Ga-$p$, Te-$p$ and Cl-$p$ orbitals [Figs. 2(b)-(e)].

Turning the SOC, however, slightly reduces the band gap to about 2.05 eV and strongly modifies the electronic band structures of the GaTeCl ML. In comparison with the band structures calculated without SOC [Fig. 2(a)], one can see that a sizable band splitting produced by the SOC is observed due to the inversion symmetry breaking, except for the time-reversal-invariant $\bar{k}$ points. This splitting is particularly visible along the the $\Gamma - X$ and $X - M$ symmetry lines located in the proximity of the CBM. However, due to the protection of the glide mirror symmetry $\bar{M}_{xy}$, the band crossing appears along both the $\Gamma - X$ and $X - M$ symmetry lines, forming a hourglass-shaped band dispersions similar to that observed on bulk BiInO$_3$ and monolayer GaTe. Along the $\Gamma - X$ line, we find that the split bands are fully spin-polarized oriented in the out-of-plane ($z$) direction, while all components of the spin polarization vanish in the split bands along the $X - M$ line [Fig. 3].
FIG. 3. Spin polarization projected to the spin-split bands calculated for \( \vec{k} \) along \( \Gamma - X - M - Y - \Gamma \) symmetry line. Color bars represent expectation values of spin component \( \langle S_x \rangle \), \( \langle S_y \rangle \), and \( \langle S_z \rangle \).

The vanishing spin polarization in the split bands along the \( X - M \) line indicates that the BSVSP effect is achieved, which is similar to that observed on the SnTe ML\(^{23}\).

The fully out-of-plane spin-polarized bands along the \( \Gamma - X \) line can be explained by using unidirectional Rashba effect induced by the in-plane ferroelectricity\(^{39,41,42}\). The existence of the in-plane ferroelectric polarization along the \( y \) direction naturally develops an in-plane
electric field, $\vec{E} = E_y \hat{y}$, and produces a unidirectional Rashba SOC described by the following Hamiltonian\cite{39,41,42}, $H_{\Gamma-X} = \alpha_R k_x \sigma_z$, where $\alpha_R$ is the Rashba parameter that is proportional to the magnitude of the in-plane electric field $E_y$, and $\sigma_z$ is the $z$ component of the Pauli matrices. We noted here that the similar form of $H_{\Gamma-X}$ can also be deduced by considering the little group of the wave vector $\vec{k}$ at the $\Gamma$ point belonging to the $C_{2v}$ point group similar to that reported on various 2D ferroelectric materials such as WO$_2$Cl\cite{39}, SnTe\cite{41,42}, and SnSe\cite{43} MLs. Therefore, the spin orientation along the $\Gamma - X$ ($k_x$) line is completely locked in the out-of-plane direction, forming a fully unidirectional out-of-plane spin polarization [Fig. 3]. This spin polarization is expected to maintain the persistent spin helix state\cite{44,45} along the $\Gamma - X$ line, which suppresses the DP mechanism of the spin relaxation\cite{46} and induces an extremely long spin lifetime\cite{47}.

The vanishing spin polarization as a manifestation of the BSVSP effect in the split bands along the $X - M$ symmetry line, on the other hand, cannot be explained in term of the unidirectional Rashba effect. Recently, based on the group theory analysis, the emergence of the BSVSP effect has been proposed for both symmorphic and non-symmorphic systems satisfying the following two-simultaneous conditions\cite{23}: (i) the little space group associated with the wave vector $\vec{k}$ possess 1D double-value irreducible representation (IR); (ii) the little point group associated with $\vec{k}$ should be a non-pseudo polar point group (detailed analysis based on the point group theory can be found in the supplementary of Ref. 2). In our system, the crystal symmetry is isomorphic to the $Pmn2_1$ space group whose corresponds to the point group $C_{2v}$\cite{33}. Along the $X - M$ line, the little space group of $\vec{k}$ belongs to $C_{2v}$ point group. Therefore, we find that there exists 1D double-value IR of the little space group along the $X - M$ line. At the same time, the little point group of $\vec{k}$ along the $X - M$ line also belongs to $C_{2v}$ point group, which is non-pseudo polar. All these facts confirmed that the split bands along the $X - M$ line sustains the BSVSP effect [see Fig. 3].

To clarify the origin of the BSVSP effect along the $X - M$ line, we evaluate the contribution of the spin polarization of each atoms in the unit cell to the spin-split bands. Here, we focused on the spin-split bands along the $X - M$ line at the CBM due to the large spin splitting [Fig. 2(a)]. Since there are six atoms in the unit cell of the GaTeCl ML, namely Ga-1, Ga-2, Te-1, Te-2, Cl-1, and Cl-2 atoms [Fig. 1(a)], we then decompose the spin polarization of the selected bands into these atoms. As shown in Fig. 4, we find that the spin polarizations are mainly dominated by the $S_x$ component of spin, which is
FIG. 4. Atomic decomposition of the spin polarization projected to the spin-split bands along the $X - M$ line. The Upper, middle, and lower panels show the decomposition of the spin polarization on the Ga, Te, and Cl atomic pairs in the unit cell. Color bars represent expectation values of spin component $\langle S_x \rangle$, $\langle S_y \rangle$, and $\langle S_z \rangle$.

originated from the contribution of the Ga atoms. These spin polarizations are opposite in the $x$ direction for different contribution of the Ga atoms at the upper (Ga-1) and lower (Ga-2) sub-layers, indicating that the spin polarizations are locally emerged. Such local and opposite spin polarizations found in the bands along the $X - M$ line are analogous to the
TABLE I. Transformation role for wave vector \((k)\), spin \((\sigma)\), and sublattice \((\tau)\) Pauli matrices under \(C_{2v}\) point group symmetry operations for the \(X\) point in the first Brillouin zone. \(K\) denotes complex conjugation.

| Symmetry operation | \((k_x, k_y)\) | \((\sigma_x, \sigma_y, \sigma_z)\) | \((\tau_x, \tau_y, \tau_z)\) |
|--------------------|----------------|---------------------------------|--------------------------|
| \(T = i\sigma_y \tau_z K\) | \((-k_x, -k_y)\) | \((-\sigma_x, -\sigma_y, -\sigma_z)\) | \((-\tau_x, \tau_y, \tau_z)\) |
| \(C_{2y} = i\sigma_y \tau_x\) | \((-k_x, k_y)\) | \((-\sigma_x, \sigma_y, -\sigma_z)\) | \((\tau_x, -\tau_y, -\tau_z)\) |
| \(M_{yz} = \sigma_x \tau_x\) | \((-k_x, k_y)\) | \((\sigma_x, -\sigma_y, -\sigma_z)\) | \((\tau_x, -\tau_y, -\tau_z)\) |
| \(M_{xy} = i\sigma_z\) | \((k_x, k_y)\) | \((-\sigma_x, -\sigma_y, \sigma_z)\) | \((\tau_x, \tau_y, \tau_z)\) |

hidden spin-polarization effect \(^{17,18}\) observed on the centrosymmetric layer compounds \(^{17–22}\). Since the orientations of the local spin polarization are opposite in the \(x\) direction, they should cancel each other so that the net spin polarizations is zero, thus maintaining the BSVSP effect in agreement with total spin polarization shown in Fig. 3.

To further demonstrate the microscopic origin of the BSVSP effect along the \(X - M\) line at the CBM, we construct \(\vec{k} \cdot \vec{p}\) effective Hamiltonian describing the band structure around the high symmetry \(X\) point. Here, the \(\vec{k} \cdot \vec{p}\) Hamiltonian can be derived based on the theory of invariant \(^{48,49}\). For the particular high symmetry point in the first Brillouin zone, the little group of the wave vector \(\vec{k}\) is characterized by a point group \(G\), where the matrix representation for the chosen basis functions is given by \(\{D(g) : g \in G\}\), where \(g\) is the symmetry operations in the point group. The derived Hamiltonian should satisfy the following invariant condition \(^{49}\):

\[
H(\vec{k}) = D(g)H(g^{-1}\vec{k})D^{-1}(g), \quad \forall g \in G. \quad (5)
\]

At the \(X\) point, the little group of the wave vector \(\vec{k}\) belongs to the \(C_{2v}\) point group. Therefore, the wave vector \(\vec{k}\) and spin vector \(\vec{\sigma}\) can be transformed according to the symmetry operations in this point group. Taking into account the spin and sublattice degree of freedom in the \(X\) point, the corresponding transformations are given in Table I. Collecting all terms which are invariant under these symmetry operations, we obtain the following effective Hamiltonian:

\[
H_X = E_0 + \lambda \tau_z \sigma_z + \alpha k_y \tau_y \sigma_x + \beta k_x \tau_y \sigma_y + \gamma k_x \tau_0 \sigma_z + \delta k_x \tau_z \sigma_0, \quad (6)
\]

where \(E_0 = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y}\) is the free electron contribution with \(m_{x,y}\) being the effective mass.
along the \( k_x \) and \( k_y \) directions. Here, \( \lambda, \alpha, \beta, \gamma, \) and \( \delta \) are independent parameters, \( \sigma_0 \) and \( \tau_0 \) are the \( 2 \times 2 \) identity matrices. Along the \( X-M \) line, we have \( k_x = 0 \), so the Hamiltonian of Eq. (6) can be written as

\[
H_{X-M} = E_{0_y} + \lambda \tau_z \sigma_z + \alpha k_y \tau_y \sigma_x,
\]

where \( E_{0_y} = \frac{\hbar^2 k_y^2}{2m_y} \). At the \( X \) point, the \( \lambda \tau_z \sigma_z \) term in Eq. (7) splits the states into two doublets (\( \Psi_1, \Psi_2 \)) separated by \( \Delta = 2 \lambda \). Solving eigenvalue problem involving the Hamiltonian of Eq. (7) leads to the solution for each doublets as follows:

\[
\Psi_1^\pm = \frac{\phi(\vec{k}, \vec{r})}{\sqrt{2}} \begin{pmatrix} \pm 1 \\ 1 \end{pmatrix}, \quad E_{\Psi_1}^\pm = E_{0_y} + \lambda \pm \alpha k_y
\]

\[
\Psi_2^\pm = \frac{\phi(\vec{k}, \vec{r})}{\sqrt{2}} \begin{pmatrix} \mp 1 \\ 1 \end{pmatrix}, \quad E_{\Psi_2}^\pm = E_{0_y} - \lambda \pm \alpha k_y,
\]

where \( \phi(\vec{k}, \vec{r}) \) is the spatial part of the wavefunctions. By fitting the band dispersion of Eq. (8) to the DFT energy band along the \( X-M \) in the CBM, yield the following parameters: \( \lambda = 0.09 \) eV and \( \alpha = 2.27 \) eV Å. Importantly, the calculated \( \alpha \) is much larger than that observed on various 2D materials\(^{9-13} \), which is sufficient to support the room temperature spintronics functionality.

The BSVSP effect can be confirmed by calculating the spin polarization projected to the atom in the unit cell. Since the bands along the \( X-M \) line at the CBM are mainly dominated by the Ga-s orbital [Fig. 2(b)], we can write the local part of the wave functions as \( \phi_{Ga-1}^s(\vec{k}, \vec{r}) \) and \( \phi_{Ga-2}^s(\vec{k}, \vec{r}) \), where Ga-1 and Ga-2 represent the Ga atoms located at the upper and lower sub layers, respectively, in the unit cell [see Fig. 1(b)]. Due to the existence of the glide mirror plane \( \bar{M}_{x,y} \), we obtain that \( \phi_{Ga-1}^s(\vec{k}, \vec{r}) = -\phi_{Ga-2}^s(\vec{k}, \vec{r}) \). Therefore, the expectation values of the spin operators projected to the Ga-1 and Ga-2 atoms can be calculated from the relation \( \langle S^\pm \rangle = \frac{\hbar}{2} \langle \Psi_{1,2}^\pm | \vec{\sigma} | \Psi_{1,2}^\pm \rangle \), resulting in that

\[
\begin{align*}
\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \rangle_{\Psi_{1,Ga-1}^\pm}^\pm &= \pm \frac{\hbar}{2} (1, 0, 0) \\
\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \rangle_{\Psi_{1,Ga-2}^\pm}^\pm &= \mp \frac{\hbar}{2} (1, 0, 0) \\
\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \rangle_{\Psi_{2,Ga-1}^\pm}^\pm &= \mp \frac{\hbar}{2} (1, 0, 0) \\
\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \rangle_{\Psi_{2,Ga-2}^\pm}^\pm &= \pm \frac{\hbar}{2} (1, 0, 0).
\end{align*}
\]
This shows that both Ga-1 and Ga-2 atoms contribute to the local spin polarization having opposite direction along the $x$ direction, which is consistent well with our DFT results shown in Fig 4. Therefore, the net spin polarization becomes zero, giving rise to the BSVSP effect that is in agreement with our DFT results presented in Fig. 3.

We noted here that the existence of the BSVSP effect with large band splitting in the present system can be access experimentally in spirit of the experimental observation of the hidden spin polarization effect in 2D materials. The GaTeCl ML is a semiconductor with substantial band gap, and in order to observed BSVSP effect, an electron doping is required. Recently, the electron doping techniques in various 2D materials are under rapid development realizing by ion liquid gating technique, thus application of the electron doping in GaTeCl is plausible. Since the BSVSP effect is observed in the proximity of the CBM, electron doping can move the interesting band close to the Fermi level. Therefore, the BSVSP effect in the interesting bands can be resolved by using spin-polarized angle-resolved photoelectron spectroscopy.

C. Tunable spin polarization by an external electric field

Although the the BSVSP effect leads to the large bands splitting along the $X – M$ line, which is beneficial for spintronics, the vanishing spin polarization in these bands may induce the undesired effect of losing the spin information. Therefore, inducing the spin polarization is the important task for realization spintronic devices. Since the BSVSP effect along the $X – M$ line is protected by the non-pseudo-polar $C_{2v}$ point group, reducing this point group symmetry may exhibits the non-zero spin polarization. For this propose, we apply an external out-of-plane electric field $\vec{E} = E_z \hat{z}$ perpendicular to the GaTeCl ML thin film, which can be realized by introducing a gate voltage. Introducing the out-of-plane external electric field is expected to break both the glide mirror plane $\bar{M}_{xy}$ and two-fold screw rotation axis $\bar{C}_{2y}$ in the crystal of the GaTeCl ML, implying that the point group symmetry reduces to the pseudo-polar $C_s$ point group. Therefore, the non-zero spin-polarization is allowed in the bands along the $X – M$ line.

Fig. 5(a) shows the calculated spin polarization projected to the bands along the $X – M$ line under the influenced of 1.0 GV/Å out-of-plane electric field. By comparing the bands with and without an external electric field [see Fig. 3 and Fig. 5(a)], we find that the
FIG. 5. Elecetric field effect on the spin polarization. (a) The spin polarization projected to the band structures of GaTeCl ML along the $X - M$ line an external out-of-plane electric field $E_z = 1.0 \text{ GV/Å}$ is shown. The colours indicate spin polarization components ($S_x$, $S_y$, $S_z$). (b) The calculated spin polarization as a function of out-of-plane electric field. The spin polarizations are calculated at certain the $\vec{k}$ point in the lowest conduction band along the $X - M$ line as indicated in black point in Fig. 5(a).

Band crossing at the $\vec{k}$ along the $X - M$ line breaks due to the external electric field, so that the Hourglass band dispersion splits into two pair of the split bands. In contrast to the system without the external electric field, the split bands along the $X - M$ line exhibit significant spin polarization, which is dominated by the $S_x$ component of spin [Fig. 5(a)]. Moreover, by evaluating the spin polarization at certain $\vec{k}$ along the $X - M$ line, one can observe that the magnitude of the spin polarization enhances linearly by increasing the magnitude of the external electric field [Fig. 5(b)], indicating that the spin polarization can be effectively tuned by an external electric field. Interestingly, we find that the orientation
of the spin polarizations can be fully reversed by switching the direction of the external electric field. These tunable and reversible spin polarization by the external electric field enable the controlled of the spin-dependent properties, which is the hint for realization spintronic devices.

The large spin polarizations in the split bands along the $X - M$ line induced by the out-of-plane external electric field can further be understood by considering the $\vec{k} \cdot \vec{p}$ Hamiltonian around the $X$ point. By including the out-of-plane electric field contribution, the total $\vec{k} \cdot \vec{p}$ Hamiltonian can be rewritten as

$$H_{X}^{E_z} = H_{X} + H_{E_z} = H_{X} + \alpha_{E_z} \tau_y \sigma_0,$$  \hspace{1cm} (10)

where $H_{X}$ is given in Eq. (6) and $\alpha_{E_z} = \frac{E_z |\phi(\vec{k}, \vec{r})| z |\phi(\vec{k}, \vec{r})\rangle}{\sqrt{(\alpha k_y)^2 + \alpha_{E_z}^2 \pm \lambda}}$. Here, $E_z$ is the magnitude of the out-of-plane external electric field. Along the $X - M$ line, the Hamiltonian of Eq. (10) can be simplified to

$$H_{X-M}^{E_z} = E_0 y + \lambda \tau_z \sigma_z + \alpha k_y \tau_y \sigma_x + \alpha_{E_z} \tau_y \sigma_0.$$  \hspace{1cm} (11)

This Hamiltonian leads to the solutions:

$$\Psi_{1}^{\pm} = \frac{\phi(\vec{k}, \vec{r})}{\sqrt{\left(\frac{(\alpha k_y)^2 + \alpha_{E_z}^2}{(\alpha k_y)^2 + \alpha_{E_z}^2 \pm \lambda}\right)^2 + 1}} \left( \pm \frac{\sqrt{(\alpha k_y)^2 + \alpha_{E_z}^2}}{1} \right), \ \ E_{\Psi_1}^{\pm} = E_0 y + \lambda \pm \sqrt{(\alpha k_y)^2 + \alpha_{E_z}^2}.$$  \hspace{1cm} (12)

$$\Psi_{2}^{\pm} = \frac{\phi(\vec{k}, \vec{r})}{\sqrt{\left(\frac{(\alpha k_y)^2 + \alpha_{E_z}^2}{(\alpha k_y)^2 + \alpha_{E_z}^2 \pm \lambda}\right)^2 + 1}} \left( \pm \frac{\sqrt{(\alpha k_y)^2 + \alpha_{E_z}^2}}{1} \right), \ \ E_{\Psi_2}^{\pm} = E_0 y - \lambda \pm \sqrt{(\alpha k_y)^2 + \alpha_{E_z}^2}.$$  \hspace{1cm} (12)

For the case of the external electric field $E_z = 1.0$ GV/Å the parameters $\lambda$, $\alpha$, and $\alpha_{E_z}$ can be obtained by fitting the energy dispersion of Eq. (12) to the DFT energy band of Fig. 5(a), and we find that $\lambda = 0.11$ eV, $\alpha = 2.12$ eVÅ and $\alpha_{E_z} = 0.03$ eV.

Furthermore, by using Eq. (12), the calculated expectation values of the spin operators
can be expressed as
\[
\left( \langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \right)_{\psi^+}^\pm = \pm \frac{\hbar \alpha E_z \sqrt{\frac{(\alpha k_y)^2}{\alpha E_z} + 1}}{2 \sqrt{(\alpha k_y)^2 + \alpha^2 E_z}} (1, 0, 0)
\]
\[
\left( \langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle \right)_{\psi^-}^\pm = \mp \frac{\hbar \alpha E_z \sqrt{\frac{(\alpha k_y)^2}{\alpha E_z} + 1}}{2 \sqrt{(\alpha k_y)^2 + \alpha^2 E_z}} (1, 0, 0).
\]  

(13)

It is clearly seen from Eq. (13) that the electric field induces the significant spin polarization along the \( x \) direction, which is consistent well with our DFT results shown in Fig. 5(a). Moreover, switching the direction of the electric field from \( E_z \) to \(-E_z\) revers the sign of \( \alpha E_z \) to \(-\alpha E_z\), leading to reversing the spin polarization in the \( x \) direction that is also in agreement with our DFT results shown in Fig. 5(b).

Now, we discuss the possible applications of the electric field-driven spin polarization in GaTeCl ML. Here, we propose a possibility to observe a Hall effect similar to the valley Hall effect previously reported on the 2D transition metal dichalcogenides. As mentioned previously that introducing an external electric field in the GaTeCl ML produces the large spin polarization in the split bands along the \( X - M \) line at the CBM [Fig. 5(a)-(b)]. Accordingly, such spin polarization is expected to occur in the two states located at the \( \vec{k} \) and \(-\vec{k}\) near the CBM. This implies that the Berry curvatures should be observed with opposite sign. By using polarized optical excitation, it is possible to create imbalance population of the electron in these two states, and hence a charge Hall current can be detected.

Finally, we discuss another possible application of the GaTeCl ML in term of the reversible spin polarization effect induced by switching the external electric field. Such reversible spin polarization may be implemented in the magnetic tunnel junctions, where at the interface of a magnetic tunnel junction, the Rashba SOC induces a tunneling spin Hall effect and tunneling anomalous Hall effect (AHE). Since the magnitude of the tunneling AHE is linearly depends on the SOC parameter, the tunneling AHE effect is more experimentally accessible for the systems having larger the SOC parameter. In our system, we found that large the spin-orbit parameter (\( \alpha = 3.1 \text{ eVÅ} \)) is observed when the electric field \( E_z = 1.0 \text{ GV/Å} \) indicating that this material is a favorable candidate for detecting the AHE effect experimentally. Since, in our system, the spin polarization can be reversed by switching the direction of the electric field, it is expected that the reversible AHE effect by the electric field is also achieved. Therefore, we conclude that the present system is promising candidate
for spintronic applications.

IV. CONCLUSION

In summary, we have investigated the emergence of the BSVSP effect in the 2D nonsymorphic GaXY (X = Se, Te; Y = Cl, Br, I) family by performing first-principles density-functional theory calculations. By considering the GaTeCl ML as a representative example, we have found that the BSVSP effect is observed in the split bands along the $X - M$ line in the proximity of the CBM. By deriving the $\vec{k} \cdot \vec{p}$ Hamiltonian obtained from the symmetry analysis, we have confirmed that the BSVSP effect along the $X - M$ line is originated from the cancellation of the local spin polarization, enforced by the non-pseudo-polar $C_{2v}$ point group symmetry of the wave vector $\vec{k}$. We also found that large spin polarization in the split bands along the $X - M$ line can be effectively induced by applying an external out-of-plane electric field, thus offering an electrically controllable spin polarization for spintronic applications.

The BSVSP effect found in the present study is solely dictated by the non-pseudo-polar $C_{2v}$ point group of the wave vector in the systems having the non-symmetric $Pnm2_1$ space group symmetry. Therefore, we expect that the BSVSP effect discussed here is also shared by other materials having the similar symmetry. These allowed us to implement our analysis provided here to be directly applied to these materials. Recently, there are a number of other 2D materials that are predicted to maintain the similar symmetry of the crystals, which opens a possibility to further to resolve the BSVSP effect in these materials. For example, the better resolved of the BSVSP effect are expected to occur in 2D single-elemental multiferroic materials such as As, Sb, and Bi due to the stronger SOC\cite{55,56}. Therefore, we expect that our predictions will stimulate further theoretical and experimental efforts in the exploration of the BSVSP effect in the 2D-based ferroelectric materials, broadening the range of the 2D materials for future spintronic applications.

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