Spin Hall effect in prototype Rashba ferroelectrics GeTe and SnTe

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Ferroelectric Rashba semiconductors (FERSCs) have recently emerged as a promising class of spintronics materials. The peculiar coupling between spin and polar degrees of freedom responsible for several exceptional properties, including ferroelectric switching of Rashba spin texture, suggests that the electron’s spin could be controlled by using only electric fields. In this regard, recent experimental studies revealing charge-to-spin interconversion phenomena in two prototypical FERSCs, GeTe and SnTe, appear extremely relevant. Here, by employing density functional theory calculations, we investigate spin Hall effect (SHE) in these materials and show that it can be large either in ferroelectric or paraelectric structure. We further explore the compatibility between doping required for the practical realization of SHE in semiconductors and polar distortions which determine Rashba-related phenomena in FERSCs, but which could be suppressed by free charge carriers. Based on the analysis of the lone pairs which drive ferroelectricity in these materials, we have found that the polar displacements in GeTe can be sustained up to a critical hole concentration of over ~10^{21}/cm^3, while the tiny distortions in SnTe vanish at a minimal level of doping. Finally, we have estimated spin Hall angles for doped structures and demonstrated that the spin Hall effect could be indeed achieved in a polar phase. We believe that the confirmation of spin Hall effect, Rashba spin textures and ferroelectricity coexisting in one material will be helpful for design of novel all-in-one spintronics devices operating without magnetic fields.

RESULTS AND DISCUSSION

Electronic properties and SHE
Spin Hall materials are usually found either among elemental metals with strong SOC or novel topological phases, such as Weyl and Dirac nodal line semimetals where spin–orbit-protected gaps between the electronic bands are crossed by the Fermi

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Surprisingly, despite much smaller polar displacement, the electronic properties of the ferroelectric SnTe are quite similar to those described above. The strong SOC combined with the small band gap (0.33 eV) induces giant Rashba splittings (parameters) of the valence and conduction bands along ZU path, estimated to approximately 180 and 290 meV (4.0 and 8.3 eVÅ, respectively), again in good agreement with earlier hybrid functional calculations.\(^3\)

As a next step, we will analyze the intrinsic SHE in both compounds. By using Bilbao Crystallographic Server\(^{35,36}\) we have determined non-zero elements of \(\sigma_{xy}^s\) and \(\sigma_{yx}^s\) expressed them in terms of four independent components identified in the ferroelectric phase (space group no. 160). The third rank tensor of SHC can be written by treating different spin polarizations as separate matrices in the following form:

\[
\sigma_i^s = \begin{pmatrix}
\sigma_{xx}^s & 0 & 0 \\
0 & -\sigma_{xx}^s & \sigma_{yx}^s \\
0 & -\sigma_{xx}^s & 0
\end{pmatrix}, \quad \sigma_i^s = \begin{pmatrix}
0 & -\sigma_{xx}^s & -\sigma_{yx}^s \\
-\sigma_{xx}^s & 0 & 0 \\
\sigma_{yx}^s & 0 & 0
\end{pmatrix}
\]

We have also performed an analogous symmetry analysis for the paraelectric phase (space group no. 225) and found only one independent component of the SHC tensor; more specifically, the elements of the matrices above are all identical, except for \(\sigma_{xx}^s\) which vanishes in such a case.

Figure 2c–c’ shows SHC components \(\sigma_{xx}^s\), \(\sigma_{xy}^s\), and \(\sigma_{yx}^s\) representing typical experimental geometries. We note that the elements \(\sigma_{xy}^s = \sigma_{yx}^s\) describe either rarely occurring configurations with spin polarizations aligned along spin/charge current or so-called longitudinal spin currents flowing in the direction of charge current. Because it is not yet clear whether they should be classified as SHEs\(^{37}\) we have omitted them in the discussion below (\(\sigma_{xx}^s\) is reported in the Supplementary Fig. 1). The plotted SHCs strongly suggest a sizable SHE in either ferroelectric (blue) or centrosymmetric (red) configuration. It emerges due to the significant impact of SOC on the electronic states, as deduced from the comparison between fully-relativistic and scalar-relativistic electronic structures. Nevertheless, it is evident that the magnitudes of SHCs are not identical in the two phases. Although the difference could arise either from the unit cell deformation or the polar displacement itself, a closer analysis revealed that the component \(\sigma_{xy}^s\) changes mostly because of the deviation from the cubic unit cell, while the modifications in \(\sigma_{xx}^s\) and \(\sigma_{yx}^s\) arise predominantly from differences in the internal positions. As the latter leads to the IS breaking and Rashba spin-splitting in several regions of the BZ, we are convinced that it must be also a cause of a slight change in the magnitudes of SHC.

Finally, we note that in both materials the enhancement in the ferroelectric phase is rather small; for example, the feature that may really contribute to SHE in polar GeTe is a small peak of \(\sigma_{xx}^s\) which is reported in the Supplementary Fig. 1). The reliable value of the band gap is relevant for the estimation of Rashba spin splittings. They can be easily noticed in Fig. 2a, especially close to the valence band maximum (VBM) and highest conduction band minimum (HBM) along the ZU direction. Their values, 250 meV and 100 meV for valence and conduction bands, respectively, are again in excellent agreement with the HSE calculations and with experimental results reporting giant RE in bulk electronic states of GeTe.\(^5\) The corresponding Rashba parameters (6.4 and 2.4 eVÅ) are comparable with the values in different polar materials, such as BiTeI.\(^3\)
Doping-induced evolution of polar displacements

The idea of realizing SHE in a device based on FERSM raises the question whether ferroelectricity, the key property of these materials, can be sustained upon doping which is required to achieve a non-zero SHC. In fact, the existence of ferroelectric metals has been debated for several years, as not only do the conduction charges screen the external electric fields, but they also suppress the Coulomb interactions that give rise to polar distortions. Although true ferroelectric metals are rare, it has been shown that the polar phase can survive in some materials upon doping. For example, ferroelectric distortions in BaTiO$_3$ are driven by the mixing with the anion screening the Coulomb interaction. We note, however, that the Coulomb interactions that give rise to polar distortions.

Figure 3a shows the evolution of polar displacement in GeTe as a function of charge carrier concentration. We can immediately notice that n- and p-type doping yield two completely different structural scenarios. In case of the former, the displacements are enhanced, similarly as in the previous studies of lone-pair-driven ferroelectrics. In contrast, p-type doped structures reveal a rather fast decay of polar distortions which vanish above the critical hole concentration of $n = 0.13$e/u.c. corresponding to about $2.2 \times 10^{21}$/cm$^3$, closely resembling the behavior of BaTiO$_3$ with ferroelectric instability ensured by the Coulomb force. This indicates that the lone pairs in GeTe might become less active upon p-type doping. We also notice that the volumes of the unit cell, Fig. 3b, follow quite similar trend, i.e. a larger displacement tends to increase the volume, while paraelectric structures favor smaller unit cells. Finally, ferroelectric to paraelectric transition in p-type doped regime is further confirmed by the phonon calculations of the doped cubic cells shown in Fig. 3c. Ferroelectric instabilities manifest as the imaginary frequencies of phonons that soften close to the point of phase transition.

In order to shed more light on these intriguing findings, we have calculated the electron localization function (ELF) which helps to identify regions associated with electron pairs. Figure 3d compares ELF plotted for selected configurations from Fig. 3a–c as well as for an undistorted structure. The lone pairs are seen as pronounced red regions around the Ge atoms, rather spherical in the centrosymmetric configuration (upper left) and distorted in the ferroelectric structure (upper right). The asymmetric lobe confirms the activity of the lone pair in the polar phase and demonstrates dominant role that it plays in the mechanism of ferroelectricity. Furthermore, the comparison of the heavily p- and n-type 'ferroelectrics' (bottom right and left, respectively) clearly shows that in the former the lobes resemble those observed in the centrosymmetric structure. In contrast, the asymmetric lobe in the electron-doped configuration is even more enhanced with respect...
that the ferroelectric switching is possible in semiconductor. Recent experimental study by Kolobov et al. showed polarization reversal, which can be challenging in a doped material. Their bonding/antibonding with the anion and light blue, respectively) resulting from a delicate balance of it is thus not surprising that the lone pair remains unaffected by since this effect occurs predominantly at the top of valence bands, this material. We believe that the weaker vacancies. We believe that the successful realization of their bonding/antibonding with the anion p states of the cation (dark and light blue, respectively) resulting from a delicate balance of their bonding/antibonding with the anion p states (orange lines). Since this effect occurs predominantly at the top of valence bands, it is thus not surprising that the lone pair remains unaffected by n-type doping which shifts the Fermi level in opposite direction (Fig. 4a). On the other hand, in the presence of holes as shown in Fig. 4c, all the involved states reconstruct, slightly hybridizing with conduction bands which in turn suppresses the distortion.

In SnTe, the calculations of structural parameters with varying carrier concentration revealed trends very similar to those observed in GeTe. We emphasize that the polar displacement, even without doping, is very tiny ($r \approx 0.01$). Moreover, as can be observed in Fig. 5a, $r$ decays much faster than in GeTe; the polar phase is completely suppressed at the carrier concentration of $n = 0.03 \text{e}/\text{u.c.}$ equivalent to around $4.0 \times 10^{20}/\text{cm}^3$, a doping commonly observed in experiments. We believe that the weaker ferroelectricity in this material can be assigned to a smaller and less active lone pair, resulting in a decreased tendency to a covalent bond formation.

Finally, let us comment on the practical realization of polarization reversal, which can be challenging in a doped semiconductor. Recent experimental study by Kolobov et al. based on piezoelectric force microscopy have demonstrated that the ferroelectric switching is possible in p-type doped epitaxial GeTe films. As estimated above, the polar displacements should survive even at the high doping level of over $10^{21} / \text{cm}^3$ above the typically measured values, but the applied electric field might still be screened by free carriers induced by the vacancies. We believe that the successful realization of ferroelectric switching in GeTe samples could be related to a strong electric field applied locally with the PFM tip which allows to switch the domains. As pointed out by Kolobov et al., the reduced thickness of the film might also play a role in the overall mechanism of the switching. These indicate that the ferroelectric switching in this material has to be further explored from both fundamental and practical sides; ideally, the polarization reversal should be achieved by applying an opposite voltage with the electrode contacts. On the other hand, the ferroelectric switching has never been reported in a similar rhombohedral SnTe, most likely due to the weak ferroelectricity and low temperature of phase transition, which also impedes the realization of FERSC in this material.

SHE in doped FERSCs Finally, we will focus on the SHE in the doped structures discussed in the previous section. Figure 6 reports the values of spin Hall angle, defined as a ratio of spin and charge conductivity. We have compared the values estimated for XTe at moderate and high concentrations of holes with the calculations for known spin Hall materials. The highest SHEs in GeTe within the considered range of carrier concentrations are $\sim 30-80 (\text{n}/\text{e})\Omega^{-1}\text{cm}^{-1}$ with the maximum value found at $n = 0.1 \text{e}/\text{u.c.} = 2.0 \times 10^{21}/\text{cm}^3$ for $\sigma^z$. The calculated spin Hall angle $\theta_{\text{SH}} \approx 0.01$ (green circle) is lower than in case of Pt and much below the value estimated for (nodal line) semimetal IrO$_2$. It can be assigned to the large charge conductivity in doped GeTe. On the other hand, $\theta_{\text{SH}}$ is higher at $n = 0.02 \text{e}/\text{u.c.} = 3 \times 10^{20}/\text{cm}^3$ (green square), as the charge conductivity changes faster than the SHC. This confirms that the sizable SHE could be explored in GeTe at hole concentrations of $10^{20}-10^{21}/\text{cm}^3$, which genuinely sustains the polar phase and is typically observed in experiments. In fact, recent results based on unidirectional spin Hall magnetoresistance in Fe/GeTe bilayer seem to be in good agreement with the above estimation. In those experiments, the SHE was observed in GeTe with holes concentration of $\sim 2.2 \times 10^{20}/\text{cm}^3$. 

Fig. 3 Evolution of crystal distortions with varying doping concentration in GeTe. Panel a shows the relative displacement $r$ of the atom from the centrosymmetric 0.5a position (black diamonds) and the angle between lattice vectors (red squares), b reports the changes in the unit cell volume (blue circles) and c the corresponding phonon frequencies (green circles). The negative numbers indicate imaginary values of the frequency. Dashed lines denote the phase transition. d Electron localization function plotted in the plane of distortion [0-11] for the centrosymmetric (upper left) and distorted (upper right) structures without doping and assuming the same rhombohedral unit cell for both. The bottom panels report p-type (left) and n-type doped (right) polar phases. In this case, the unit cells correspond to the relaxed volumes displayed in b. The highest localization is displayed in red, thus the orange/redish lobes are interpreted as the lone pairs of Ge.
Analogous trends can be noticed for SnTe displayed as blue square and circle in Fig. 6. We have found that the SHCs are much above those estimated for GeTe, similarly as in case of previously reported 2D-XTe. Notably, the values of SHCs continuously grow with doping, achieving 170–250 (Ω×cm)−1 for hole concentrations of 0.02–0.1|e|/u.c., which results in very high spin Hall angles of 0.03–0.15. Because the polar distortions of SnTe are suppressed already at 0.02|e|/u.c., the giant SHE should rather be attributed to the paraelectric phase. In fact, the estimated spin Hall angle is in good agreement with the experimental value of 0.01 measured in the high-temperature rocksalt structure by Ohya et al. Although it has been suggested that the topological surface states could enhance the efficiency of SHE, our analysis shows that the large spin Hall angle can be entirely assigned to the strong SOC of bulk electronic states in the cubic structure. Thus, despite the realization of FERSC seems difficult in this material, it is extremely promising for spintronics applications based on SHE.

Summary
In summary, we have studied SHE in prototype Rashba ferroelectrics GeTe and SnTe. Although such an idea might appear contradictory, we have demonstrated that the SHE could be indeed observed in a doped polar (or ferroelectric) material. We have explored several aspects related to the realization of SHE in polar structures. First, we have noticed that the Rashba splittings of the electronic bands can enhance SHC, but they play a minor role at the hole concentrations usually observed in the considered materials. Second, we have investigated the evolution of polar
distortions under carrier doping and found that the lone pair driven ferroelectricity is robust against electron injection, whereas in the presence of holes the polar displacements can be sustained up to ~0.13 (0.03)  Å/Åc in GeTe (SnTe). Finally, we have reported spin Hall angles for both materials at the typical concentrations of holes 10^{20}–10^{21}/cm^3. The values in GeTe are close to 0.01 and refer to the polar phase, while giant SHE in SnTe characterized by the angles of ~0.1 is likely to be found in paraelectric structures. In conclusion, our results indicate that the SHE could be realized in FERSCs. This opens a new perspective to integrate different functionalities within one material, and combine spin injection/detection with electric spin manipulation in a device similar to recently presented all-electric spin transistor.54 We believe that our study will stimulate further search of FERSCs with complementary spin-dependent electronic properties, whereby the interplay of charge-to-spin conversion, Rashba-related physics and ferroelectricity could bring novel spintronics applications.

METHODS

First-principles calculations based on DFT were performed using QUANTUM ESPRESSO package55,56 interfaced with the AFLWfr infrastructure.57 We treated the exchange and correlation interaction within the generalized gradient approximation (GGA)58 and the ion–electron interaction with the projector augmented-wave fully-relativistic pseudopotentials59 from the psilibrary database.60 The electron wave functions were expanded in a plane wave basis set with the cutoff of 85 Ry. The electronic properties were calculated using the pseudo-hybrid Hubbard density functional ACBNO.61 We remark that this parameter-free alternative of traditional DFT plane wave basis set with the cutoff of 85 Ry. The electronic properties code65 following the Kubo formula:66,67

\[
\sigma^\alpha_{ij} = \frac{e}{h} \sum_k \sum_n f_n (k) \Omega_{ij}^n (k),
\]

(1)

\[
\Omega_{ij}^n (k) = \frac{2 \text{Im} \left< \hat{v} \hat{\rho}^{n,k} \hat{v}^{\dagger} \hat{\rho}^{n,k} \right> - (E_n - E_m)^2}{(E_m - E_n)^2},
\]

(2)

where the spin Berry curvature of nth band assuming spin polarization along k and spin (charge) current along \( \hat{J}_s \) is the Fermi-Dirac distribution function and \( \hat{J}_v = \{ s_v, v_\} \) is the spin current operator, where s and v stand for spin and velocity operators, respectively. In order to properly resolve the rapid variation of spin Berry curvatures, we have interpolated the k-points mesh to 48 × 48 × 48 using the adaptive meshing in the final SHC calculations. The corresponding convergence test is reported in the Supplementary Information.

DATA AVAILABILITY

Data are available from the authors upon reasonable request.

CODE AVAILABILITY

The PAOFLOW code can be downloaded from http://aflowlib.org/src/paoflow.

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