Hidden spin polarization in inversion-symmetric bulk crystals

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Spin–orbit coupling can induce spin polarization in nonmagnetic 3D crystals when the inversion symmetry is broken, as manifested by the bulk Rashba and Dresselhaus effects. We establish that these spin-polarization effects originate fundamentally from specific atomic site asymmetries, rather than, as generally accepted, from the asymmetry of the crystal space group. This understanding leads to the recognition that a previously overlooked hidden form of spin polarization should exist in centrosymmetric crystals. Although all energy bands must be doubly degenerate in centrosymmetric materials, we find that the two components of such doubly degenerate bands could have opposite polarizations, each spatially localized on one of the two separate sectors forming the inversion partners. We demonstrate such hidden spin polarizations in particular centrosymmetric crystals by first-principles calculations. This new understanding could considerably broaden the range of currently useful spintronic materials and enable the control of spin polarization by means of operations on the atomic scale.

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If two quantum mechanical wavefunctions are degenerate, one can choose their linear combination such that the spin polarization of each state is not unique and only the sum of the spin polarization of the two states is meaningful. A key observation here is that in the R-2 and D-2 effects, the spin polarization of the energetically degenerate bands is spatially segregated into a dominant spin texture for one real-space sector, whereas the opposite spin texture is associated with its inversion partner. This type of R-2 and D-2 doubly degenerate bands is different from the common notion of spin-degenerate bands where both spin-up and spin-down wavefunctions occur in the same real-space sector—that is, there is no spatial separation between two spin-subbands. Such local SOC-induced spin polarization, segregated into different real space domains, is clearly apparent from DFT calculations reported here, because in such calculations the spin degrees of freedom of each bulk state can be projected onto individual real-space sectors.

### Bulk symmetry, site symmetry and spin polarization

The basic concepts of symmetry used in this paper are illustrated in Fig. 1. One can distinguish the presence or absence of inversion symmetry in the bulk space group (centrosymmetric versus non-centrosymmetric, respectively) from the presence or absence of such inversion symmetry in the atomic site point group. The latter is the subgroup formed by the subset of all symmetry operations of the crystal space group that leave that atomic site invariant. The net spin polarization of a bulk crystal is the sum over all atomic sites of the local spin polarizations. One can then classify all crystal systems into three general spin polarization cases by considering different combinations of bulk space group and site point group. This is explained in the cases shown in Fig. 1a–c.

**Figure 1** | The three classes of spin polarization in nonmagnetic bulk crystals. **a.** Absence of spin polarization in centrosymmetric crystals if all atomic sites are inversion symmetric. As the local environment (crystal field) of centrosymmetric atomic sites does not produce spin-orbit coupling induced spin polarization, the total (bulk) spin polarization is absent as well. **b.** Net bulk spin polarizations (R-1 and D-1 effects): a local site dipole field or the site inversion asymmetry leads to local Rashba or local Dresselhaus effects, respectively. In combination with a non-centrosymmetric space group, these local effects produce bulk R-1 (Rashba) and D-1 (Dresselhaus) effects, respectively. **c.** Compensated (hidden) bulk spin polarization (R-2 and D-2 effects): a local site dipole field or the site inversion asymmetry leads to local Rashba or local Dresselhaus effects, respectively, as in **b.** In combination with a centrosymmetric space group, these local effects produce bulk R-2 (Rashba) and D-2 (Dresselhaus) effects, respectively. Here the spin polarization from each sector is concealed by compensation from their inversion partners, but is readily visible when the results from individual sectors are observed.

| Bulk symmetry: | a | Centrosymmetric | **b** | Non-centrosymmetric (bulk inversion asymmetry) | c | Centrosymmetric |
|---|---|---|---|---|---|---|
| Site symmetry: | | | | | | |
| Symmetry schematic: | Absence of spin splitting and spin polarization | Site dipole field induced net spin polarization | Site inversion asymmetry induced net spin polarization | Site dipole field induced spin polarization compensated by its inversion counterpart | Site inversion asymmetry induced spin polarization compensated by its inversion counterpart |
| Effect/consequence: | | | | | | |
| Name: | | | | | | |

![Diagram showing the three classes of spin polarization](image)

**The three classes of spin polarization in nonmagnetic bulks**

**Absence of spin polarization** (Fig. 1a). When all the site point groups contain inversion symmetry (point groups $C_{iv}$, $C_{ih}$, $D_{2h}$, $C_{3v}$, $D_{2d}$, $S_6$, $D_{6h}$, $C_{3h}$, $D_{4h}$, $T_d$, and $O_h$), there is no SOC-induced local spin polarization and thus the bulk spin polarization vanishes too (Fig. 1a and Table 1f). This is the case in crystal structures such as NaCl-type ($Pm\bar{3}m$), CsCl-type ($Pm\bar{3}m$), CaTiO$_3$-type perovskite ($Pm\bar{3}m$) and Mg-type hexagonal close packed ($P6_3/mmc$) structures. For example, the $\beta$-phase (NaCl-type) of SnTe—a topological crystalline insulator with topologically protected states on surfaces—is found here to have vanishing spin polarization in the bulk (Table 1f). However, we will show below that such bulk spin polarization can be controlled by tuning the atomic arrangement (and, thus, the symmetry), for example changing the $\beta$-phase having no spin polarization to an $\alpha$-phase having strong R-1 polarization (Table 1c).

**Net bulk spin polarization: R-1 and D-1 effects** (Fig. 1b). In these cases, the energy bands have non-zero net spin polarization. We next identify the pertinent combinations of bulk inversion asymmetry and site point groups leading to these macroscopic spin polarization effects (Table 1).

The D-1 effect (Table 1a,b) is associated with a non-centrosymmetric space group (bulk inversion asymmetry). In this case either all sites have non-polar point group symmetry ($D_3$, $D_3$, $D_3$, $S_6$, $D_{2d}$, $C_{3h}$, $D_{4h}$, $T_d$ and $O_h$), or some sites have polar point group symmetry ($C_{3v}$, $C_{3h}$, $C_{3v}$, $C_{4h}$, $C_{6v}$, $C_{6h}$, $C_{6v}$ and $C_{m}$) and all the site dipoles add up to zero. The simplest example (Table 1a) is the zinc-blende structure, where the bulk space group is $F43m$ and the site point group is $T_d$ for both atom species, such as InAs, GaSb and GaAs (ref. 3). A similar example is the half-Heusler materials, also having bulk space group $F43m$ and site point group...
Distortion (which induces polar point groups on the atomic sites) is removed by deforming the lattice to the centrosymmetric $\beta$-phase (the total energy rises by $\sim 0.01 \text{ eV/atom}$), the spin polarization disappears, as it now belongs to the unpolarized class, as illustrated in Table 1f.

### Compensated (hidden) spin polarization: R-2 and D-2 effects (Fig. 1c)

These can arise in crystal structures where inversion symmetry is present in the bulk space group, but not in the site point groups (Fig. 1c). This is the case when the individual sites carry either a local dipole field (for R-2) or a site inversion asymmetric crystal field (for D-2). A combination of a bulk centrosymmetric space group with a site dipole field leads to the bulk R-2 effect, whereas a combination of a global centrosymmetric space group with site inversion asymmetric results in the bulk D-2 effect (Fig. 1c).

We next explain the R-2 and D-2 effects in greater detail.

The D-2 effect (Table 1d) originates from the combination of a centrosymmetric global space group with site inversion asymmetry. Specifically, all atoms have non-polar site point groups and at least one site must have an inversion asymmetric site point group. The calculated band structure shown in Fig. 3b clearly illustrates the large band splitting ($\sim 400 \text{ meV}$) in the vicinity of the $L$ point in the Brillouin zone between CB1 and CB2 and between VB1 and VB2. The corresponding spin texture, projected onto the real-space sectors $\alpha$ and $\beta$, are shown as brown and green arrows, respectively, in Fig. 3c,d. Even though all the bands are energetically doubly degenerate as a result of bulk
inversion symmetry, we see that each of the branches of the two-fold degenerate band has opposite spin polarizations in real space. This real-space separation originates from the separate local site Dresselhaus SOC, as indicated by the brown branch projected on the \(C\) plane containing the \(A-H\) and \(A-L\) directions near the \(A\) point indicated by solid boxes in \(b\). We see in Fig. 4c,d that the spin polarizations from \(\alpha\)-sector (\(\text{CaBi}_0\)) layer and the green branch projected on the \(\beta\)-sector (\(\text{CaBi}_1\)) layer.

Centrosymmetric bulk silicon was always assumed to be a spin polarization-free material (so it is assumed not to disturb an externally injected spin polarization\(^{14}\)). It is an ideal material for long spin lifetime because the D-1 effect is absent and the effect of the nuclear spin of Si vanishes\(^7\). However, we illustrate in Supplementary Section B that bulk diamond-like silicon has compensated D-2 spin polarization (the class shown in Table 1d) because the site point group of Si atoms is non-centrosymmetric \(T_D\), which leads to a local atomic Dresselhaus spin polarization.

| Crystal structure and site point groups of each atomic site. | 
| --- | 
| \(\alpha\)-SnTe (\(R\) \(3m\)) | 
| Sn (\(C_{\text{mmm}}\)) | 
| Te (\(C_{\text{mmm}}\)) | 
| \(\omega\)-SnTe (\(R\) \(3m\)) | 
| | 
| Band structure around the A point along the A-H and A-L directions in the Brillouin zone. The two lowest conduction bands (CB1 and CB2) and two highest valence bands (VB1 and VB2) are shown in red. | 
| | 
| Spin polarization (contributed by the entire unit cell) is represented by brown arrows for the states of spin-split CB1 + CB2 and VB1 + VB2 bands in the \(k\)-plane containing the A-H and A-L directions near the A point indicated by solid boxes in | 
| | 
| Corresponding 2D diagram of the spin polarizations of CB1 and VB1, respectively. The arrows indicate the in-plane spin direction and the colour scheme shows the out-of-plane spin component. The magnitude of each spin vector is renormalized to unity for simplicity unless otherwise noted. Note that the magnitude of spin vectors varies with the \(k\)-points and bands depending on the strength of spin-orbit coupling and the magnitude of spin splitting. | 

Figure 2 | Rhombohedral \(\alpha\)-SnTe (\(R\) \(3m\)) with R-1 (dominant over D-1) spin textures. a. Crystal structure and site point groups of each atomic site. b. Band structure around the A point along the A-H and A-L directions in the Brillouin zone. The two lowest conduction bands (CB1 and CB2) and two highest valence bands (VB1 and VB2) are shown in red. c. Spin polarization (contributed by the entire unit cell) is represented by brown arrows for the states of spin-split CB1 + CB2 and VB1 + VB2 bands in the \(k\)-plane containing the A-H and A-L directions near the A point indicated by solid boxes in b, respectively. e, f. Corresponding 2D diagram of the spin polarizations of CB1 and VB1, respectively. The arrows indicate the in-plane spin direction and the colour scheme shows the out-of-plane spin component. The magnitude of each spin vector is renormalized to unity for simplicity unless otherwise noted. Note that the magnitude of spin vectors varies with the \(k\)-points and bands depending on the strength of spin-orbit coupling and the magnitude of spin splitting. | 

recently discovered to have similar properties to cuprate- and iron-based superconductors\(^{14}\). Figure 4a shows the crystal structure of LaOBiS\(_2\), having a centrosymmetric bulk space group and non-centrosymmetric polar site point group \(C_{\text{v}}\) for Bi, S and La atoms, as well as a non-centrosymmetric non-polar site point group \(S_{\text{c}}\) for O atoms. The unit cell of LaOBiS\(_2\) can be divided into three sectors: two inversion-partner BiS\(_2\) layers, termed the \(\alpha\)-sector and \(\beta\)-sector in Fig. 4a, and the central La\(_2\)O\(_2\) layer, which does not affect the low-energy (near band gap) spectrum. The calculated band structure as shown in Fig. 4b clearly illustrates large band splitting (~120 meV) in the vicinity of the X point in the Brillouin zone between CB1 and CB2 and between VB1 and VB2. These are induced mainly by the large site dipole field as well as by the site inversion asymmetry in the BiS\(_2\) layers. The corresponding spin textures projected on sectors \(\alpha\) and \(\beta\) are shown in Fig. 4c,d. They manifest two branches of spin polarization (indicated in Fig. 4c,d by green and brown arrows) corresponding to the two BiS\(_2\) real-space sectors shown in Fig. 4a. We see in Fig. 4c,d that the spin polarizations from the two inversion-symmetric BiS\(_2\) layers have opposite directions and compensate each other. The 2D spin textures of CB1 and VB1 are shown in Fig. 4e,f. We see both helical (mainly in Fig. 4f) and non-helical (mainly in Fig. 4e) spin textures, suggesting that the R-2 effect is accompanied by the D-2 effect. The distribution of R-2 and D-2 effects on each band depends on the specific band character.
Figure 3 | NaCaBi (P63/mmc) with D-2 effect. a, Crystal structure and site point group of each atomic site. The two boxed real-space sectors (CaBi layers) forming the inversion partners used for spin projection are labelled α-sector and β-sector. b, Band structure near the L point along the L–(−H) and L–H directions in the Brillouin zone. The CB1+CB2 and VB1+VB2 band pairs are shown in red. c, d, Projected local spin polarization is represented by green (on the α-sector) and brown (on the β-sector) arrows for CB1+CB2 and VB1+VB2 bands in the k-plane containing the L–H and L–A directions near the L point indicated by solid boxes in b, respectively. The band crossing at the L point is due to both time-reversal symmetry and fractional translation operations (namely, a screw axis $6\bar{3}$ and a glide plane $c$ along the [0001] direction). We illustrate the compensated spin polarization near the band-crossing L point for simplicity. Note that band crossing is not necessary for compensated spin polarization.

Discussion

Physical generality of the observation. The concept that opposing local effects can mutually compensate in an extended crystal is common to the present discussion on spin polarization and a much earlier work on pyroelectricity\(^{19}\) which discussed classic electro-elasticity and compensation by molecular units (‘sectors’). In the present study we point out that the polar/nonpolar point group symmetry of sites carries the essential information. The connection to point group symmetry allows us to accomplish two new results. First, to identify other properties previously thought to exist only in non-centrosymmetric crystals (for example, spin polarization, piezoelectricity, and second-harmonic generation) as belonging to this general class of hidden effects in centrosymmetric crystal structures. This is demonstrated in Table 1 and Supplementary Section C, which show how these three types of observables emerge in specific combinations of site point groups and space groups. Second, the focus on site symmetries further allows us to systematically predict actual materials that would show such hidden compensation effects; for example, NaCaBi shows the D-2 effect whereas LaOBl$\text{S}_2$ shows the R-2 effect, as described in what follows.

How can one find actual materials with the R-2 or D-2 effect? Our objective is to transform the understanding of the symmetry underpinning the R-1, D-1, R-2 and D-2 effects to a search algorithm of actual materials that will manifest these effects, and then verify our understanding by calculating the respective spin texture for such prototypical materials. This is done by the following design principles: look for compounds (for example, in the Inorganic Crystal Structure Database\(^{20}\)) that have centrosymmetric space groups but with at least one of the Wycko positions lacking inversion symmetry and belonging to either polar (for R-2) or nonpolar (for D-2) point groups (listed in Table 1). Out of the 230 space groups, 92 are centrosymmetric; out of the 32 point groups, 21 are non-centrosymmetric\(^{19}\). To find materials that have a significant R-2 or D-2 spin polarization, look for compounds that have heavy elements located on atomic sites with a large dipole field; the latter can be readily obtained from an electronic structure calculation within first-principles DFT by computing the gradient of the self-consistent electrostatic potential at various lattice sites. For LaOBl$\text{S}_2$, we find a rather large dipole field of $1.8 \times 10^5$ kV cm$^{-1}$ on the Bi site (see details in Supplementary Section D). We find...
Potential advantages of compensated over non-compensated spin polarization. In addition to the obvious increase in the number of systems that can be amenable to spin-polarization based applications, the currently predicted spin polarization in centrosymmetric materials (the R-2 or D-2 effect) might have some advantage over the more conventional R-1 or D-1 effect in non-centrosymmetric systems. Indeed, in the former case one could sensitively manipulate the effect via the application of symmetry-breaking external perturbations such as an external electric field. In contrast, the more ordinary bulk Rashba effect in non-centrosymmetric crystals (R-1) is difficult to manipulate or reverse by an external electric field because the internal field (for example, $0.4 \times 10^5$ kV cm$^{-1}$ on the Sn site in α-SnTe, see Supplementary Section D) is usually much stronger than the external field. Thus, the hidden spin polarization may provide a new route to manipulate the electron’s spin.

Methods

In this work we evaluate the band structure by density functional theory (DFT; ref. 23) using the projector-augmented wave (PAW) pseudopotentials$^{24}$ with the exchange-correlation of Perdew–Burke–Ernzerhof (PBE) form$^{25}$ as implemented in the Vienna Ab-initio Simulation Package (VASP; ref. 26). We choose the energy cutoff in the range 300–550 eV, and the reciprocal space grids of $10 \times 10 \times 10, 18 \times 18 \times 6, 8 \times 8 \times 6, 12 \times 12 \times 12$ and $13 \times 13 \times 4$ for ZrCoBi, α-SnTe, NaCaBi, St, and LaOBiS$_2$, respectively. The crystal structures are taken from refs 20,27,28 and the atomic positions are fully relaxed under a tolerance of $10^{-5}$ eV Å$^{-1}$. Spin–orbit coupling is taken into account, although calculated by a
perturbation $\sum_{i,j} V_{i+j} \mathbf{L} \cdot \mathbf{S}(l,m)_j(l,m)_i$ to the pseudopotential, where $\{i,j\}$ is the angular momentum eigenstate of the $i$th atomic site. The spin polarization is evaluated by projecting the calculated wavefunction $\langle \psi \rangle$ on the spin and orbital basis of each atomic site $C_{ijkl} = \langle \psi \rangle \langle \phi_i \otimes \phi_j \| \phi_i \otimes \phi_j \rangle$ and then summing $C_{ijkl}$ for a given spin direction and sector that contains a number of atomic sites in the unit cell. The Wigner–Seitz radii for constructing $\{i,j\}$ used in this study are listed in the pseudopotentials of the VASP simulation package. In the future, we will use advanced numerical methods to project the wavefunction onto any shape of volume of the sector.

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