Zeeman-type spin splitting in nonmagnetic three-dimensional compounds

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Despite its potential for device application, the nonmagnetic Zeeman effect has only been predicted and observed in two-dimensional compounds. We demonstrate that noncentrosymmetric three-dimensional compounds can also exhibit a Zeeman-type spin splitting, allowing the splitting control by changing the growth direction of slabs formed by these compounds. We determine the required conditions for this effect: (i) noncentrosymmetric including polar and nonpolar point groups, (ii) valence band maximum or conduction band minimum in a generic k-point, i.e., non-time-reversal-invariant momentum, and (iii) zero magnetic moment. Using these conditions as filters, we perform a material screening to systematically search for these systems in the AFLLOW-ICSD database. We find 20 candidates featuring the Zeeman-type effect. We also find that the spin splitting in confined systems can be controlled by an external electric field, which in turns can induce a metal–insulator transition. We believe that this work will open the way for the discovery of novel fundamental effects related to the spin polarization control.

npj Quantum Materials (2019) 4:41; https://doi.org/10.1038/s41535-019-0182-z

INTRODUCTION

The manipulation of inversion and time-reversal (TR) symmetries have been the cornerstone of novel phenomena allowing the generation and control of spin-polarized states in crystalline materials, the principal goal of spintronics.1–4 The TR-symmetry breaking, which is usually induced by external magnetic fields or the intrinsic magnetic order, can lead to a separation in energy of bands with opposite spin, i.e., Zeeman spin splitting.5–7 In nonmagnetic compounds, the combination of the atomic-site polarity and bulk point group results in all possible structural configurations leading to intrinsic spin-polarized states.8–10 For instance, in bulk inversion asymmetry (IA) materials, the spin polarization is always accompanied by a spin splitting typically referred to as either Dresselhaus11 or Rashba effect12,13 according to the spin-texture orientation (see Fig. 1a). The split bands have the opposite helical in-plane spin-texture in Rashba semiconductors and the same helicity in band inverted Rashba semiconductors.14 In the Dresselhaus effect, the spin polarization is parallel to k ((Σ)) if k0 = 0 and kπ = 0. The band dispersion curves related to these effects, which are represented in Fig. 1b, have been characterized by spectroscopic measurements for many surfaces and interfaces,15–18 and can be described by a simplified Hamiltonian model,

\[
\mathcal{H} = \mathcal{H}_0 + \Omega(k) \cdot \sigma
\]

where \(\mathcal{H}_0 = \frac{\hbar^2 k^2}{2m} I\), \(\Omega(k)\) is the spin–orbit coupling (SOC) field, and \(\sigma\) are the Pauli matrices. Here, \(k_x = k_x^0 + k_x^2\), \(m\) is the effective mass of electrons, and \(I\) is the 2 × 2 unitary matrix. The specific form of \(\Omega(k)\) depends on the material symmetry.19,20 For instance, in a two-dimensional system with C2 point group, the Rashba and Dresselhaus fields are written as \(\Omega_1 = \lambda_1 (k_x, k_y, 0)\) and \(\Omega_2 = \lambda_2 (k_x, k_y, 0)\), respectively. The strength of the Rashba (Dresselhaus) field is given by the parameter \(\lambda_1\) (\(\lambda_2\)). The parameter \(\lambda_2\) is different from zero in systems featuring a nonzero electric dipole,21 which can be intrinsic or, as originally proposed by Rashba, induced by interfacing semiconductors or external electric fields.12,13 The Rashba effect is typically used for the electrical control of the spin polarization.22 For these reasons, IA materials have historically been the most promissory candidates for spintronic devices.2–4

Besides the Rashba and Dresselhaus effects, another kind of spin splitting in nonmagnetic IA compounds, whose spin texture is similar to the one observed in the magnetic Zeeman effect, is the so-called Zeeman-type spin splitting (See Fig. 1a). Despite its potential for device application, this nonmagnetic effect has only been predicted and observed in the two-dimensional WSe2 and MoS2.23 Unlike the Rashba and Dresselhaus splitting, the Zeeman-type splitting does not have a band crossing (see Fig. 1a) and has been related to the effect of an electric dipole or an external electric field.23 This suggests that this effect can only be induced in two-dimensional systems. Indeed, it has not been explored in three-dimensional compounds.

Here, we demonstrate that IA three-dimensional compounds can also exhibit a Zeeman-type spin splitting, allowing the splitting control by changing the growth direction of slabs formed by these compounds. For this purpose, we first establish the conditions for nonmagnetic spin-split bands. Using these conditions as filters, we perform a material screening in the AFLLOW-ICSD database,26,27 i.e., a systematic search of fabricated materials. We find 20 binary three-dimensional compounds featuring the Zeeman-type effect. Aside from the prediction of large Zeeman splitting in the three-dimensional version of layered systems exhibiting this effect (the VBM in MoS2 and WS2 have a spin splitting of 187 and 510 meV, respectively), we also find large spin splitting in compounds that are not formed by van der Waals layered materials, such as, OsC, WN2, and SnTe, with splittings.
Fig. 1 Spin polarized states preserving the TR-symmetry. a Schematic representation of the band structure and spin-texture of systems featuring the Rashba, Dresselhaus, and nonmagnetic Zeeman effects. The arrows stand for the spin polarization orientation. In the Rashba and Dresselhaus effects, the bands (green and purple) cross each other at the origin of the BZ (Γ is a TR-invariant point). b Filters used in the materials prediction for each spin polarization phenomenon. The band structure without SOC is represented in black. After considering the SOC, for IA compounds, the bands split. The up and down spins are represented in blue and red, respectively. For compounds with IS, we have also represented each band separately to make evident the different spin components.

The Zeeman-type effect is the spin discrimination as a consequence of the inversion symmetry (IS) breaking at non-TR-invariant k-points, rather than the effect of an intrinsic electric dipole, as we discuss below. We then define the conditions that a material should satisfy to exhibit the Zeeman-type effect. Design principles are typically used as filters to predict or select compounds from the materials databases, e.g., AFLLOW and materials project. By combining the materials screening with high-throughput density functional theory (DFT) calculations (see section "Methods"), we have an efficient approach to predict novel Zeeman-type semiconductors.

The Zeeman-type effect is the spin discrimination as a consequence of the inversion symmetry (IS) breaking at non-TR-invariant k-points, rather than the effect of an intrinsic electric dipole, as we discuss below. We then define the conditions that a material should satisfy to exhibit the Zeeman-type effect: (i) IA and TR-symmetry (noncentrosymmetric bulk and nonmagnetic moment) and (ii) the VBM and CBM must take place at a non-TR-invariant k-point. In addition, a total electric dipole is not needed, allowing the presence of the Zeeman-type effect in compounds with polar and nonpolar point groups. These conditions are summarized in Fig. 1b. Specifically, the Zeeman-type splitting is related to noncentrosymmetric nonmagnetic materials, i.e., only compounds with bulk point groups Cn, Cnv, Dn (with n = 1, 2, 3, 4, and 6), Sv, D2n, C3v, D3v, T, Td, and O could feature the nonmagnetic Zeeman effect. When the VBM or CBM take place at a TR-invariant k-point, the compounds with this bulk point groups are classified as Rashba or Dresselhaus semiconductors (see Fig. 1b). In addition, materials in other symmetries could feature the hidden-spin-polarization, which is characterized by spin-degenerated bands, as represented in Fig. 1b.

We use the previously established conditions as filters for a systematic search of nonmagnetic Zeeman materials. We perform a materials screening in the AFLLOW database, which contains information of ~59,000 fabricated materials. After eliminating compounds with the same formula, space group, and the number of atoms in the unit cell, we obtain 32,553 entries. In this work we will focus on binary compounds, what leads to a total of 8360 materials, which in turn can be divided into 1326 IA and 7034 IS materials. Among the IA compounds, we find 587 nonmagnetic gaped and 739 gapless magnetic materials. Finally, only 20 nonmagnetic IA compounds exhibit either the CBM or the VBM at non-TR-invariant k-points. Detailed information of the predicted Zeeman-type materials is presented in Table 1.

Some materials in the ICSD database have been fabricated under specific conditions of pressure and temperature; therefore, these compounds could be above the boundary of the convex Hull, i.e., the phase diagram representing the set of the lowest possible potential energy states obtained from both single materials and mixtures of those materials. Remarkably, in the selected compounds, we find systems forming the boundary of the convex hull (E_AH = 0), suggesting that they are in the most stable structural configuration, such as, WN2 and RuSi, FeSi, Ir3Ge3, Ir3Te3, Cs3Te3 in the space groups P6/m2, P213, P213, Pm21, Cc, and Cmc21, respectively. We find that for RuGe, OsSi, MoO3, WS2, and Ti3Te5 the energy above the convex hull is less than 30 meV/atom, which means that these materials could be easily synthesized.

For WS2 and MoS2 (space group P6/mmc), the bulk is centrosymmetric and the site point group D3h and C3v of the Mo and S atoms are noncentrosymmetric, which results in a hidden Dresselhaus spin polarization. However, in the noncentrosymmetric space group R3m, the VBM of these materials has a giant Zeeman-type splitting about 510 and 187 meV, as shown in Table 1. We also find that compounds with the same formula but with different structure could exhibit different splitting values. For instance, Bi2O3 (space group R3m) has a...
splitting of 81 meV in the CBM, whereas the VBM of this compound in the $P4mm_2$ space group has a splitting of 15 meV. This is expected since the on-site SOC is not the unique property related to the spin splitting. Indeed, systems formed by atoms with a relatively weak SOC could also have large splitting values, e.g., $\Delta_{2Y} = 192$ meV in Mn$_2$Ge.

Surfaces and electrical control

Since surfaces and two-dimensional confinement affect the symmetry and the total electric dipole, we here explore the spin splitting in the surfaces of Zeeman-type semiconductors and its possible electrical control. For illustrative purposes, we will present here the results for SnTe (one of the materials with the largest splitting). We consider three growth directions corresponding to planes parallel, oblique, and perpendicular to the Sn–Te bonding along the axis normal to the surface (111) (see Fig. 2a), i.e., planes at the crystallographic directions (10T), (110), and (111), respectively. We find that the spin splitting change according to the growth direction of the slab. Specifically, the splitting is near zero for the plane (10T) and increases as the angle between the plane and the bonding increases. Thus, the (110) and (111) planes exhibit a splitting of 50 and 491 meV (see Fig. 2c–e). Consequently, the slab (10T) is an insulator, whereas the (110) and (111) surfaces are metallic. This insulator–metal transition is a remarkable effect arising from large spin splittings in nonmagnetic Zeeman semiconductors. If the spin splitting in the VBM is greater than the band gap, the highest energy band can cross the Fermi energy, leading to majority spin channels for given non-TR-invariant k-point, as shown for SnTe in Fig. 2c–e. The TR-symmetry imposes that a given k-point and its respective TR-partner $-k$ have opposite spin polarization, which in turn implies that the spin filtering requires the breaking of the valley symmetry. However, we find that the metal–insulator transition can be induced and controlled in a specific slab by manipulating the Zeeman splitting, which can be used for application in spintronics. For instance, a perpendicular external electric field $E = E_z$ could modify the electric dipole induced by the surface. For SnTe slab along the (111) surface, an applied electric field $E = E_z$ decreases the spin splitting, leading to a metal–insulator transition for $E_z = 0.12$ eV/Å. By increasing the electric field, the band gap opens again due to the change on the electric dipole orientation, resulting in an insulator–metal transition for $E_z = 0.145$ eV/Å.

**DISCUSSION**

The Zeeman-type splitting in the so far proposed layered materials has been interpreted in terms of a nonzero intrinsic dipole. This interpretation, based on the common understanding of the Rashba effect, implies that compounds in which the atomic dipoles add up to zero, e.g., ZB GaAs, cannot exhibit this splitting, which is not necessarily correct, as we discuss below. GaAs (space group $F43m$) is a historical example of Dresselhaus semiconductors. In this IA compound, the dipoles add up to zero due to the tetrahedral chemical environment imposed by the crystal symmetry, as represented in Fig. 3a. Thus, although the Rashba terms do not contribute to the Hamiltonian describing the GaAs band structure, the spin splitting reaches high values ($\approx 120$ meV) at the high symmetry point $W$ (see Fig. 3b), as early reported in ref. 3. On the other hand, for ZB binary semiconductors, the position of the CBM and VBM can change according to the chemical composition (AB):

| Compound | $\Delta_{2X}$ (meV) | $\Delta_{2Y}$ (meV) | $E_F$ (eV) | $E_{\text{vH}}$ (eV) | $E_g$ (eV) | Space group | Exp. | Theory | ICSD code |
|----------|---------------------|---------------------|-----------|------------------|----------|-------------|------|--------|-----------|
| Ge$_2$As$_4$ | 13                  | –                   | 0.005     | 0.05             | 0.155    | $P4mm$    | –    | 44     | 163833    |
| SnS      | 49                  | –                   | $-0.495$  | 0.28             | 0.166    | $F4mm$    | 45   | 31     | 43409     |
| OsC      | 332                 | 340                 | 0.772     | 0.772            | 0.279    | $P2_1,3$  | –    | 46     | 168277    |
| Mn$_2$Ge | 192                 | 141                 | 0.137     | 0.253            | 0.132    | $F4mm$    | 47   | –      | 184947    |
| RuGe     | 97                  | 101                 | $-0.281$  | 0.013            | 0.185    | $P2_1,3$  | 48   | –      | 637744    |
| OsSi     | 346                 | 202                 | $-0.367$  | 0.012            | 0.512    | $P2_1,3$  | 49   | –      | 647777    |
| FeSi     | 70                  | 17                  | $-0.511$  | 0                | 0.181    | $P2_1,3$  | 50–52| –      | 633542    |
| RuSi     | 85                  | 81                  | $-0.647$  | 0                | 0.261    | $P2_1,3$  | 53–55| –      | 85209     |
| WS$_2$   | –                   | 38                  | $-0.277$  | 0.066            | 0.034    | $P6_2,22$ | 56,57| –      | 652549    |
| WN$_2$   | 433                 | 125                 | $-0.521$  | 0                | 1.070    | $P6m2$    | 58   | –      | 290433    |
| Bi$_2$O$_3$ | –                  | 81                  | $-1.562$  | 0.092            | 2.416    | $R3m$     | 59   | –      | 168810    |
| MoS$_2$  | 187                 | –                   | $-1.303$  | 0.003            | 1.422    | $R3m$     | 60–62| –      | 435600    |
| WS$_2$   | 510                 | –                   | $-1.26$   | 0.004            | 1.841    | $R3m$     | 63,64| –      | 202367    |
| Ir$_2$Ge$_3$ | 16                 | –                   | $-0.34$   | 0                | 0.128    | $P4c2$    | 65–67| –      | 42909     |
| Ti$_2$Te$_3$ | 156            | 197                 | $-0.167$  | 0.024            | 0.445    | $Cc$      | 68   | –      | 26282     |
| GeO$_2$  | 7                   | –                   | $-0.533$  | 1.561            | 0.985    | $P3121$   | 69   | –      | 53869     |
| SnTe     | 491                 | –                   | $-0.034$  | 0.252            | 0.240    | $F4mm$    | 28   | –      | 53956     |
| Bi$_2$O$_3$ | 15                 | –                   | $-1.486$  | 0.168            | 0.149    | $P4mm$    | 59   | –      | 168808    |
| In$_2$Te$_5$ | –                | 31                  | $-0.233$  | 0                | 1.041    | $Cc$      | 70,71| –      | 640615    |
| Cs$_3$Te$_3$ | 53               | 209                 | $-0.755$  | 0                | 0.637    | Cmc21     | 72,73| –      | 53245     |

The calculated electronic properties are in agreement with the results reported in the material project$^{31,32}$ and AFFLOW-ICSD$^{26,27}$ repositories.
Rashba and Dresselhaus fields given by $\Omega_R(k) = \lambda_R (n \times k)$ and $\Omega_D(k) = \lambda_D \left( k_x (k_y^2 - k_z^2), k_y (k_x^2 - k_z^2), k_z (k_x^2 - k_y^2) \right)$, respectively. Here, $n$ is a unitary vector along the direction of the electric dipole. Accordingly, the spin splitting generated by these odd-in-$k$ effective magnetic fields is:

$$\Delta(k) = \epsilon^\uparrow(k) - \epsilon^\downarrow(k) = |\Omega_R(k)| + |\Omega_D(k)|,$$

where $\epsilon^\uparrow(k)$ and $\epsilon^\downarrow(k)$ are the eigenvalues of the Hamiltonian $\mathcal{H}$. In order to show that the Zeeman splitting is typically larger than the Rashba and Dresselhaus splitting, we consider an illustrative case: $\lambda_R = 0$ and $n = z$. Thus, the spin splitting becomes $\Delta(k) = \lambda_D |k_z|$. In the Rashba effect, the momentum offset $k_R$ usually reaches small values between $10^{-2}$ and $10^{-1}$ Å$^{-1}$ (see Fig. 1b).$^3$ Therefore, although the parameter may be large ($\lambda_R = 1$ eV Å), the splitting values are always limited to some meV.$^3$ This is also valid in compounds in which the atomic dipoles add up to zero, where $\lambda_R = 0$ and $\Delta(k) = \Omega_D(k)$. Since the non-TR-invariant high symmetry $k$-points are at the boundary of the BZ, Zeeman-type splitting are always larger than Rashba and Dresselhaus splitting. In addition, due to the spin splitting position in the BZ, the Zeeman-type effect offers alternative mechanisms for spin polarization control.

In the WSe$_2$ monolayer, an in-plane electric dipole generates an out-of-plane effective magnetic field, which can be locally described in terms of the Hamiltonian in Eq. (1). The effective magnetic field $\mathcal{H}_e$ comes from the SOC interaction and forbids spin degenerated states at non-TR-invariant $k$-points. Thus, the spin splitting and the spin-texture are consequence of the intrinsic effective magnetic field, but not the origin. Specifically, the spin direction depends on the direction of the effective magnetic field. For example, in MoS$_2$ case, the effective magnetic field is along the $z$-axis and hence, only the expected value of the spin operator $S_z$ is different from zero. The same analysis can be applied to the SnTe compound. For instance, in this compound, the total electric dipole is zero, and hence, only the Dresselhaus term contributes to the effective magnetic field. Therefore, at the $k_{xy}$ plane, by imposing $\lambda_R = 0$, the effective magnetic field along the $X-W$
symmetry line is written as \( \mathbf{Q}_0(\mathbf{k}) \approx (k_x, k_y, 0, 0) \), since in this direction \( k_x = 0 \) and \( k_y = 0 \). In our density functional calculations, we obtain that the spin texture of the SnTe band structure is dominated by \( S_z \) spin components at this plane, as shown in Fig. 2b. Since the Dresselhaus effective magnetic field can also lead to the Zeeman-type spin texture, electric dipoles are a sufficient condition but not necessary for this effect, as we initially proposed in the design principles.

The proposed design principles for the Zeeman-type effect are also applicable to the two-dimensional compounds with external electric fields in which the VBM or CBM take place at a non-TR-symmetry \( k \)-point. The external electric field is the key ingredient to break the IS, generating a perpendicular effective magnetic field and consequently, a \( S_z \) spin component. For instance, this specific behavior has been found for \( k \)-points near the high symmetry point \( K \) in the graphene band structure with a perpendicular electric field,\(^{35,36}\) but it was not related with the Zeeman-type effect. For \( k \)-points far from the \( K \) point, the spin texture is the observed in the common Rasha effect.\(^{37}\)

The spin splitting can be controlled by changing the growth direction of slabs. For instance, when the systems are confined along the (10T) direction, we can write \( (k_z) = 0 \). Consequently, the Zeeman spin splitting at the \( W \) point (\( S \)-point in the equivalent two-dimensional BZ, as shown in Fig. 2b) vanishes. Different from the Rashba and Dresselhaus splitting at TR-invariant \( k \)-points, the non-magnetic Zeeman effect does not allow the spin polarization electrical control, but the metal–insulator transition mediated by the electrical control of the splitting size. Specifically, an external electric field does not change the spin polarization, but the splitting size. Thus, the electric field can bring states to the Fermi energy. This control mechanism is different from the recently reported in the magnetic Zeeman splitting.\(^{38}\) As previously discussed, the electrical control of the spin splitting can also be achieved in these materials according to the growth direction of the slab.

In conclusion, we demonstrate that IA three-dimensional non-magnetic compounds can exhibit a Zeeman-type spin splitting, providing the possibility to grow slabs in which the electrical dipole is perpendicular to the surface and hence, allowing the electrical control of the spin splitting. The required conditions for this effect are: valence band maximum or conduction band minimum in a non-TR-invariant \( k \)-point, IA, and zero magnetic moment. Using these conditions as filters, we perform a material screening and high-throughput ab initio calculations to systematically search for these materials in the AFLOW-ICSD database. We find 20 candidates featuring this splitting. Our calculated spin splittings can be as large as 433, 510, and 491 meV for the compounds WN\(_2\) (P6\(_3\)m1), WS\(_2\) (R3m), and SnTe (F4\(_3\)m), respectively. We also demonstrate that the spin splitting in slabs of these compounds depends on the growth direction and can be controlled by an external electric field. We believe that this work will open the way for the discovery of novel fundamental effect related to the spin-polarization control.

METHODS

The ab initio calculations were performed within the DFT using Perdew–Burke–Emzerhof generalized gradient approximation\(^{19}\) exchange-correlation functional and the Hubbard on-site terms\(^{40,41}\) as implemented in the Vienna Ab initio Simulation Package.\(^{2,43}\) All the specific settings of the calculations without SOC (e.g., cutoff energies, \( k \)-point sampling, effective U parameters, atomic configurations) were the same to those used on the AFLOW database.\(^{2,42}\) We have then included the spin–orbit interaction keeping the zero magnetic moment.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGEMENTS

This work was financed by FAPESP (grants 18/11856-7 and 17/02317-2), and CNPq. This work was performed using the computational infrastructure of the LNCC supercomputer center (Santos Dumont).

AUTHOR CONTRIBUTIONS

C.M.A. performed the materials screening and the band structure calculations. All authors participated on the conceptual development of the project, analysis of the results and shaping the manuscript.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the npj Quantum Materials website (https://doi.org/10.1038/s41535-019-0182-z).

Cometing interests: The authors declare no competing interests.

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