Topological node line semimetal state in two-dimensional tetragonal allotrope of Ge and Sn

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Abstract
Realizing semimetal states in two-dimensional (2D) materials are of great importance for their future application in novel quantum devices at the nanoscale. Using first-principles calculations based on density functional theory, we propose a new 2D tetragonal allotrope of Ge and Sn, 2D T-Ge and T-Sn, which consists of repeated square and octagon rings. The calculated cohesive energy, \textit{ab initio} molecular dynamic simulations and phonon dispersions indicate that 2D T-Ge and T-Sn are stable at room temperature and possibly synthesized in the experiments under appropriate growth conditions. In the absence of spin–orbital coupling (SOC), 2D T-Ge and T-Sn are node line semimetals and the nodal loop in 2D T-Ge and T-Sn are protected by the combination of the spatial inversion $P$ and time-reversal $T$ symmetries. Remarkably, when SOC is included, 2D T-Ge and T-Sn are still node line semimetals although small gap is opened along the nodal loop, which are identified by nontrivial $Z_2$ invariant and topological edge states at the sample boundaries. Furthermore, our calculations show that node line semimetal states in 2D T-Ge and T-Sn are robust with the biaxial strains in the range of $-3\%$ to $3\%$. Our results provide a new 2D material platform for realization of 2D topological node line semimetals and innovative applications of topological node line semimetals.

1. Introduction

Following the successful preparation of graphene [1–3], two-dimensional (2D) materials have attracted extensive attentions due to their unusual physical properties and innovative applications [4–6]. In analogy to graphene, other group IV elements, such as Si, Ge and Sn, can also form stable 2D honeycomb crystals, namely silicene, germanene and stanene. Intriguingly, all of silicene, germanene and stanene are 2D topological insulator (also called quantum spin Hall (QSH) insulator) [7, 8], and their band gaps are larger than that of graphene because spin–orbit coupling (SOC) greatly increase as the atomic indices and degree of buckling increase. It is worth noting that allotropes of many 2D materials are predicted to be stable and possess exotic physical properties even superior to their original counterparts. Body-centered tetragonal carbon (bct-carbon) allotrope, which consists of square and octagon rings, was predicted to be a transparent carbon polymorph [9–11]. Furthermore, 2D tetragonal allotrope of C (T-graphene) originated from bct-carbon was predicted to be stable. Liu et al theoretically demonstrated that different from planar T-graphene, buckled T-graphene possess Dirac-like fermions and high Fermi velocity [12, 13], while Huang et al claimed that buckled T-graphene is a normal metal as planar T-graphene [14]. Also, it was theoretically proposed that 2D tetragonal allotrope of Si (T-silicene) is stable and is nodal line semimetal [15]. Inspired by the experimental investigations for atomic structure of grain boundaries in single layer 1H-MoS$_2$ [16], a tetragonal allotrope of single layer MX$_2$ ($M = Mo, W, Nb; X = S, Se, Te$) [17–21], which consists of repeated square and octagon rings, was theoretically predicted. Interestingly, tetragonal allotrope of single layer MX$_2$ ($M = Mo, W; T = S, Se, Te$) were proposed to be QSH...
insulator [18–20]. Moreover, it was theoretically proposed that except for single layer puckered and buckled honeycomb lattice structures [22], group V elements, including P, As, Sb and Bi, can form a stable 2D tetragonal allotrope composed of buckled square and octagon rings [23–26]. Remarkably, 2D tetragonal allotrope of Bi was predicted to be a QSH insulator with a sizable band gap about 0.41 eV [25, 26]. It is therefore imperative to investigate 2D tetragonal allotrope of Ge and Sn.

As a novel class of quantum materials, topological metals and semimetals [27–29], have been extensively studied in recent years. In view of future application in novel quantum devices at the nanoscale, of particular interest among these new quantum materials are a large family of 2D topological metals and semimetals. In this respect, Young et al theoretically proposed symmetry protected 2D Dirac semimetals in which Dirac cones at high-symmetry points are not gapped by SOC [30]. On the other hand, Honeycomb–Kagome lattice Hg2As2 [31], Lieb lattice BeH2 and Be2C [32], single layer MX (M = Pd, Pt; X = S, Se, Te) [33], single layer Bi2C [34], 2D compounds X2Y (X = Ca, Sr and Ba; Y = As, Sb and Bi) [35], β12-borophene [36] and pentagonal group p-IVX2 (IV = C, Si, Ge, Sn, Pb; X = S, Se, Te) [37] were predicted to be 2D node line semimetals, in which the conduction and valence bands touch near the Fermi level at extended loops. More intriguingly, single layer Cu2Si [38] and CuSe [39] have been experimentally demonstrated to be 2D node line semimetals. Up to now, single layer HfGeTe [40] have been theoretically proposed to be 2D Z2 topological metal.

In this paper, based on first-principles calculations, we propose a new 2D tetragonal allotrope of Ge and Sn, which consists of repeated square and octagon rings, and explore their stability, geometry structure, band structure and topological property as well as the effects of biaxial strain on their stability, geometry structure, band structure and topological property. Our calculations show that in the absence of SOC, 2D tetragonal allotrope of Ge and Sn are 2D node line semimetals protected by the combination of the spatial inversion P and time-reversal T symmetries. Furthermore, in the presence of SOC, 2D tetragonal allotrope of Ge and Sn remain topological node line semimetal states and they survive the topological states under the biaxial strains in the range between –3% and 3%.

2. Computational details

Our calculations were carried out using density-functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP) [41–43]. The projector–augmented wave [44] method was used to describe the ion–electron interaction and the exchange correlation energy was approximated by the generalized gradient approximation (GGA) [45] in the form proposed by Perdew, Burke and Ernzerhof (PBE). The energy cutoff of plane wave basis was set as 500 eV and the convergence threshold for energy was set to be 1 × 10^{-6} eV. A vacuum space of more than 20 Å was adopted along the direction normal to the plane of 2D material to avoid the interaction between the neighboring slabs. All structures were fully relaxed, including atomic positions and lattice constants, until the maximal force on each atom was smaller than 0.01 eV Å−1. Considering the large computational burden of HSE calculations as well as the underestimation of band gap by GGA, the PBE functional was used for structural optimization, and then the Heyd–Scuseria–Ernzerhof (HSE06) [46] hybrid functional was employed to calculate more accurately band structure of the optimized structure by using PBE functional. The Brillouin zone (BZ) was sampled by using a 11 × 11 × 1 k-point mesh. The SOC was included in the self-consistent calculations of band structure. The ab initio molecular dynamic (MD) simulations in the canonical (NVT) ensemble were performed via the VASP code and the temperature was maintained at 300 K by Nosé–Hoover method. Phonon dispersion curves were calculated using the density functional perturbation theory as implemented in the VASP combined with the PHONOPY code [47], in which a 4 × 4 × 1 supercell was employed. The s and p orbitals of Ge and Sn atoms were projected as the original orbitals to construct the maximally localized Wannier functions (MLWFs) by using the WANNIER90 code [48, 49]. The \( \mathbb{Z}_2 \) topological invariant and edge states were calculated by the software package WannierTools [50], based on the method of MLWFs.

3. Results and discussion

Figure 1 depicts the top and side views of crystal structure of 2D tetragonal allotrope of Ge and Sn, where the square area surrounded by black lines represents the unit cell. In the following, 2D tetragonal allotrope of Ge and Sn are denoted as 2D T-Ge and T-Sn, respectively. Instead of the six-membered rings in the honeycomb lattice, it can be seen from figure 1(a) that the lattice of 2D T-Ge and T-Sn consists of repeated square and octagon rings in both x and y directions, forming a square Bravais lattice with \( D_{4h} \) symmetry. In this lattice, each atom is bound to three neighboring atoms and the unit cell contains eight atoms at the corners of an octagon ring. Table 1 lists the optimized structural parameters of 2D T-Ge and T-Sn at the PBE level, including the lattice constants \( a_0 \), the bond length \( l_1 \) that constitutes the square ring, the bond length \( l_2 \) that links two square rings, and the buckling
Moreover, the bond length $d$ and the bond lengths $l_1$ and $l_2$ monotonously increase along with increasing of the atomic indices from Ge to Sn, as listed in Table 1. The bond length $l_1$ is slightly larger than $l_2$, which is similar to tetragonal allotrope of group V elements [26] and MoS$_2$ [21].

In order to examine the stability of 2D T-Ge and T-Sn, we first calculate their cohesive energy per atom, which is defined as the difference between the energy of one X (X = Ge, Sn) atom in 2D tetragonal allotrope of Ge and Sn and that of a free X atom. As shown in Table 1, the cohesive energies of 2D T-Ge and T-Sn are $-3.08$ and $-2.61$ eV/atom, respectively, which are slightly higher than that of the honeycomb counterparts [51]. Therefore, 2D T-Ge and T-Sn are only slightly less stable than the honeycomb counterparts. Combined with the earlier reported synthesis of germanene and stanene [52, 53], it is anticipated that 2D T-Ge and T-Sn, i.e. 2D tetragonal allotrope of Ge and Sn, are possibly synthesized in the experiments under appropriate growth conditions. We also perform ab initio MD simulations at 300 K using a $3 \times 3 \times 1$ supercell to check the thermal stability of 2D T-Ge and T-Sn, where the total simulation time is set to 10.0 ps with a time step is 1.0 fs. The evolution of total energy of 2D T-Ge and T-Sn during the MD simulations and structural snapshot of T-Ge and T-Sn at the end of the simulation are depicted in Figure 2. It can be seen from Figures 2(a) and (b) that the total energy of 2D T-Ge and T-Sn only fluctuate around a constant value during the entire simulations, and the structures retain their integrity without appreciable distortion until the end of the MD simulations, indicating that both 2D T-Ge and T-Sn are thermally stable at room temperature. Furthermore, we calculate the phonon dispersions to check the dynamic stability of 2D T-Ge and T-Sn. Figures 2(c) and (d) show that the frequencies of all phonon branches of 2D T-Ge and T-Sn are positive values in the whole BZ, confirming that 2D T-Ge and T-Sn are dynamically stable.

We turn to calculate the electronic properties of 2D T-Ge and T-Sn using the HSE06 hybrid functional. Figures 3(a) and (d) depict the band structure of 2D T-Ge and T-Sn without SOC, respectively. As depicted in Figures 3(a) and (d), in the absence of SOC, both 2D T-Ge and T-Sn are semimetals, where the valence and conduction bands exhibit linear dispersion in the vicinity of the Fermi level and cross near the Fermi level to form two nodal points along the high-symmetric $\Gamma-X$ directions in the BZ. A detail scan of the crossing points for the whole BZ clearly shows that all crossing points of the valence and conduction bands in 2D T-Ge and T-Sn form a nodal loop around the $\Gamma$ point, as depicted in Figures 3(b) and (e). To reveal the energy dispersions of the nodal loop, three-dimensional (3D) band structure around the $\Gamma$ point near the Fermi level in 2D T-Ge and T-Sn are calculated and depicted in Figures 3(c) and (f). The calculated 3D band structures around the $\Gamma$ point show that the energies of the nodes in the loop of 2D T-Ge and T-Sn vary within the range of $-68$ to $+2$ meV along the loop. In contrast, the energy variation along the nodal loop in node line semimetals is typically

Table 1. Cohesive energy $E_c$, lattice constant $a_0$, bond lengths $l_1$ and $l_2$, and buckling height $d$ of 2D T-Ge and T-Sn.

|           | $E_c$ (eV/atom) | $a_0$ (Å) | $l_1$ (Å) | $l_2$ (Å) | $d$ (Å) |
|-----------|----------------|-----------|-----------|-----------|---------|
| T-Ge      | $-3.08$        | 8.01      | 2.48      | 2.41      | 0.72    |
| T-Sn      | $-2.61$        | 9.22      | 2.87      | 2.80      | 0.88    |

Figure 1. Top (a) and side (b) views of the crystal structure for 2D T-Ge and T-Sn. $l_1$ represents the bond length constituted the square. $l_2$ represents the bond length connected two squares. $d$ represents the buckling height. $m_1$ and $m_2$ represent two mirror reflection planes.

Figure 2. The evolution of total energy of 2D T-Ge and T-Sn during the MD simulations and structural snapshot of T-Ge and T-Sn at the end of the simulation. The calculated 3D band structures around the $\Gamma$ point in 2D T-Ge and T-Sn are calculated and depicted in Figures 3(c) and (f). The calculated 3D band structures around the $\Gamma$ point show that the energies of the nodes in the loop of 2D T-Ge and T-Sn vary within the range of $-68$ to $+2$ meV along the loop.
hundreds of meV, such as >200 meV for Cu3PdN [54], >300 meV for TiB2 [55], and >800 meV for the elemental Be crystal [56], indicating that the nodal loop in 2D T-Ge and T-Sn are very flat in energy and momentum space. The orbit-projected analysis of the composition of the electronic states manifests that conduction and valence bands around the Fermi level of 2D T-Ge and T-Sn are mainly arose from the $p_z$ orbital of Ge and Sn atoms, respectively, as illustrated in figures 3(a) and (d).

Figure 2. Fluctuation of total energy during the MD simulations for 2D T-Ge (a) and T-Sn (b) and phonon dispersions of 2D T-Ge (c) and T-Sn (d). The insets depict the structural snapshot of T-Ge and T-Sn at the end of simulations.

Figure 3. Band structure of unstrained T-Ge (a) and T-Sn (d) without SOC. Red and blue dots denote $p_{xy}$ and $p_z$ atomic orbitals, respectively, and the size of symbols is proportional to the contribution weight of atomic orbital. The Fermi level is set to zero and indicated by dotted line. Nodal loop formed by crossing points of the valence and conduction bands in the BS of 2D T-Ge (b) and T-Sn (c) 3D band structure around $\Gamma$ point for 2D T-Ge (c) and T-Sn (f) without SOC.
In general, the nodal loop is protected by two typical protection mechanisms in the absence of a SOC system \[57–60\], i.e. the combination of the spatial inversion \( P \) and time-reversal \( T \) symmetries as well as mirror reflections symmetry. As known, the crystal structure of 2D T-Ge and T-Sn possess the inversion \( P \) and the mirror reflections symmetries. In addition, the time-reversal symmetry \( T \) is also preserved due to no magnetic ordering in 2D T-Ge and T-Sn. The nodal loop in 2D T-Ge and T-Sn are protected by the combination of \( P \) and \( T \) symmetries in the absence of SOC. To explore the role of the combination of \( P \) and \( T \) symmetries, we introduce the following artificial perturbations to the crystal structure of 2D T-Ge and T-Sn. First, we artificially apply 3% uniaxial strain to 2D T-Ge and T-Sn along \( x \) axis, as depicted in figure 4(a), which breaks mirror reflections symmetries \( m_1 \) and \( m_2 \) but preserves inversion \( P \). It can be seen from figure 4(b) that under 3% uniaxial strain, the nodal loop in 2D T-Ge and T-Sn are intact. In the second case, along the \( z \) axis we artificially shift one Ge (Sn) atom in the unit cell by a displacement of 0.1 Å, as depicted in figure 4(c), which preserves a mirror reflection symmetry \( m_2 \) but breaks inversion \( P \). As a result, the nodal loop in 2D T-Ge and T-Sn are gapped, as depicted in figure 4(d). These results clearly demonstrate that the nodal loop in 2D T-Ge and T-Sn are protected by the combination of \( P \) and \( T \) symmetries rather than the mirror reflections symmetry.

As shown in figures 5(a) and (b), the inclusion of SOC opens small gaps along the nodal loop in 2D T-Ge and T-Sn, while the shape of the bands near the Fermi level are essentially unchanged. The calculated 3D band structures around the \( \Gamma \) point show that the gap varies depending on the position along the nodal loop in 2D T-Ge and T-Sn from less than 11 and 22 meV to a maximum of 19 and 36 meV, respectively. Similar to 2D compounds \( X_2Y (X = \text{Ca, Sr and Ba}; Y = \text{As, Sb and Bi}) \) [35], SOC opens small gaps along the nodal loop in 2D T-Ge and T-Sn. Although opening small gaps along the nodal loop, SOC essentially do not change the shape of the bands near the Fermi level, thus 2D T-Ge and T-Sn are still node line semimetals with four electron pockets on the \( \Gamma - S \) directions and four hole pockets on the \( \Gamma - X \) directions.

It has been reported that except topological edge states, the \( \mathbb{Z}_2 \) topological invariant is also used to identify the topological properties for 2D node line semimetal [31, 32, 35]. In the following, we identify the topological properties of 2D T-Ge and T-Sn by calculating the \( \mathbb{Z}_2 \) topological invariant and topological edge states. Here we study the \( \mathbb{Z}_2 \) topological invariant and topological edge states by using the WannierTools package. Using the DFT bands as the input, we construct the MLWFs via the HSE06 method. As depicted in figures 6(a) and (d), the
DFT and MLWFs fitted band structure of 2D T-Ge and T-Sn are in very good agreement with each other. We first calculate the $Z_2$ topological invariant of 2D T-Ge and T-Sn by directly tracking the evolution of the Wannier charge centers (WCCs). The evolution of WCCs along $k_x$ for 2D T-Ge and T-Sn in figures 6(b) and 6(e) show that the evolution lines cross arbitrary reference line parallel to $k_x$ odd times, yielding $Z_2 = 1$, which identifies that 2D T-Ge and T-Sn are node line semimetals. In order to further identify the topological properties of 2D T-Ge and T-Sn, we calculate the edge states of semi-infinite 2D T-Ge and T-Sn with a boundary along $x$ axis via the iterative Green's function method as implemented in the WannierTools package. It can be seen from figures 6(c) and 6(f) that each edge has a single pair edge states in the bulk band gap of 2D T-Ge and T-Sn and a pair edge states linearly cross at the X point, which further prove the nontrivial properties of 2D T-Ge and T-Sn.

Finally, we investigate the effect of external biaxial strain on the electronic properties and topological properties of 2D T-Ge and T-Sn. The applied biaxial strain is defined as $\varepsilon = (a - a_0)/a_0$, where $a$ and $a_0$ are the lattice constant of strained and unstrained systems. The positive and negative values of $\varepsilon$ refer to the tensile and compressive strains. In this work, the applied external biaxial strains are within the range of $\pm$3%. Under each strain, all atoms are fully relaxed with fixed lattice constrain. As depicted in figure 7, the calculated phonon dispersions indicate that 2D T-Ge and T-Sn are dynamically stable when tensile and compressive strains reach up to 3% and $-3\%$ respectively. Figure 8 depicts the band structure of 2D T-Ge and T-Sn without and with SOC under $-3\%$ and $3\%$ strains. In the absence of SOC, nodal points along the high-symmetric $\Gamma$ and $\Gamma-X$ directions and the nodal loop around the $\Gamma$ point are robust with the strains in the range of $-3\%$ to $3\%$, as
depicted in figures 8(a) and (c), while the biaxial strains just tune the shape and position of nodal loops. Remarkably, figures 8(b) and (d) show that the SOC opens small gaps along the nodal loop in 2D T-Ge and T-Sn under the biaxial strains in the range of $-3\%$ to $3\%$, which are similar to that of 2D compounds $X_2Y$ ($X = \text{Ca, Sr}$).
and Ba; Y = As, Sb and Bi [35]. Furthermore, the calculated \(Z_2\) topological invariant and topological edge states unambiguously identify that under strains in the range of \(-3\% to 3\%\), both 2D T-Ge and T-Sn remain node line semimetal states in the absence and in the present of SOC. The robustness of topological properties against biaxial strain of 2D T-Ge and T-Sn imply their experimental realization and potential application in spintronics.

4. Conclusion

In conclusion, using first-principles calculations, we predict a new 2D tetragonal allotrope of Ge and Sn, which consists of repeated square and octagon rings. The calculated cohesive energy, \textit{ab initio} MD simulations and phonon dispersions indicate that 2D T-Ge and T-Sn are stable at room temperature and have potential to be synthesized in the future. In the absence of SOC, both 2D T-Ge and T-Sn are node line semimetals, where all crossing points of the valence and conduction bands in 2D T-Ge and T-Sn form a nodal loop around the \(\Gamma\) point, and the nodal loops around the \(\Gamma\) point are preserved with the strains in the range of \(-3\% to 3\%\). The nodal loop in 2D T-Ge and T-Sn are protected by the combination of \(P\) and \(T\) symmetries rather than the mirror reflections symmetry. When SOC is included, 2D T-Ge and T-Sn are still topological node line semimetals, which is identified by nontrivial \(Z_2\) invariant and topological edge states. Furthermore, the node line semimetal states of 2D T-Ge and T-Sn are robust with the biaxial strains in the range of \(-3\% to 3\%\). Our findings provide a new 2D material platform for realization of 2D topological node line semimetal and innovative applications of topological node line semimetals.

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References

[1] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183
[2] Han M Y, Ozsílma B, Zhang Y and Kim P 2007 Phys. Rev. Lett. 98 206805
[3] Nair R R, Blake P, Grigorenko A N, Novoselov K S, Booth T J, Stauber T, Peres N M R and Geim A K 2008 Science 320 1308
[4] Wang F et al 2018 Chem. Soc. Rev. 47 6296–341
[5] Wang Z, Jingjing Q, Wang X, Zhang Z, Chen Y, Huang X and Huang W 2018 Chem. Soc. Rev. 47 6128–74
[6] Xu R, Zou X, Liu B and Cheng H-M 2018 Mater. Today 21 391–418
[7] Liu C-G, Feng W and Yao Y 2011 Phys. Rev. Lett. 107 076802
[8] Xu Y, Yan B, Zhang H-J, Wang J, Xu G, Tang P, Duan W and Zhang S-C 2013 Phys. Rev. Lett. 111 136804
[9] Schultz P A, Leung K and Stachel E B 1999 Phys. Rev. B 59 733–41
[10] Umemoto K, Wentzcockt R M, Saito S and Miyake T 2011 Phys. Rev. Lett. 106 125504
[11] Zhou X-F, Qian G-R, Dong X, Zhang L, Tian Y and Wang H-T 2010 Phys. Rev. B 82 134126
[12] Liu Y, Wang G, Huang Q, Guo L and Chen X 2012 Phys. Rev. Lett. 108 225305
[13] Liu Y, Wang G, Huang Q, Guo L and Chen X 2013 Phys. Rev. Lett. 110 026404
[14] Huang H, Li Y, Liu Z, Wu J and Duan W 2013 Phys. Rev. Lett. 110 026903
[15] Wu H, Qian Y, Du Z, Zhu R, Kan E and Deng K 2017 Phys. Lett. A 381 3754–9
[16] van der Zande A M et al 2013 Nat. Mater. 12 554–61
[17] Zhu L and Zhang T 2015 J. Nanopart. Res. 17 220
[18] Ma Y, Kou L, Li X, Dai Y, Smith S C and Heine T 2015 Phys. Rev. B 92 085427
[19] Nie S M, Song Z, Weng H and Fang Z 2015 Phys. Rev. B 91 235434
[20] Sun Y, Felsert C and Yan B 2015 Phys. Rev. B 92 165421
[21] Li W, Guo M, Zhang G and Zhang Y-W 2014 Phys. Rev. B 89 205402
[22] Zhang S et al 2018 Chem. Soc. Rev. 47 982–1021
[23] Ersan F, Aktürk E and Ciraci S 2016 Phys. Rev. B 94 245417
[24] Zhang Y, Lee J, Wang W-L and Yao D-X 2015 Comput. Mater. Sci. 110 109–14
[25] Li Pand Luo W 2016 Sci. Rep. 6 25423
[26] Kou L Z, Tan X, Ma Y D, Tahini H, Zhou L, Sun Z Q, Aijun D, Chen C F and Smith S C 2015 2D Mater. 2045010
[27] Armitage N P, Mele E J and Vishwanath A 2018 Rev. Mod. Phys. 90 015001
[28] Burkov A A 2016 Nat. Mater. 15 1145

8
[29] Chiu C-K, Teo J C Y, Schnyder A P and Ryu S 2016 Rev. Mod. Phys. 88 035005
[30] Young S M and Kane C L 2015 Phys. Rev. Lett. 115 126803
[31] Jin-Lian L, Wei L, Xue-Yang L, Chong-Qi Y, Jue-Xian C, Xin-Gao G and Hong-Jun X 2017 Chin. Phys. Lett. 34 057302
[32] Yang B, Zhang X and Zhao M 2017 Nanoscale 9 8740–6
[33] Jin Y, Wang R, Zhao J-Z, Du Y-P, Zheng C-D, Gan L-Y, Liu J-F, Xu H and Tong S Y 2017 Nanoscale 9 13112–8
[34] Zhou P, Ma Z S and Sun L Z 2018 J. Mater. Chem. C 6 1206–14
[35] Niu C, Buhl P M, Bihlmayer G, Wortmann D, Dai Y, Blügel S and Mokrousov Y 2017 Phys. Rev. B 95 235138
[36] Gupta S, Kutana A and Yakobson B I 2018 J. Phys. Chem. Lett. 9 2757–62
[37] Zhang R-W, Liu C-C, Ma D-S and Yao Y 2018 Phys. Rev. B 97 125312
[38] Feng B et al 2017 Nat. Commun. 8 1007
[39] Guo L et al 2018 Adv. Mater. 30 1707055
[40] Gao L et al 2018 Adv. Mater. 30 1707055
[41] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–86
[42] Kresse G and Hafner J 1993 Phys. Rev. B 47 558–61
[43] Kresse G and Hafner J 1994 Phys. Rev. B 49 14251–69
[44] Blöchl P E 1994 Phys. Rev. B 50 17953–79
[45] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865–8
[46] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207–15
[47] Allè D 2009 Comput. Phys. Commun. 180 2622–33
[48] Mostofi A A, Yates J R, Lee Y-S, Souza I, Vanderbilt D and Marzari N 2008 Comput. Phys. Commun. 178 685–99
[49] Nicola M and David V 1997 Phys. Rev. B 56 12847–65
[50] Wu Q, Zhang S, Song H-F, Troyer M and Soluyanov A A 2018 Comput. Phys. Commun. 224 405–16
[51] Matusalem F, Marques M, Teles I K and Bechstedt F 2015 Phys. Rev. B 92 045436
[52] Dávila M E, Xian L, Cahangirov S, Rubio A and Le Lay G 2014 New J. Phys. 16 095002
[53] Zhu F, Chen W-J, Xu Y, Gao C-L, Guan D-D, Liu C-H, Qian D, Zhang S-C and Jia J-F 2015 Nat. Mater. 14 1020
[54] Kim Y, Wieder B J, Kane C L and Rappe A M 2015 Phys. Rev. Lett. 115 036806
[55] Zhang X, Yu Z-M, Sheng X-L, Yang H Y and Yang S A 2017 Phys. Rev. B 95 235116
[56] Li R, Ma H, Cheng X, Wang S, Li D, Zhang Z, Li Y and Chen X-Q 2016 Phys. Rev. Lett. 117 096401
[57] Feng X, Yue C, Song Z, Wu Q and Wen B 2018 Phys. Rev. Mater. 2 014202
[58] Li S, Liu Y, Fu B, Yu Z-M, Yang S A and Yao Y 2018 Phys. Rev. B 97 245148
[59] Zhang R-W, Liu C-C, Ma D-S, Wang M and Yao Y 2018 Phys. Rev. B 98 035144
[60] Zhang X, Yu Z-M, Zuo Z, Wu W, Wang S, Sheng X-L and Yang S A 2018 Phys. Rev. B 97 235150