Coexistence of giant Rashba spin splitting and quantum spin Hall effect in H–Pb–F

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Rashba spin splitting (RSS) and quantum spin Hall effect (QSHE) have attracted enormous interest due to their great significance in the application of spintronics. In this work, we theoretically proposed a new two-dimensional (2D) material H–Pb–F with coexistence of giant RSS and quantum spin Hall effec by using the *ab initio* calculations. Our results show that H–Pb–F possesses giant RSS (1.21 eV·Å) and the RSS can be tuned up to 4.16 eV·Å by in-plane biaxial strain, which is a huge value among 2D materials. Furthermore, we also noticed that H–Pb–F is a 2D topological insulator (TI) duo to the strong spin–orbit coupling (SOC) interaction, and the large topological gap is up to 1.35 eV, which is large enough for for the observation of topological edge states at room temperature. The coexistence of giant RSS and quantum spin Hall effect greatly broadens the potential application of H–Pb–F in the field of spintronic devices.

Keywords: coexistence, Rashba spin splitting, quantum spin Hall effect, spin–orbit coupling

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1. Introduction

Due to the rise of spintronics, SOC has attracted great attention.[1] SOC is the interaction between the spin of an electron and its motion in an electric field, which establishes a relationship between orbital motion and spin degrees of freedom.[2,3] SOC provides the possibility to control the spin of electrons, which makes the system produce new excellent properties, such as spin ballistic transport, current-induced spin polarization, spin galvanic effect,[4–6] and so on. Among them, the most attractive properties are RSS and 2D QSHE.[7] For RSS, one of the most important prerequisites for its realization is the breaking of the system space inversion symmetry and it has very important potential application value for spin field effect transistor (FET) without external magnetic field.[8] In recent years, a large number of materials with RSS phenomenon have been found experimentally and theoretically. Such as MoS_2/Bi_2Te_3 heterojunction (0.27 eV·Å–2.5 eV·Å),[9] semihydrogenated graphene and topological insulator heterojunction (0 eV·Å–0.783 eV·Å),[10] MoS_2/Bi (1.097 eV·Å),[11] Janus bilayer transition metal dichalcogenides (0 eV·Å–0.38 eV·Å), O-PTl (1.736 eV·Å),[12] and Pb coverd Bi_2Se_3 (1.98 eV·Å)[13] are predicted theoretically. However, these theoretically predicted structures are difficult to realize experimentally. Moreover, Au/W (110) quantum wells (0.16 eV·Å),[14] InGaAs/GaAs quantum dots (0.08 eV·Å–0.12 eV·Å),[15] Au (0.33 eV·Å),[16] and so on are realized experimentally. However, these splitting values are too small that it is difficult to be applied in spintronic devices. Therefore, it is still of great significance to explore materials with giant RSS.

The 2D QSHE has potential applications in topological spintronic devices because of its one-dimensional edge state protected by time inversion symmetry. At present, a large number of 2D TI have been found experimentally and theoretically, such as hexagonal lattice materials,[17,18] III–V bilayers,[19–21] HgX (X = Te, Se),[22] $ZrTe_5$/$HfTe_5$,[23] triangle lattice systems of Au/GaAs(111) surface and mxenes,[24,25] and transition metal halide.[26] However, only a few materials have been proved to have 2D topological edge states by experiments, such as InAs/GaSb[27] and HgTe/CdTe[28] quantum wells, Bi coverd Bi_2Te_3.[29] And the band gap of these 2D topological materials is usually small, so that the observation temperature required for the experiment is extremely low (10 K), which greatly limits the experimental research and potential application of these materials. Thus it is still a challenge to find 2D topological insulators with large band gaps. In recent years, some studies have shown that RSS can coexist with QSHE in the same material. However, the RSS or topological band gap are very small, which greatly limits its potential application. Therefore, can we design a 2d structure with broken spatial inversion symmetry, so that RSS and QSHE can coexist perfectly in this structure?

According to previous studies, we find that the electronic properties of 2D materials can be greatly changed by adsorbing X (X = H, F, Cl, Br)[30,31] atoms. Recently, 2D plumbene has been successfully prepared experimentally[32] and it is

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proved to be a normal insulator,[30,33] but it has strong SOC that it would be easy to induce topological phase transition. Hence, in this paper, on the basis of first-principles calculations, we theoretically propose a 2D material H–Pb–F with spatial inversion symmetry breaking. Based on our calculation results, we note that the material has a giant RSS coefficient (1.21 eV·Å) near the Fermi surface, and the splitting can be further increased to 4.16 eV·Å under biaxial stress (−12%). In addition, by calculating the topological invariants and topological edge states near the Fermi surface, we also find that the material is a 2D topological insulator with a huge topological band gap (1.23 eV). The coexistence of giant RSS and huge topological band gap would greatly expand the applications of the material in spintronic devices.

2. Computational details

All calculations are performed with the density functional theory (DFT) by using the plane wave basis, as implemented in the Vienna *ab initio* simulation package (VASP)[34,35] package, with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation for the exchange–correlation potential.[36,37] The Brillouin zone integration was sampled by a $9 \times 9 \times 1$ k-grid mesh, and the plane-wave energy cutoff is 400 eV. The vacuum layer is set to 20 Å to avoid interaction between adjacent cells. For structural optimization, the crystal structures were fully relaxed until the residual force is less than 0.01 eV/Å, and the convergence threshold for energy is 1×10^{-6} eV. The calculations are implemented in the presence of SOC. The topological edge states, invariants, and phonon dispersion of materials are calculated by using wannier90,[38] Wannier tools,[39] and PHONOPY,[40] respectively.

3. Results and discussion

Figures 1(a)–1(c) show the crystal structure of 2D layered material H–Pb–F, with one H atom and one F atom are adsorbed on both sides of the plumbene respectively. The space group of H–Pb–F is P3M1(156), and the lattice constants are 5.345 Å and $c = 25$ Å. The bond lengths between F–Pb, Pb–Pb, and H–Pb are 2.215 Å, 3.123Å, and 1.9Å, respectively. The bond angles of F–Pb–Pb and H–Pb–Pb are 99.2°, and the position of H, Pb(H), Pb(F), and F are (0.333, 0.667, 0.614), (0.333, 0.667, 0.538), (0, 0, 0.518) and (0, 0, 0.433). The buckling height of Pb–Pb in the z-axis direction is about 0.49 Å. In addition, in order to verify the stability of H–Pb–F crystal structure, we calculated the phonon spectrum of the material by utilizing PHONOPY, as shown in Fig. 1(d). It can be seen from the phonon spectrum that the acoustic and optical branches are well separated, and the absence of any imaginary frequency, which strongly proves that the 2D H–Pb–F crystal is dynamically stable.

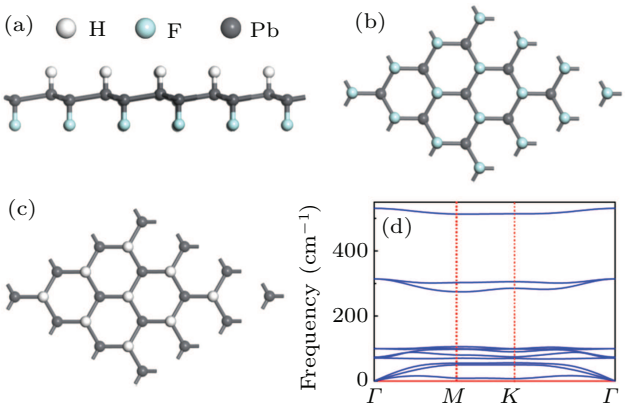


Fig. 1. (a)–(c) Side, bottom, and top view of the crystal structure of H–Pb–F nanosheet. (d) Phonon dispersion of 2D H–Pb–F along the high symmetry points in Brillouin zone.

Next, we studied the effect of SOC on the electronic properties of H–Pb–F. The band structure without SOC is shown in Fig. 2(a), it can be seen that the energy band of the system is closed at the Fermi surface, showing semimetallic properties. As the interaction of SOC included (Fig. 2(b)), the system opens a band gap of about 0.96 eV near the Fermi surface. In order to avoid the underestimation of the electronic band gap by PBE method, we further consider the hybrid functional HSE06 and find that the band structures without and with SOC (Figs. 2(c) and 2(d)) are similar with that of PBE and band gap of HSE+SOC is expanded to 1.23 eV. In addition, we can also see that when the SOC interaction is taken into account, the electron energy band near the Fermi surface appears obvious splitting phenomenon. Since the intrinsic system is a strong SOC material with broken spatial inversion symmetry, we further calculated the work function of the system and found that there is an obvious electrostatic potential difference ($\Delta\Phi = 2.29$ eV) between the upper and lower surfaces of the system. $\Delta\Phi > 0$ means that there is an intrinsic electric field along the Z axis in the crystal structure H–Pb–F. This effective electric field and broken spatial inversion symmetry result in strong RSS in H–Pb–F. Furthermore, we calculate the RSS coefficient of the system by using formula $\alpha_R \sim 2\Delta E_R/\Delta k_R$, where ΔE_R and Δk_R are the energy and momentum offsets, respectively, and the Rashba parameter is 1.21 eV·Å.

In order to explore the relationship between the intrinsic electric field inside the H–Pb–F crystal structure and Rashba splitting degree, we further studied the strain effects on the the work function and RSS of H–Pb–F under biaxial stresses. It is found that the work function of H–Pb–F decreased significantly with the increase of biaxial stress (−12% to 18%) as shown in Fig. 3(a), which indicates that the increase of biaxial stress significantly weakened the intrinsic electric field in the H–Pb–F crystal structure. In addition, we also noticed that the H–Pb–F possesses giant RSS coefficient (1.21 eV·Å) without any stress, and the degree of RSS decreased significantly with the increase of biaxial stress (−12% to 18%) as shown

in Fig. 3(b). Previous studies have shown that the magnitude of this effective electric field is positively correlated with the degree of RSS,[41] and thus our calculation results are very consistent with the previous research reports. Notably, under the biaxial stress of −12%, the RSS coefficient reaches 4.16 eV·Å, which is a huge value among 2D materials, and it has great application potential in spintronic devices without external magnetic field.

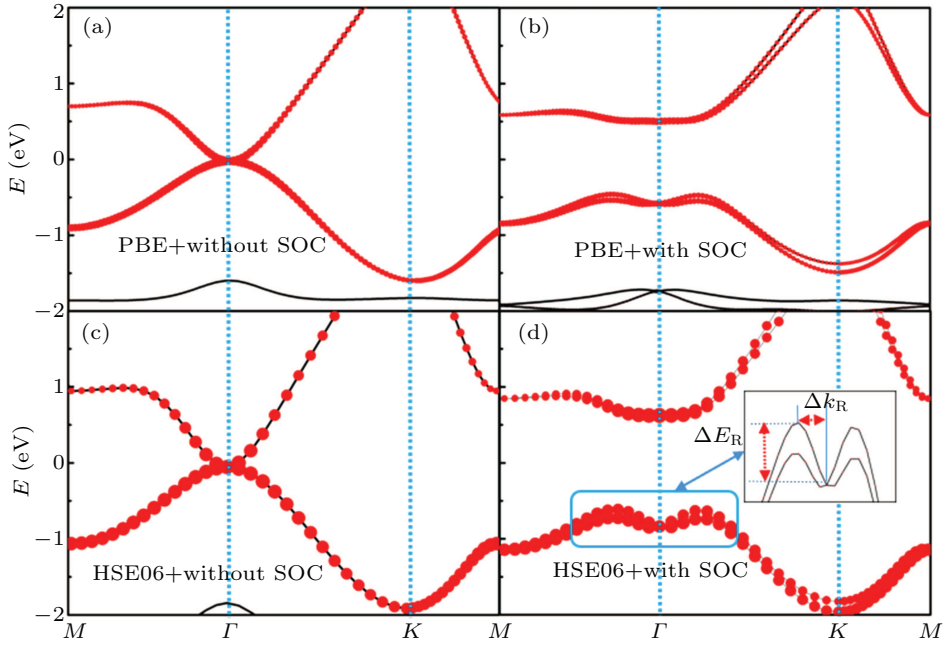


Fig. 2. (a)–(d) Band structures without and with SOC of 2D H–Pb–F from PBE and HSE06, where the red dot represents the $p_{x,y}$ orbital contribution of Pb atoms.

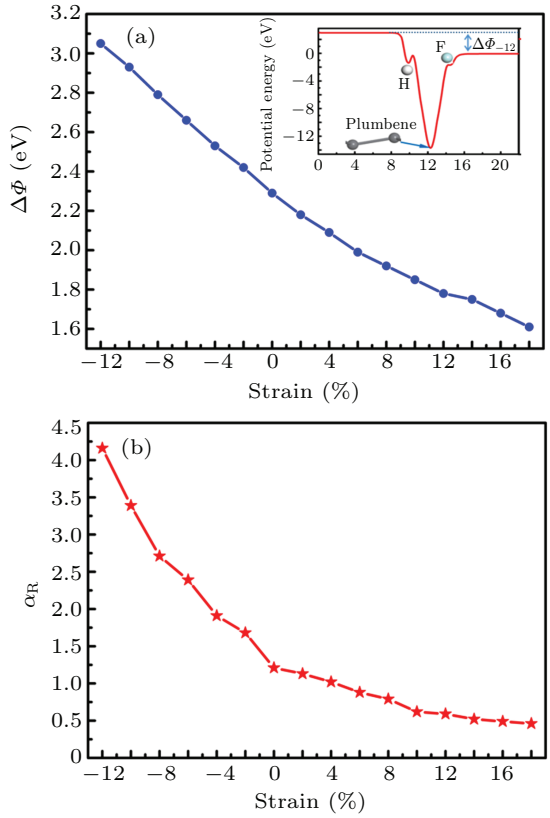


Fig. 3. The variations of electrostatic potential difference $\Delta\Phi$ (a) and RSS α_R (b) of H–Pb–F with the biaxial stress of −12% to 18%. The inset in panel (a) shows the work functions of H–Pb–F under −12% biaxial stress.

By analyzing the contribution of atomic orbitals to electronic properties, we find that the energy band near the Fermi surface is mainly contributed by the p_{xy} orbitals of Pb atoms, Figs. 2(a)–2(d), and the s-orbital lies below the p_{xy} orbital and the contribution of p_z orbital is far away from the Fermi surface. Therefore, we systematically demonstrated the energy band evolution of H–Pb–F at G point, Fig. 4(a). One can see that p_{xy} orbitals split into the bonding (p_{xy}^+) and anti-bonding (p_{xy}^-) states duo to the chemical bonding and crystal field splitting between Pb–Pb atoms, where the superscripts + and − represent the bonding and anti-bonding states, respectively. Moreover, when SOC is inculded, the p_{xy}^+ orbit is further split into $|\Phi_1^+\rangle$ and $|\Phi_2^+\rangle$ near the Fermi surface resulting in the band gap opening.

Noticeably, there was no band inversion during the band evolution, because the lattice constant of H–Pb–F (5.34 Å) was so large that the hybridization of s and p_{xy} orbitals of Pb atoms was too weak, making s orbitals always below p_{xy} orbitals. It is worth noting that the H and F atoms adsorbed on the upper and lower surfaces of plumbene act as an orbital filter, selectively removing the p_z orbitals from the plumbene, so that the system maintains a nontrivial six band lattice with $Z_2 = 1$. In fact, SOC only plays the role of opening the Fermi band gap, and has nothing to do with the formation of nontrivial band orders. It has been mentioned more than once in previous studies, such as the well-known 2D TI graphene and silicene.[42–44] QSH phase in H–Pb–F is attributed to the s–p

band inversion, which is similar to the results of Bi_2Se_3.[45] and HgTe/CdTe quantum wells.[28] Another important feature of 2D is that it has a topologically protected gapless edge state. And thus we calculated the energy band structure of H–Pb–F nanoribbons by using the Green's function method, and the tight binding parameters used in this method are from VASP and wannier90, as shown in Fig. 4(b). One can clearly see that the edge states appear in the bulk band gap and cross linearly at G point, which means that H–Pb–F is a 2D TI with a large topological nontrivial band gap.

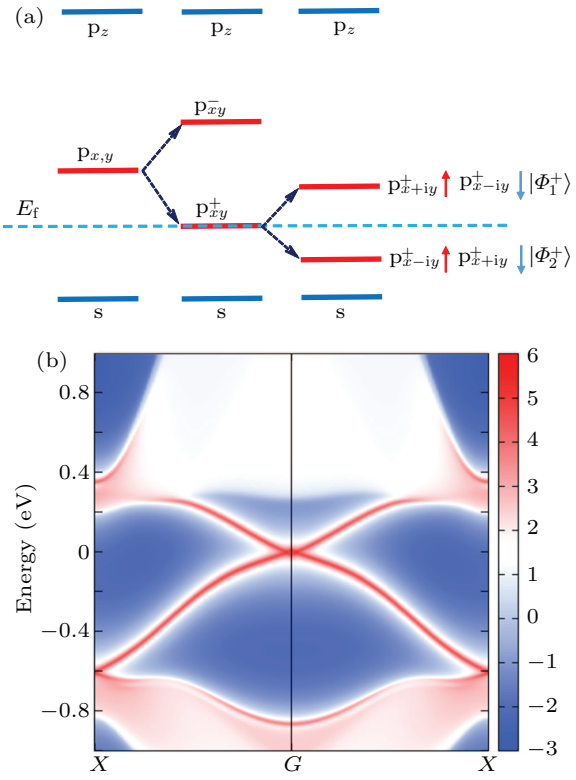


Fig. 4. (a) Schematic diagram of the evolution of energy bands at G for H–Pb–F. (b) Edge states of H–Pb–F on the zigzag edges.

For the experimental realization of 2D TI, there are two main problems: the destruction of the topological band gap by biaxial stress and substrate effect. Therefore, it is still of great significance to find a 2D TI with large topological band gap that is not damaged by stress and substrate effect. And thus we continue to explore the topological band gap changes of H–Pb–F under different biaxial stresses and the influence of substrate effect on its topological band gap, as shown in Figs. 5(a) and 5(b). Firstly, it can be clearly seen that biaxial strain can effectively modulate the non-trivial band gap, with a large band gap of 1.025 eV obtained by using the PBE generalized gradient approximation and 1.35 eV obtained by using the HSE06 functional approximation at -8% compression strain. Consequently, H–Pb–F has a huge nontrivial topological band gap, which is much larger than other 2D materials with large band gap. The opening of this huge gap is mainly caused by the strong SOC related to the p_{xy} orbitals of Pb atoms at the G point, and SOC only plays the role of opening the Fermi band gap, and has nothing to do with the formation of nontrivial band orders, and the topological characteristic of H–Pb–F monolayer is confirmed by the Z_2 topological order due to s–p_{xy} band inversion. In comparison with the pristine plumbene, the lattice constant of H–Pb–F is slightly larger, and the vertical height difference of Pb atoms in Z direction is significantly reduced due to the weakly hybridization between π and σ orbitals, as listed in Table 1. The buckling between atoms has a great influence on the energy band of hexagonal lattice materials, and the similar cases have been reported in the study of halogenated germanene and stanene monolayers.[46–48]

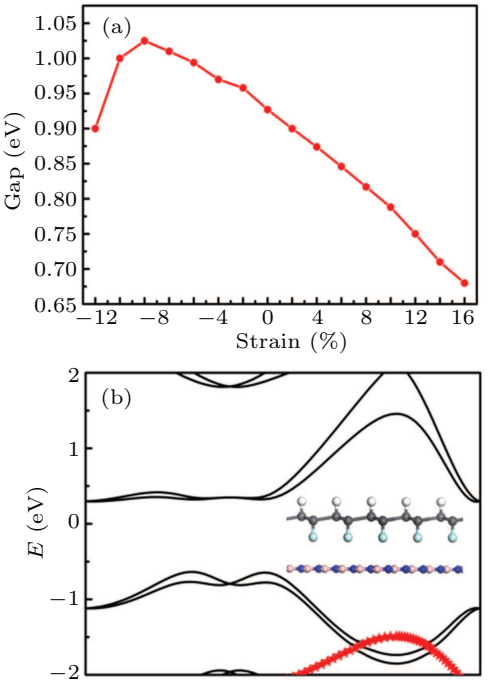


Fig. 5. (a) The bandgap of 2D H–Pb–F as a function of external biaxial strain (red stars). (b) PBE band structure of O-PTl(1 1 1)-(1 × 1)/BN(1 1 1)-(2 × 2), with the red stars-lines contributed by BN substrate.

Table 1. The present crystal parameters include the lattice constant a, the vertical height difference of Pb atoms in Z direction Δd, and topological invariant Z_2.

Monolayer	a (Å)	Δd (Å)	Z_2
Pb	4.923	0.929	0
H–Pb–F	5.345	0.494	1

In addition, we studied the effect of BN substrate on the topological band gap of H–Pb–F by using the H–Pb–F (111)-(1 × 1)/BN (111)-(2 × 2) system, and the H–Pb–F layer has a lattice mismatch of 2.06%. As shown in the band structure in Fig. 5(b), H–Pb–F still retains the properties of TI under the effect of SOC, and is not affected by the substrate BN. Our results show that the nontrivial topological band gap of H–Pb–F can be well preserved under both biaxial stress and substrate effects. Moreover, because H–Pb–F can well retain the nontrivial topological band gap under the stress of -12% to 18%, there are many kinds of substrate materials used for the syn-

thesis of this material, which is very helpful for the successful preparation of experiments.

4. Conclusion

In summary, we predicted a stable hexagonal lattice structure H–Pb–F based on the first principle calculation. According to our results, the composition of the band structure of H–Pb–F near the Fermi surface is mainly contributed by the p_{xy} orbitals of Pb atoms. Under the influence of SOC, H–Pb–F has a giant RSS coefficient as high as 4.16 eV·Å appears near the Fermi surface due to the lack of spatial inversion symmetry, and the splitting is tunable under the effect of biaxial stress, and it has great application potential in spintronic devices without external magnetic field. In addition, we also found that under the influence of SOC, a large topological nontrivial band gap of 1.35 eV was opened near the Fermi surface, and the nontrivial topologies were testified by calculating Z_2 topological invariants and topologically protected edge states, and thus it provides a good platform for observing QSHE at room temperature. Our comprehensive study revealed that the coexistence of giant RSS and quantum spin Hall effect in H–Pb–F can greatly expand the application range and enhances the potential application value of this material in spintronic devices.

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References

[1] Žutić I, Fabian J and Sarma S D 2004 *Rev. Mod. Phys.* **76** 323
[2] Bychkov Y A and Rashba E I 1984 *J. Exp. Theor. Phys. Lett.* **39** 78
[3] Dresselhaus G 1955 *Phys. Rev.* **100** 580
[4] Lu J P, Yau J B, Shukla S P and Shayegan M 1999 *Phys. Rev. Lett.* **81** 1282
[5] Kuhlen S, Schmalbuch K, Hagedorn M, Schlammes P, Patt M, Lepsa M, Guntherodt G and Beschoten B 2012 *Phys. Rev. Lett.* **109** 146603
[6] Strecker K E, Partridge G B, Truscott A G and Hulet R G 2002 *Nature* **417** 150
[7] Qi X L, Wu Y S and Zhang S C 2006 *Phys. Rev. B* **74** 085308
[8] Rezavand A and Ghobadi N 2021 *Physica E* **132** 114768
[9] Peng Q, Lei Y, Deng X, Deng J, Wu G, Li J, He C Y and Zhong J X 2022 *Physica E* **135** 114944
[10] Xue W M, Li J, Peng X Y, He C Y, Ouyang T, Zhang C X, Tang C, Li Z Q, Liu H T and Zhong J X 2019 *J. Phys.: Condens. Matter* **31** 365002
[11] Lee K, Yun W S and Lee J D 2015 *Phys. Rev. B* **91** 125420
[12] Xue W M, Li J, Peng X Y, He C Y, Ouyang T, Zhang C X, Tang C, Li Z Q, Lu D L and Zhong J X 2020 *J. Phys. D: Appl. Phys.* **53** 025302
[13] Yang H, Peng X Y, Wei X L, Liu W L, Zhu W, Xiao D, Stocks G M and Zhong J X 2012 *Phys. Rev. B* **86** 155317
[14] Varykhalov A, Sanchez-Barriga J, Shikin A M, Gudat W, Eberhardt W and Rader O 2008 *Phys. Rev. Lett.* **101** 256601
[15] Huang S M, Badrutdinov A O, Serra L, Kodera T, Nakaoka T, Kumagai N, Arakawa Y, Tayurskii D A, Kono K and Ono K 2011 *Phys. Rev. B* **84** 085325
[16] LaShell S, McDougall B A and Jensen E 1996 *Phys. Rev. Lett.* **77** 3419
[17] Zhang R W, Zhang C W, Ji W X, Li P, Wang P J, Li S S and Yan S S 2016 *Appl. Phys. Lett.* **109** 182109
[18] Ezawa M 2012 *New J. Phys.* **14** 033003
[19] Zhou P, Xue L and Sun L Z 2017 *J. Mater. Chem. C* **5** 4268
[20] Li X, Dai Y, Ma Y, Wei W, Yu L and Huang B 2015 *Nano Res.* **8** 2954
[21] Crisostomo C P, Yao L Z, Huang Z Q, Hsu C H, Chuang F C, Lin H, Albao M A and Bansil A 2015 *Nano Lett.* **15** 6568
[22] Li J, He C Y, Meng L J, Xiao H P, Tang C, Wei X L, Kim J, Kioussis N, Stocks G M and Zhong J X 2015 *Sci. Rep.* **5** 14115
[23] Weng H, Dai X and Fang Z 2014 *Phys. Rev. X* **4** 011002
[24] Si C, Jin K H, Zhou J, Sun Z and Liu F 2016 *Nano Lett.* **16** 6584
[25] Weng H, Ranjbar A, Liang Y, Song Z, Khazaei M, Yunoki S, Arai M, Kawazoe Y, Fang Z and Dai X 2015 *Phys. Rev. B* **92** 075436
[26] Zhou L, Kou L, Sun Y, Felser C, Hu F, Shan G, Smith S C, Yan B and Frauenheim T 2015 *Nano Lett.* **15** 7867
[27] Knez I, Du R R and Sullivan G 2012 *Phys. Rev. Lett.* **109** 186603
[28] König M, Wiedmann S, Brüne C, Roth A, Buhmann H, Molenkamp L W, Qi X L and Zhang S C 2007 *Science* **318** 766
[29] Miao L, Yao M Y, Ming W, Zhu F, Han C Q, Wang Z F, Guan D D, Gao C L, Liu C, Liu F, Qian D and Jia J F 2015 *Phys. Rev. B* **20** 91
[30] Zhao H, Zhang C W, Ji W X, Zhang R W, Li S S, Yan S S, Zhang B M, Li P and Wang P J 2016 *Sci. Rep.* **6** 20152
[31] Chen H, Yan P L, Li J, He C Y, Zhang C X, Tang C and Zhong J X 2020 *J. Appl. Phys.* **127** 084301
[32] Yuhara J, He B, Matsunami N, Nakatake M and Le Lay G 2019 *Adv. Mater.* **31** 1901017
[33] Huang Z Q, Hsu C H, Chuang F C, Liu Y T, Lin H, Su W S, Ozolins V and Bansil A 2014 *New J. Phys.* **16** 105018
[34] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
[35] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
[36] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[37] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
[38] Mostofi A A, Yates J R, Lee Y S, Souza I, Vanderbilt D and Marzari N 2008 *Comput. Phys. Commun.* **178** 685
[39] Wu Q, Zhang S, Song H F, Troyer M and Soluyanov A A 2018 *Comput. Phys. Commun.* **224** 405
[40] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **4063** 4066
[41] Zhu L Y, Zhang T T, Chen G B and Chen H B 2018 *Phys. Chem. Chem. Phys.* **20** 30133
[42] Kane C L and Mele E J 2005 *Phys. Rev. Lett.* **95** 226801
[43] Fu L, Kane C L and Mele E J 2007 *Phys. Rev. Lett.* **98** 106803
[44] Kane C L and Mele E J 2005 *Phys. Rev. Lett.* **95** 146802
[45] Zhang H, Liu C X, Qi X L, Dai X, Fang Z and Zhang S C 2009 *Nat. Phys.* **5** 438
[46] Si C, Liu J W, Xu Y, Wu J, Gu B L and Duan W H 2014 *Phys. Rev. B* **89** 115429
[47] Xu Y, Yan B H, Zhang H J, Wang J, Xu G, Zhang P Z, Duan W H and Zhang S C 2013 *Phys. Rev. Lett.* **111** 136804
[48] Hong L, Ge J, Shuang S and Liu D Q 2022 *Acta Phys. Sin.* **71** 016301 (in Chinese)