Topological phase transition in layered XIn$_2$P$_2$ ($X = \text{Ca, Sr}$)

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Abstract

Based on fully relativistic first-principles calculations, we studied the topological properties of layered XIn$_2$P$_2$ ($X = \text{Ca, Sr}$). Band inversion can be induced by strain without SOC, forming one nodal ring in the $k_z = 0$ plane, which is protected by the coexistence of time reversal and glide mirror symmetries. Including SOC, a substantial band gap is opened along the nodal line and the line-node semimetal would evolve into a topological insulator. These results reveal a category of materials showing quantum phase transition from trivial semiconductors and topologically nontrivial insulators by tuneable elastic strain engineering. Our investigations provide a new perspective about the formation of topological line-node semimetal under stain.

Keywords: first-principles calculations, topological insulator, line-node semimetal

(Some figures may appear in colour only in the online journal)

1. Introduction

Topological insulator (TI) [1, 2] is a new kind of material possessing gapped bulk states and exotic metallic surface states. The robust surface state in a 3D system, sheltered against backscattering from nonmagnetic impurities as long as the bulk gap remains open and the time-reversal symmetry is preserved [2–8]. The unique feature of the surface state has attracted enormous attention in theoretical calculations and experimental observations [3, 8], not only because of their theoretical importance but also because of their great potential applications [9–11]. Recently, the topological properties have been extended into a variety of three dimensional (3D) topological semimetal (TSM) systems [12–16]. In most Weyl/Dirac semimetals, conduction bands overlap with valence bands at certain momentum points. For instance, the topological properties of Na$_3$Bi [17, 18] and Cd$_2$As$_3$ [19, 20] semimetals have been experimentally confirmed. However, in line-node semimetals, the band crossing points around the Fermi level ($E_F$) form a closed loop. Many systems have been proposed as line-node semimetals including Mackay–Terrones crystal (MTC) [21], Bernal stacked graphene bilayer [22], antiperovskite Cu$_3$PdN [23] and so on. Such line-node band structure has been measured by the angle-resolved photoelectron spectroscopy (ARPES) in PbTaSe$_2$ [24] and ZrSiS [25]. Interestingly, in addition to these materials, researchers also found node line structures in the photonics crystals [26] and spin liquids [27]. Their intriguing properties characterizing topological nodal line semimetals include drumhead like nearly flat surface states [23], unique Landau energy levels [22], long-range Coulomb interactions [28], which open an important route to achieve high-temperature superconductivity [29–31].

The topological line-node semimetal could be driven into 3D TI or Dirac semimetal by the SOC and strain. For example, CaTe [32] is a TSM, possessing the nodal rings without SOC, exhibiting Dirac semimetal behavior when SOC is included. When it was applied by appropriate strain, it becomes a strong topological insulator [32, 33]. However, the CaAgX ($X = \text{P, As}$) can be driven into a TI phase from line-node semimetal by taking into account of SOC [34]. Bulk CaIn$_2$P$_2$ and SrIn$_2$P$_2$ are layered semiconductors with indirect-gap and direct-gap respectively. They have been investigated with their electronic and optical properties [35]. Up to now, their topological properties have not been studied. In this study, we find that the indirect-gap semiconductor can be changed into ‘direct’-gap
by applying uniaxial strain slightly. Further increasing strain, the compound undergoes a transition from trivial insulator to a line-node semimetal with a nodal ring in the $k_z = 0$ plane. When SOC is taken into account, the compounds become a nontrivial topological insulator with $Z_2$ index (1000). Our results provide a new perspective to understand the effect of strain and SOC on the formation of topological line-node semimetal and insulator.

2. Crystal structure and method

The ternary compound CaIn$_2$P$_2$ is isostructural with SrIn$_2$P$_2$ and crystallizes in a hexagonal structure with the space group P63/mmc [36]. The alkaline earth cations X (Ca or Sr) are located at a site with 3 m symmetry; In and P are located at sites with 3 m symmetry. The lattice constants of CaIn$_2$P$_2$ and SrIn$_2$P$_2$ are $a = b = 4.022$ Å, $c = 17.408$ Å, and $a = b = 4.094$ Å, $c = 17.812$ Å, respectively [24]. The corresponding unit cell of the XIn$_2$P$_2$ (X = Ca, Sr) compounds is depicted in figure 1(a). It contains two chemical formula units, the layers of X$^{2+}$ cations are separated by [In$_2$P$_2$$^{2-}$ layers. The atoms positioned at the following Wyckoff positions: X (Ca, Sr): 2a (0, 0, 1/2), In: 4f (2/3, 1/3, 0.329) and P: 4f (1/3, 2/3, 0.396). The bulk Brillouin zone (BZ) and projected surface Brillouin zones of (001) plane are illustrated in figure 1(b).

Firstly, we perform density functional calculations by using the WIEN2K package [37], with the modified Becke–Johnson exchange potential (mBJ) to get the accurate band gap [38]. The valence configurations of the Ca, Sr, P and In atoms are as Ca $3s^23p^64s^2$, Sr $4s^24p^65s^2$, P $3s^23p^3$ and In $4d^{10}5s^25p^1$, respectively. The plane-wave cutoff parameter $R_{MT}k_{max}$ is set to 7 and a $12 \times 12 \times 3$ K-mesh is used for the BZ integral. The SOC interaction is included by using the second-order variational procedure. The tight binding model based on maximally localized Wannier functions (MLWF) method [39, 40] has been constructed in order to investigate the surface states. The surface Green’s function of the semi-infinite system, whose imaginary part is the local density of states to obtain the dispersion of the surface states, can be calculated through an iterative method [41–43]. To confirm the compounds are dynamically stable, the phonon spectrum was calculated by using the PHONON code [44].

3. Results and discussion

The electronic band structures of the unstrained and 5% strained CaIn$_2$P$_2$ ($\alpha/\alpha_0 = 1.05$) with SOC are depicted in figures 2(a) and (b). The unstrained CaIn$_2$P$_2$ has an indirect band gap about 0.5 eV, which agrees with previous studies [35]. In figure 2(a), the $\Gamma^8$ band was pushed down, while the $\Gamma^8$ was pushed up, when we induced tensile stress in the $a$-$b$
are identical, yielding a + + + + − + + + . The irreducible representations of the $Z_2$ typical 3D topological insulator $S$-axis to $Z$ value of zero for all four inversion, the products of parities of inversion symmetry in our compounds. Before the band momenta $(1 \Gamma \ldots \Gamma)$ from knowledge about the parity of each pair of Kramer changes its sign while all other seven topological invariants $(v_0; v_1 v_2 v_3)$ were calculated in Kane [46], we calculate directly the SOC that induces the $\Gamma$ band-invertion [45]. From the inset in figure 2(b), we can see a band gap about 35 meV. It is well known that the inversion of bands with opposite parity is a strong indication of the formation of topologically nontrivial phases. This suggests that the strain induces a topological phase transition in $\text{CaIn}_2\text{P}_2$. Additionally, the stability of unstrained and 5% strained compound $\text{CaIn}_2\text{P}_2$ has been checked by computing the phonon dispersion, as illustrated in figure 3. Here, we did not find imaginary frequency neither in the strained nor in the 5% strained $\text{CaIn}_2\text{P}_2$.

To confirm the topological nature of $\text{CaIn}_2\text{P}_2$, all four $Z_2$ topological invariants $(v_0; v_1 v_2 v_3)$ [46] were calculated before (zero strained) and after (5% strained) the band inversion structures. Following the method developed by Fu and Kane [46], we calculate directly the $Z_2$ topological invariants from knowledge about the parity of each pair of Kramer’s degenerate occupied energy bands at the eight time-reversal momenta $(1 \Gamma, 3 \Gamma, 1 \Lambda, 3 \Lambda)$, because of the existence of inversion symmetry in our compounds. Before the band inversion, the products of parities $\delta_i$ are identical, yielding a value of zero for all four $Z_2$ topological invariants, i.e. a topologically trivial state (0;000). When the bands with $\Gamma^8$ and $\Gamma^8$ symmetries switch around $E_F$, see figures 2(a) and (b), $\delta_i$ changes its sign while all other seven $\delta_i$ remain unchanged. The parities of time-reversal momenta are listed in table 1. It gives rise to a topological state with $Z_2$ class (1;000) and confirms that the strain induces a topological phase transition.

Generally, the band inversion is generated by SOC, formatting the topologically nontrivial state, similar to the prototypical 3D topological insulator SrTe$_2$Pb and Bi$_2$Te$_2$ [6, 47]. However, in our study, the band inversion was induced by the strain only, without considering any SOC. Then, what role does the strain and SOC play in the topological phase transformation of $X\text{In}_2\text{P}_2$? In figure 4, we take SrIn$_2$P$_2$ as the example to answer the question. Figure 4 shows the orbital characteristic band structure (around the $\Gamma$ and near Fermi energy) of SrIn$_2$P$_2$ under the different strains. To quantify the effects of strain and SOC on the band inversion in SrIn$_2$P$_2$, we temporally switch off the SOC in figures 4(a) and (b). For the unstrained compound (figure 4(a)), there is a direct band gap about 0.3 eV, with the In-s state above the P-p state, indicating a trivial topological insulator. When we induce the strain with $a = 5\%a_0$ and without SOC, the In-s state was pushed down the P-p state, resulting a band inversion. The band inversion happens along the $M$–$\Gamma$–$K$ direction, resulting in the nodal ring from the crossing between the valence band and the conduction band in the $k_z = 0$ plane. The glide symmetry $G_z = M_z | (0,0,1/2)$ is the combination of mirror reflection symmetry $M_z: (x,y,z) \rightarrow (x,y,-z)$ and a translation by a half lattice vector $\tau_z = (0,0,1/2)$. Thus, the eigenvalue of $G_z$ is the product of the eigenvalue of $M_z$ and the phase factor induced by $\tau_z$. The irreducible representations of the little group of $k$ points in the $k_x$-$k_y$ plane are determined by the eigenvalue of $M_z$. As the Hamiltonian without SOC is spin-rotation invariant, i.e. $M_z^2 = 1$, the eigenvalue of $M_z$ is $+1$ or $-1$. According to this argument, the two bands with different representations will not induce a band gap when they cross each other. Therefore, the appearance of the nodal ring in the absence of SOC is protected by the glide mirror symmetry. Therefore, the strained SrIn$_2$P$_2$ formed a line-node band structure (figure 4(b)), which indicates that the band inversion is caused by the strain rather than the SOC. For the 5% strained compound, when we include SOC, there is a band gap about 35 meV exactly at the Fermi energy. Comparing the three figures in figure 4, we can draw the conclusion that lattice strain induces the band inversion while SOC opens the band gap.

To gain further insight into the mechanism of the strain induced band inversion, we study the electronic structure of unstrained SrIn$_2$P$_2$ around $E_F$ in more detail. Without SOC, the projected band structure of SrIn$_2$P$_2$ has been shown in figure 5(a). It shows that the valence bands $\Gamma_6$ and $\Gamma_4$ are dominated by the P-p states, while the conduction bands $\Gamma_2$ and $\Gamma_3$ are mainly composed of In-s state. Both the valence bands and conduct bands are doubly degenerated at the A-point, and they split up into $\Gamma^+ / \Gamma^−$ and $\Gamma^− / \Gamma^+$ -bands, respectively. As a result, the $\Gamma^+$ and $\Gamma^−$ bands give rise to the conduction band minimum and valence band maximum, respectively. The relative position of the $\Gamma^+$ and $\Gamma^−$ bands decides whether a band inversion occurs or not. We have determined the four parameters $\Delta E (A), \Delta E (\Gamma_4), \Delta E (\Gamma_2,3), \Delta E_2$ as functions of the uniaxial strain $(a - a_0)/a_0$ (volume is fixed). In the unit cell, there are two In-P-In-P slabs in XIn$_2$P$_2$. The ‘inter-slab interactions’ come from the van der Waals forces between the two slabs. The ‘intra-slab interactions’ refers to the covalent bonds between atoms in one slab. The energy difference $\Delta E (A)$ is determined by the intra-slab covalent s-p$_z$ hybridization, while

Table 1. The parities of time-reversal invariant $k$ points with SOC and their corresponding topological invariant.

| $\Gamma$ | M | A | L | $Z_2$ |
|---------|---|---|---|------|
| SOC, strain = 0% | + | + | + | + | 0 |
| SOC, strain = 5% | - | + | + | + | 1 |

Figure 3. Phonon dispersion of 5% strained CaIn$_2$P$_2$. 
$\Delta E(\Gamma_{4,6})$ and $\Delta E(\Gamma_{2,3})$ are related to inter-slab van der Waals $p_z-p_z$ and $s-s$ interactions. This observation is in line with findings for layered transition metal dichalcogenide semiconductors, such as MoS$_2$ [48, 49].

The results are presented in figure 5(b). With increasing tensile strain in the $ab$-plane and compressive strain along the $c$-axis, the intra-slab interaction decreases, resulting in the increment of the energy split $\Delta E(\Gamma_{4,6})$. However, the inter-slab interaction increase with the $c$-axis decreasing, resulting in a strongly reduced $\Delta E(A)$, indicating strongly intra-slab covalent $s$-$p_z$ hybridization. The energy level $E_{\Gamma_4}$ (derived from P-$p_z$ orbit) increases with $c$-axis decreasing. So the band gap $E_g$ decreases with the strain increment, and the band gap closes at the critical point $\delta = 0.02$. With further increasing the strain, the band inversion takes place and the compound becomes a topological nontrivial line-node semimetal. SOC opens the band gap along the nodal ring and drives the compound into topological nontrivial insulator.
For the topological materials, the existence of the topological prevent surface states is an important character. So we calculate the (001) surface of SrIn$_2$P$_2$ by preforming the WANNIER_TOOLS package [50] in a tight-binding (TB) scheme based on the maximally localized Wannier functions (MLWFs) [39]. The surface state of SrIn$_2$P$_2$ (001) surface without and with SOC have been shown in figures 6(a) and (b), respectively. When SOC is ignored, the system is a line-node semimetal, with the bulk bands touched along $\bar{K} - \Gamma$, $\bar{\Gamma} - M$ lines and a surface state lining two touching points. This is similar to CaAgAs [34], protected by the coexistence of time-reversal and glide mirror symmetry. When SOC is included, a gap opened at the two touching points, and the compound became an topological nontrivial insulator, with two surfaces states connecting bulk valance and conduction bands (see figure 6(b)), coinciding with the previous calculated $Z_2$ (table 1).

4. Conclusion

In conclusion, by the first-principles calculations, we find the quantum phase transition in XIn$_2$P$_2$ from conventional semiconductor into the line node semimetal by strain engineering only without SOC. While SOC takes the role as opening band gap along the line node and gives rise to the nontrivial topological insulator state.

Acknowledgments

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References

[1] Moore J 2009 Nat. Phys. 5 378
[2] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045
[3] Qi X L and Zhang S C 2011 Rev. Mod. Phys. 83 1057
[4] Bernevig B A, Hughes T L and Zhang S-C 2006 Science 314 1757
[5] Kane C L and Mele E J 2005 Phys. Rev. Lett. 95 226801
[6] Zang H, Liu C-X, Qi X-L, Dai X, Fang Z and Zhang S-C 2009 Nat. Phys. 5 438
[7] König M et al 2007 Science 318 766
[8] Qi X-L and Zhang S-C 2010 Phys. Today 63 33
[9] Fu L and Kane C L 2008 Phys. Rev. Lett. 100 096407
[10] Qi X L, Hughes T L and Zhang S C 2008 Phys. Rev. B 78 195424
[11] Qi X-L, Li R, Zhang J and Zhang S-C 2009 Science 323 1184
[12] Essin A M, Moore J E and Vanderbilt D 2009 Phys. Rev. Lett. 102 146805
[13] Z Wang et al 2015 Phys. Rev. B 92 024512
[14] Yang K-Y, Lu Y-M and Ran Y 2011 Phys. Rev. B 84 045302
[15] Liu Z K and Soluyanov A A 2016 Phys. Rev. B 93 035138
[16] Lu L, Fu L, Joannopoulos J D and Soljai M 2013 Phys. Rev. B 88 125427
[17] Gao Z, Hua M, Zhang H and Zhang X 2016 Phys. Rev. B 93 035138