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<td>Citation</td>
<td>Li, C., Zhao, Y. F., Chi, B. Q., Gong, Y. Y., &amp; Sun, C. Q. (2014). The effects of chemical bonding on the topological property of half-Heusler compounds: First principle calculation. Computational Condensed Matter, 1, 8-13. doi:10.1016/j.cocom.2014.08.002</td>
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<td>Date</td>
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<td><a href="http://hdl.handle.net/10220/49514">http://hdl.handle.net/10220/49514</a></td>
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Regular article

The effects of chemical bonding on the topological property of half-Heusler compounds: First principle calculation

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A R T I C L E  I N F O

Article history:
Received 2 July 2014
Received in revised form
1 August 2014
Accepted 18 August 2014
Available online 8 November 2014

Keywords:
Half-Heusler compounds
Topological insulator
Electronic structure
First principle calculation

A B S T R A C T

The dependence of \((E_{T6} - E_{T8})\) on the lattice constants has been studied for four half-Heusler compounds. First principle simulation was carried out to calculate the electronic structure and the obtained results were compared among different compounds. It is found that the change of \((E_{T6} - E_{T8})\) with strain exhibits opposite trend for III-VIII-V half-Heusler compounds and II-VIII-VI half-Heusler compounds. Moreover, for III-V half-Heusler compounds the valent orbital are usually fixed and the conduct orbital move away from Fermi level, whereas for II-VIII-VI half-Heusler compounds the conduct orbital tend to be fixed and the valent orbital move away from Fermi level as the lattice constant is reduced. The different trends of the variation of electronic structures are caused by the different extra-nuclear electrons of IIA and IIIB group elements which change their chemical bonding.

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1. Introduction

Recent years, topological insulators (TIs) with novel surface states have attracted great attention both theoretically and experimentally [1–3]. Due to the strong spin-orbit coupling (SOC) and band inversion at Fermi level \(E_{F}\), TI has remarkable electronic properties and great potential for electronic, thermoelectric and optoelectronic [4–7], superconducting [8,9], and magnetic applications [10,11]. Up to now, HgTe [1,12,13], \(V_2\)\(V_1\) compounds [10,14,15], Heusler compounds (HCs) [16–19], thallium-based ternary chalcogenides [20–22] and organic materials [23–25] as the main candidates of TIs have been widely studied. Especially, HCs with three components have attractive numerous attention since they exhibit excellent superconducting and magnetic properties [26,27].

Several research groups have reported that MMX half-HCs with the space group F43m can be viewed as a \(M^{++}\) ion stuffing the zinc-blende \((M'X)^{P-}\) sublattice (see Fig. 1 in Ref. [14]), where \(M\) and \(M'\) are transition metal elements, \(X\) denotes main-group element. Chadov et al. have reported that \((E_{T6} - E_{T8})\) is inversely proportional to the lattice constant of III-VIII-V half-HCs in which \(M\), \(M'\) and \(X\) atoms lie in IIIB, VIIIIB and VA group, respectively [16], where \(E_{T6}\) and \(E_{T8}\) are the energies of the twofold degenerated \(\Gamma_6\) state and the fourfold degenerate \(\Gamma_8\) state at \(\Gamma\) point. In addition, Lin et al. have reported that \((E_{T6} - E_{T8})\) is inversely proportional to \((Z_{M'} + Z_X)\) for III-VIII-V half-HCs [28], where \(Z_{M'}\) and \(Z_X\) are the number of nuclear charge of \(M'\) and \(X\) elements, respectively, \(V\) is the unit-cell volume. Half-HCs with nearly zero \((E_{T6} - E_{T8})\) could be converted between TI and normal insulator (NI) by changing their lattice constants slightly, and thus have great potential application in circuit switches. However, Li et al. reported that \((E_{T6} - E_{T8})\) is inversely proportional to \(\sqrt{|\chi_M - \chi_X|}\) for II-VIII-VI half-HCs in which \(M\), \(M'\) and \(X\) atoms lie in IIA, VIIIB and VIA group, respectively, where \(\chi_M\) and \(\chi_X\) are the Pauling electronegativity, and \(\sqrt{|\chi_M - \chi_X|}\) means the degree of covalent bonding between \(M'\) and \(X\) atoms [17]. Based on the previous reports, the relationship between \((E_{T6} - E_{T8})\) and \(V\) for III-VIII-V half-HCs is converse to that for II-VIII-VI half-HCs, indicating that the nature of forming TI with half Heusler structure is ambiguous due to complex relations among each component in half-HCs. Between the two types of half-HCs, the most significant difference is the extra-nuclear electron configuration (\(s^2\) for IIA group’s atom in II-VIII-VI half-HCs, but \(d^{15}\) for IIIB group’s atom in III-VIII-V half-HCs). To understand the nature of chemical bonding of these two types of half-HCs, the effects of different extra-nuclear electrons on the chemical bonding need be analyzed, and the results are propitious to find more suitable TI candidates.

In this paper, the dependence of \((E_{T6} - E_{T8})\) on the lattice constants has been studied for two types of half-HCs, III-VIII-V half-HCs (YPdBi and YPtSb) and II-VIII-VI half-HCs (SrPtTe and BaPtTe), have
been calculated by first principle simulation. First principle simulation was carried out to calculate the electronic structures and the obtained results were compared among different compounds.

2. Computational method

All density functional theory calculations, including band structures, partial density of states (PDOS), orbital distributions of twofold degenerated states and fourfold degenerate states at Γ point are performed on the basis of the projector augmented wave [29] method implemented in the VASP 5.2 package [30]. The exchange-correlation functional the generalized gradient approximation (GGA) due to Perdew-Burke-Ernzerhof (PBE) has been used [31], including scalar-relativistic effects in addition to SOC. The kinetic energy cutoff of electron wave function is 500 eV, which is sufficiently large for the systems considered. The k-point sampling set 10 × 10 × 10 division of the reciprocal unit cell based on the Monkhorst-Pack scheme is found to be converged. The convergence tolerance of energy of 5.0 × 10−6 eV/atom, maximum force of 0.01 eV/Å, and maximum displacement of 5.0 × 10−4 Å are used. Moreover, six different strains have been considered: compressive strain with lattice constants \(a_{0.05} = a(1 - 0.5\%), a_{1\%} = a(1 - 1\%), a_{1.5\%} = a(1 - 1.5\%)\) and \(a_{2\%} = a(1 - 2\%)\), and tensile strain with lattice constants \(a_{0.05} = a(1 + 0.5\%)\) and \(a_{1\%} = a(1 + 1\%)\), respectively, where \(a\) denotes the equilibrium lattice constant.

3. Results and discussion

The equilibrium lattice constants of our results are listed in Table 1, which are similar to the previously reported simulation results [16,17], and the difference between equilibrium lattice constants is \(-1.57\%, -1.55\%, -0.19\%\) and \(-0.56\%\) for YPdBi, YPtSb, SrPtTe and BaPtTe, respectively. Moreover, the calculated results of \((E_{\text{Te}} - E_{\text{F}})\) with equilibrium lattice constant are also listed in Table 1. Comparing our and other’s results, the amounts of \((E_{\text{Te}} - E_{\text{F}})\) are similar recursively for each II-VIII-VI half-HC but different for each III-VIII-V half-HC due to the similar equilibrium lattice constant for each II-VIII-VI half-HC and different one for each III-VIII-V half-HC. While the amounts of \((E_{\text{Te}} - E_{\text{F}})\) are \(-0.01\) and \(0.22\) eV for YPdBi and YPtSb with 1.5% compressive strain, respectively (see Fig. 1), which are similar as other’s results in Table 1.

Fig. 1 shows the relationship between \((E_{\text{Te}} - E_{\text{F}})\) and lattice constant for four half-HCs. The positive values of \((E_{\text{Te}} - E_{\text{F}})\) denote NI, while negative values of \((E_{\text{Te}} - E_{\text{F}})\) indicate converse band orders compared with that of NI (see Fig. 2), which denote as TI. It is found that, similar to the previously reported results [16], \((E_{\text{Te}} - E_{\text{F}})\) is inversely proportional to the lattice constant for III-VIII-V half-HCs whereas proportional to the lattice constant of II-VIII-VI half-HCs. Moreover, III-VIII-V half-HCs transform TI to NI when the lattice constants is reduced by \(2\%\) for YPdBi and \(1\%\) for YPtSb, while II-VIII-VI half-HCs are always TIs as the strain varying from \(1\%\) to \(-2\%.\) In addition, the amount of variation of \((E_{\text{Te}} - E_{\text{F}})\) is similar for the same type of half-HCs, i.e. it increases about 0.6 eV for III-VIII-V half-HCs but reduces about 0.1 eV for II-VIII-VI half-HCs in strain range from \(1\%\) to \(-2\%.\) As mentioned above, the different or converse trends for these two types of half-HCs are caused only by different components which hold different extra-nuclear electrons: \(d^8\) for IIIB group element but \(s^2\) for IIA group element. There, the electronic structures of the two types of half-HCs need be compared in detail to analyze the nature of their chemical bonding.

Fig. 2 shows the calculated band structures of YPdBi and YPtSb with equilibrium lattice constant and 2% compressive strain, respectively. For YPdBi (see Fig. 2a) and YPtSb (see Fig. 2b) with equilibrium lattice constant, the gaps of them at Γ point are absent and the twofold degenerated \(\Gamma_6\) states (dotted line) lie below the fourfold degenerate \(\Gamma_8\) states (dashed line), which means TIs. On the other hand, when there are 2% compressive strain on YPdBi (see Fig. 2c) and YPtSb (see Fig. 2d), the twofold degenerated \(\Gamma_6\) states lying above the fourfold degenerate \(\Gamma_8\) states has an inverted band, which means NIs. Also, the band structures of SrPtTe and BaPtTe with equilibrium lattice constant and 2% compressive strain have been shown in Fig. 3. For SrPtTe (see Fig. 3a) and BaPtTe (see Fig. 3b) with equilibrium lattice constant and \(\Gamma_6\) states (dotted line) lie below the fourfold degenerate \(\Gamma_8\) states (dashed line), which means TIs. Thus, SrPtTe and BaPtTe with equilibrium lattice constant and 2% compressive strain are both TIs, and the corresponding \((E_{\text{Te}} - E_{\text{F}})\) are shown in Fig. 1.

Table 1

|         | \(a\) | \(a'\) | \(\left|a' - a\right|/a\) | \((E_{\text{Te}} - E_{\text{F}})\) | \((E_{\text{Te}} - E_{\text{F}})\) |
|---------|-------|-------|--------------------------|----------------|----------------|
| YPdBi   | 6.746 | 6.640 | -1.57%                   | -0.29          | -0.09          |
| YPtSb   | 6.626 | 6.533 | -1.55%                   | -0.09          | 0.15           |
| SrPtTe  | 6.921 | 6.908 | -0.19%                   | -0.22          | -0.25          |
| BaPtTe  | 7.193 | 7.153 | -0.56%                   | -0.13          | -0.07          |

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* Reference [17].
* Reference [16].

\(G_6\) and \(G_8\) denote TI.
of Pt-5d, Sr-4d and Te-5p electrons. For BaPtTe, the conduction band minimum consists of Pt-6s, Pt-5d, Ba-5d and Te-5p orbital mostly, and the valence band maximum is composed of Pt-5d, Ba-5d and Te-5p electrons. The PDOS of the main electronic orbits of SrPtTe and BaPtTe with equilibrium lattice constant and 2% compressive strain have been compared below, respectively. For both III-VIII-V half-HCs, the conduct orbital are fixed, while the valent orbital are moved away from $E_F$ with decreasing the lattice constant. Moreover, by comparing PDOS of the main electronic orbits near $E_F$ in Figs. 5 and 6, it is found that the amount of s and d orbits of VIII group elements in III-VIII-V half-HCs are smaller than that in II-VIII-VI half-HCs, while the amount of d orbits of IIIB group elements in III-VIII-V half-HCs are larger than that of IIA group elements in II-VIII-VI half-HCs, and the amount of p orbits of VA group elements in III-VIII-V half-HCs are similar to that of VIA group elements in II-VIII-VI half-HCs. Thus, the different changing trends of electronic structures of the two types of half-HCs are caused by the different extra-nuclear electrons of IIA and IIIB group elements which change the type of chemical bonding.

Fig. 2. Band structures of YPdBi (a) and YPtSb (b) with equilibrium lattice constant, and YPdBi (c) and YPtSb (d) with 2% compressive strains, respectively, where the dotted line marks the bands with $\Gamma_6$ symmetry and the dash line is $\Gamma_8$ symmetry.

Fig. 3. Band structures of SrPtTe (a) and BaPtTe (b) with equilibrium lattice constant, and SrPtTe (c) and BaPtTe (d) with 2% compressive strains, respectively, where the dotted line marks the bands with $\Gamma_6$ symmetry and the dash line is $\Gamma_8$ symmetry.
To analyze the chemical bonding of these HCs, the orbital distributions of twofold degenerated states and fourfold degenerate states at Γ point with equilibrium lattice constant and 2% compressive strain have been plotted in Figs. 6 and 7, respectively. Fig. 6 indicates YPdBi and YPtSb, where the blue, white and red atoms (in the web version) denote Y, Pd (or Pt) and Bi (or Sb) ones, respectively. Fig. 6a–d denote No. 1 bands of the corresponding YPdBi and YPtSb; Fig. 6e–h denote No. 2 bands of them; and Fig. 6i–l denote No. 3 bands of them, where the No. 1, 2 and 3 bands are shown in Fig. 2. Fig. 6a and c shows that the electronic orbits centre Pd (or Pt) and Bi (or Sb) atoms mostly, and the orbital configurations around Bi and Sb atoms are spherical, which means σ* orbits, while these are hybridized orbits between one Y and four Pd (or Pt) atoms, which are π* orbits. Moreover, the orbital configurations of No. 1 band of YPdBi with equilibrium lattice constant is the same as that of No. 3 band with 2% compressive strain, and Fig. 6e and i (or Fig. 6g and k) are similar as Fig. 6b and f (or Fig. 6d and h), respectively, these are π orbits around Y atoms. All above results indicate that the twofold degenerated states and fourfold degenerate states are inverted under the 2% compressive strains. Also, the blue, white and red atoms (in the web version) in Fig. 7 denote the Sr (or Bi), Pt and Te atoms, respectively. Fig. 7a–d denote No. 1 bands of the corresponding SrPtTe and BaPtTe; and Fig. 7e–f denote No. 2 bands of them. The No. 1, 2 and 3 bands are shown in Fig. 3. Fig. 7a, e, c and g show that the orbits centre Pt atoms mostly, and these are σ* orbits, which are the similar as the σ orbits in Fig. 7b, f, d and h, respectively. Fig. 7i–l denote No. 3 bands of them, and the orbits centre Pt and Te atoms mostly, which are σ orbits. And Fig. 7i and k are the same as Fig. 7j and l. All above results show that the band orders are fixed for SrPtTe and BaPtTe when the lattice constant is changed. Comparing with the orbital distributions of III-VIII-V half-HCs and II-VIII-VI half-HCs, the chemical bonding of them are different, which are caused by the different extra-nuclear electrons of IIA and IIIB group elements. The d orbits of IIIIB group elements are quite important for the chemical bonding of III-VIII-V half-HCs. Three components in III-VIII-V half-HCs contribute to the chemical bonds at Γ point, however, the most
Fig. 5. PDOS of SrPtTe (a) and BaPtTe (b) with equilibrium lattice constant. PDOS of SrPtTe with 6s (c) and 3d (e) electrons of Pt, 4d (g) electrons of Sr and 5p (i) electrons of Te, and BaPtTe with 6s (d) and 5d (f) electrons of Pt, 4d (h) electrons of Sr and 5p (j) electrons of Te with equilibrium lattice constant and 2% compressive strains, respectively.

Fig. 6. The orbital distributions of twofold degenerated states and fourfold degenerate states of YPdBi and YPtSb at Γ point with equilibrium lattice constant and 2% compressive strain, respectively.
important contributions for the chemical bonding of II-VIII-VI half-HCs are IIA and VIA group elements.

4. Conclusions

In summary, the dependence of \((E_{G6} - E_{G8})\) on the lattice constants has been studied for four half-Heusler compounds. First principle simulation was carried out to calculate the electronic structures and the obtained results were compared among different compounds. The results show that the change of \((E_{G6} - E_{G8})\) with strain exhibits opposite trend for III-VIII-V half-HCs and II-VIII-VI half-HCs. YPtSb and YPdBi transform TI to NI when the lattice constant is reduce by 1% for YPtSb and 2%, respectively, while SrPtTe and BaPtTe are always TIs as the strain in the range of 1% to 2%. Moreover, the valent orbital are usually fixed and the conduct orbital are moved away from \(E_F\) for III-VIII-V half-HCs, whereas the conduct orbital are usually fixed and the valent orbital are moved away from \(E_F\) for II-VIII-VI half-HCs when the lattice constant is reduced. The different changing trends of electronic structures of the two types of half-HCs are caused by the different extra-nuclear electrons of IIA and IIIB group elements which change their chemical bonding.

Acknowledgements

Computational resources have been provided by the Beijing Computing Center.

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