Electronic properties and topological phases of ThXY (X = Pb, Au, Pt and Y = Sb, Bi, Sn) compounds

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The electronic properties and topological phases of ThXY (X = Pb, Au, Pt, Pd and Y = Sb, Bi, Sn) compounds in the presence of spin–orbit coupling, using density functional theory are investigated. The ThPtSn compound is stable in the ferromagnetic phase and the other ThXY compounds are stable in nonmagnetic phases. Band structures of these compounds in topological phases (insulator or metal) and normal phases within generalized gradient approximation (GGA) and Engel–Vosko generalized gradient approximation (GGA_EV) are compared. The ThPtSn, ThPtBi, ThPtSb, ThPdBi, and ThAuBi compounds have topological phases and the other ThXY compounds have normal phases. Band inversion strengths and topological phases of these compounds at different pressure are studied. It is seen that the band inversion strengths of these compounds are sensitive to pressure and for each compound a second-order polynomial fitted on the band inversion strengths–pressure curves.

Keywords: topological phase, density functional theory, energy band gap, band inversion strength

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1. Introduction

ThXY (X = Pb, Au, Pt, Pd and Y = Sb, Bi, Sn) compounds have cubic MgAgAs crystal structure with $F\bar{4}3m$ space group.[1] These compounds present a rich variety of physical properties, especially semiconducting behavior which their transport properties originating from the special symmetry of the crystal structure.[1,2]

There have been some empirical calculations of the structural and electronic properties of ThPtSn compound.[3] Szajek *et al.*[4] used the van Barth–Hedin exchange correlation potential and the tight-binding linear muffin–tin orbital method in the atomic sphere approximation to calculate the electronic density of states of ThPtSn compound and used the x-ray photoemission spectra to measure the lattice parameters and the valence band of this compound. They concluded that the ThPtSn compound has a small energy gap of 32 meV, which is sensitive to details of the method being used for the exchange–correlation potential. Grytowska *et al.*[5,6] measured the lattice parameters and magnetization isotherms of ThPtSn compound with magnetometer between 1.9 K and 300 K with the magnetic field strength up to 5 T. They did not observe any splitting for Sn and Pt, due to large Pt–Sn interatomic distance. Palstra *et al.*[7] used adiabatic heat pulse technique to measure the specific heat of ThPtSn compound and used x-ray diffraction to measure the lattice parameter and Th–Th distance of this compound. They used a Foner vibrating sample magnetometer operating to determine the magnetization of ThPtSn compound, used the adiabatic heat pulse technique to measure the specific heat of this compound, and found that ThPtSn exhibits a positive magnetoresistivity and obeys the quadratic field dependence between 4 K and 100 K. To our knowledge there are no experimental and theoretical works for other ThXY compounds.

Topological phases (insulators or metals) are novel states of quantum matter in which surface states are protected by time-reversal symmetry. These states are topologically protected against back scattering. These materials have very promising technological applications in quantum computing[8] and spintronics.[9,10]

The first goal of this paper is to compare and investigate the electronic properties of ThXY compounds within generalized gradient approximation (GGA)[11] and Engel–Vosko generalized gradient approximation (GGA_EV)[12] at zero pressure. Since some physical properties of ThPtSn compound at zero pressure have already been studied by others,[1–7] the ThPtSn calculated results are compared with the previous works and we have focused on the topological phase of this compound that has not been studied by others. In addition, the topological phases of other ThXY compounds are investigated. The second goal of this paper is to study the effect of pressure on the topological phases of ThXY compounds.

2. Method of calculations

The results of this paper were attained based on the density functional theory (DFT) using the full potential linearized augmented plane wave plus local orbitals (LAPW+lo) method as implemented in the Wien2k package.[13] In LAPW+lo method, every unit cell is portioned into non-overlapping muffin-tin (MT) spheres with radii R_{MT} and interstitial region. The muffin-tin radii of Th, X, and Y atoms were selected as

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2.4 a.u., 2.3 a.u., and 2.3 a.u., respectively. The Kohn–Sham (KS) wave functions, charge density, and potential are expanded with spherical harmonics within the MT spheres and also with plane waves inside the interstitial region. In this paper, the maximum quantum number for atomic wave functions within the MT sphere was selected as $l_{\max} = 10$. The wave vector cut-off for the plane wave expansion within the interstitial region was $K_{\max} = 8/R_{\mathrm{MT}}$ (a.u.)$^{-1}$. The charge density as well as the potential was Fourier expanded inside the interstitial region up to $G_{\max} = 15$ (Ry)$^{1/2}$. 165 k-points were generated within the irreducible wedge of the Brillouin zone. The values of the $l_{\max}$, $K_{\max}$, $G_{\max}$ and the number of k-points were chosen through converging the total energy.

The exchange correlation potential was treated within GGA using the scheme of Perdew–Burke–Ernzerhof[11] and GGA_EV[12] approaches. The GGA_EV approach is based on potential optimized that has been developed for calculation of the energy band structure. The computation for the core electrons was carried out full relativistically, while for the valence electrons it was done both scalar and completely relativistically. The spin orbit coupling for the valence electrons was incorporated as a second-variational treatment[14] utilizing scalar relativistic eigenfunction as the basis.

3. Results and discussion

3.1. Structural properties

To investigate the ground state properties of ThXY (with X = Pb, Au, Pt, Pd and Y = Sb, Bi, Sn) compounds, the total energy as a function of the unit cell volume in ferromagnetic and nonmagnetic phases of these compounds is calculated using GGA. The calculated total energy–volume is fitted with the Murnaghan equation of state.[15] Due to the close similarity between the total energy–volume curves behavior of these compounds, only the curves for ThPtSn and ThPtSb compounds are shown in Fig. 1. The calculated results show that for ThPtSn the ferromagnetic phase lies lower than the nonmagnetic phase and for other ThXY compounds, the energy differences between these two phases are small, of the order of meV. Thus, at zero pressure, the ferromagnetic phase of ThPtSn and nonmagnetic phase of other ThXY compounds are the most stable phases. The equilibrium lattice parameters and bulk moduli of ThXY compounds in the stable phase are compared with available experimental values[1,2,4,5] in Table 1. The calculated equilibrium lattice parameter of ThPtSn is in acceptable agreement with the experiments.

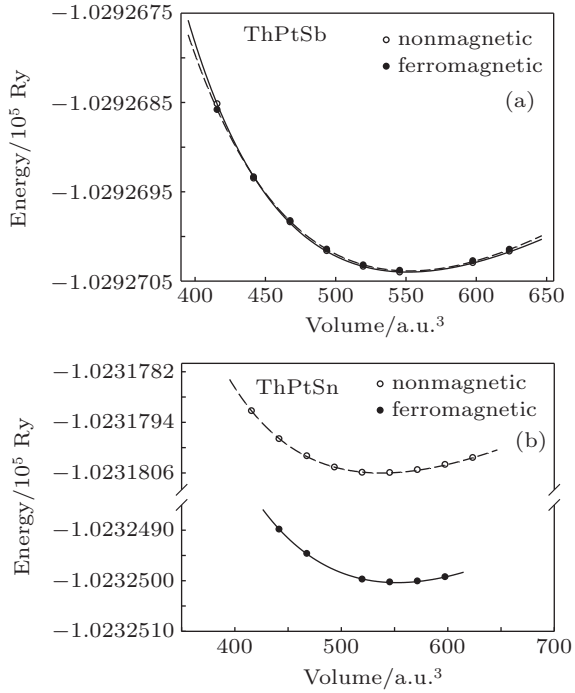


Fig. 1. The calculated total energies of ThPtSn (a) and ThPtSb (b) compounds as a function of unit cell volume in ferromagnetic and nonmagnetic phases.

The equilibrium unit cell volume of matter is related to the size of the component atoms with some adjustment for bonding in the solid. Going upward in a column of the periodic table, the bonding contribution decreases by a small value. The calculated lattice parameters of ThPdY (Y = Sb, Bi, Sn) compounds are larger than the corresponding values of ThPtY compounds. For a given row in the periodic table, the lattice parameter should increase with valence number increasing. The calculated lattice constants of ThXY compounds show that the lattice constants of ThXSb are a little larger than the corresponding values of ThXSn. This is due to the increase of the number of valence electrons, when Sn atom in ThXSn compounds is replaced with Sb. Furthermore, we also calculated the bulk moduli of these compounds. Al-Douri *et al.*[16–18] and Nourbakhsh[19] have shown that the dominant effect on the bulk moduli is from the degree of covalency and ionicity. The bulk modulus generally increases with the increase of covalency and the decrease of ionicity. The effect of decreasing ionicity is to increase the amount of bonding charge and hence to increase the bulk modulus. ThXY compounds have different degrees of covalent and ionic bonding. The calculated bulk moduli of these compounds show as follows.

Table 1. The calculated lattice parameters (in Å) and the bulk moduli (in GPa) of ThXY compounds.

		Lattice constant/Å	Bulk modulus/GPa
ThAuBi		7.1716	70.7
ThAuSb		7.0287	76.3
ThAuSn		6.9801	79.7
ThPdBi		7.0482	86.9
ThPdSb		6.9096	91.4
ThPdSn		6.8571	95.6
ThPtBi		7.0091	84.2
ThPtSb		6.8850	89.8
ThPtSn		6.8124	92.9
	Experimental	6.748[1,2]	–
		6.754[5]	
		6.736[4]	

(i) Going along a row from ThPtY to ThAuY and along a column from ThXSb to ThXBi, the bulk modulus decreases. This is due to the increase of ionicity and decrease of covalency.

(ii) The bulk modulus of ThXY compounds decreases as the atomic number of X and Y atoms increases. Going from ThPdY to ThPtY and ThXSn to ThXSb, the bulk modulus decreases. This trend is due to covalency decreasing with the nearest neighbor distance increasing.

3.2. Electronic properties

3.2.1. Electron density of states

To study the electronic properties of ThXY compounds, we have calculated the total electron density of states (DOS) within GGA and GGA_EV approaches. The calculated results indicate that the spin–orbit interaction has a considerable effect and cannot be ignored. Thus, we have studied the electronic properties and topological phases of these compounds in the presence of spin–orbit coupling. Due to close similarity between the calculated results within GGA and GGA_EV, the results within GGA are only shown in Fig. 2. The DOSs of all these compounds are similar, with some small differences in details. ThPdSn and ThPtSn compounds are semiconductor with a small band gap, while other ThXY compounds are metals. The major contribution to the occupied part of the DOS around the Fermi energy comes from the d orbitals of the Th and Y atoms. The DOS consists of a small narrow peak centered on −12 eV in ThXBi. This peak shifts toward higher energy level when Bi is replaced by Sb and further by Sn. This peak comes from the d orbital of Y atoms. The DOS above the Fermi energy originates mainly from the f orbital of Th, partially mixed with some d orbitals.

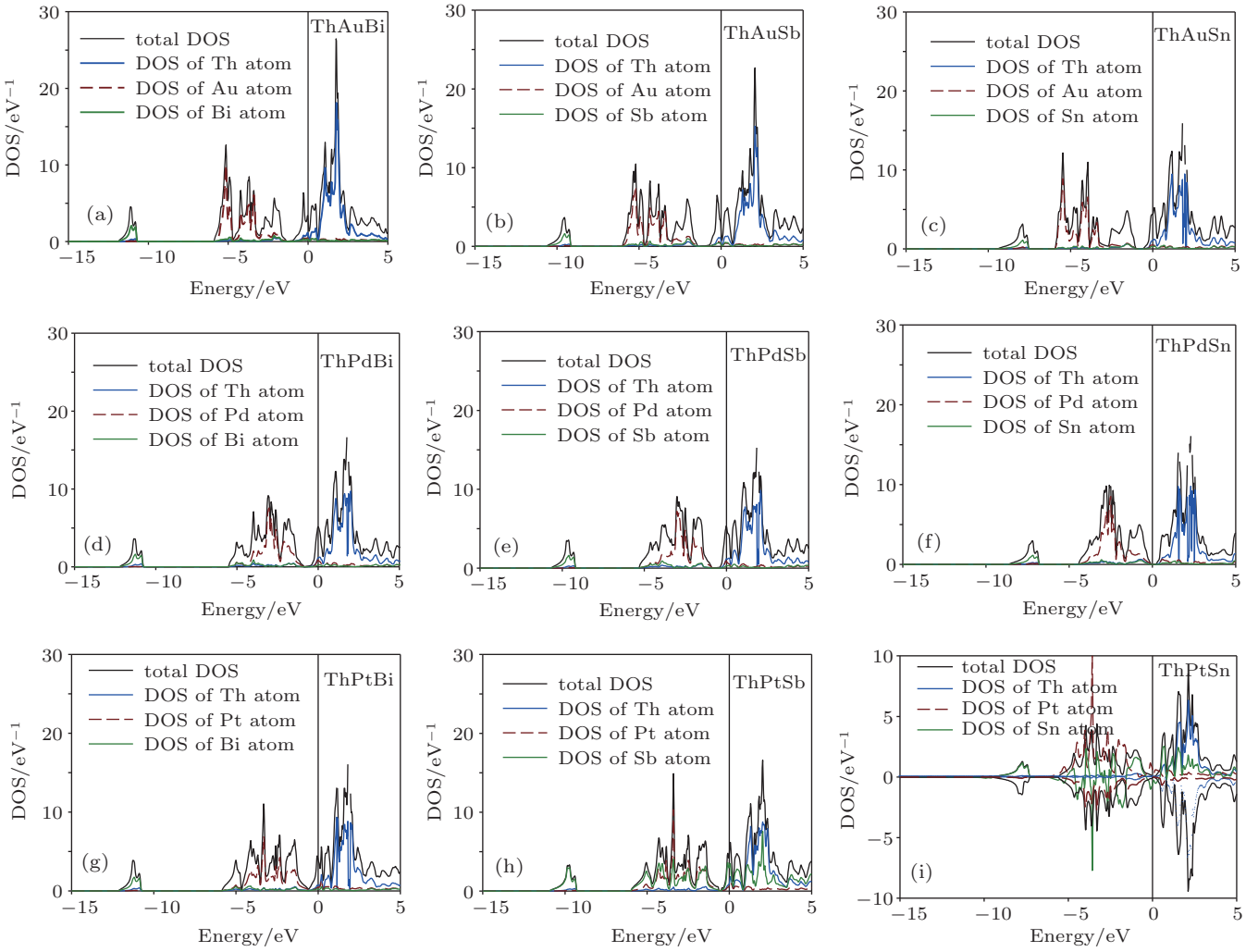


Fig. 2. (color online) The calculated total and partial electron densities of states of ThXY compounds within GGA approach. (a) ThAuBi, (b) ThAuSb, (c) ThAuSn, (d) ThPdBi, (e) ThPdSb, (f) ThPdSn, (g) ThPtBi, (h) ThPtSb, (i) ThPtSn.

3.2.2. Band structure

The band structures of these compounds within GGA approach are calculated. The calculated results show that in ThPtSn and ThPdSn, the valence band's maximum and the conduction band's minimum occur at the Γ point; hence these two semiconductor compounds have small direct energy band

gaps. The calculated energy band gap and available experimental value are given in Table 2. The calculated energy band gap of ThPtSn is smaller than the experimental value.

In band structure calculation, based on the DFT, the GGA usually underestimates the energy band gap. Engel and Vosko,[12] in the GGA_EV improved the GGA for band structure calculations, with optimizing exchange potential (V_x). In some previous papers[19–21] the GGA_EV was applied for band structure calculation of solids and compared the results with GGA calculations. It has been shown that the GGA_EV improves the determination of band gap and some other electronic properties. We have calculated the band structure of ThXY compounds within GGA_EV using the calculated equilibrium lattice parameters (as obtained in Section 3.1) within GGA in the presence of spin–orbit coupling. Due to the close similarity between the band structures of these compounds, the band structures are only given for ThPtBi, ThPdSb, and ThPtSn compounds in Fig. 3. The calculated energy band gaps of ThPtSn and ThPdSn within GGA_ EV are given in Table 2. The band gap of ThPtSn within GGA_EV is improved considerably, compared to the experimental results.

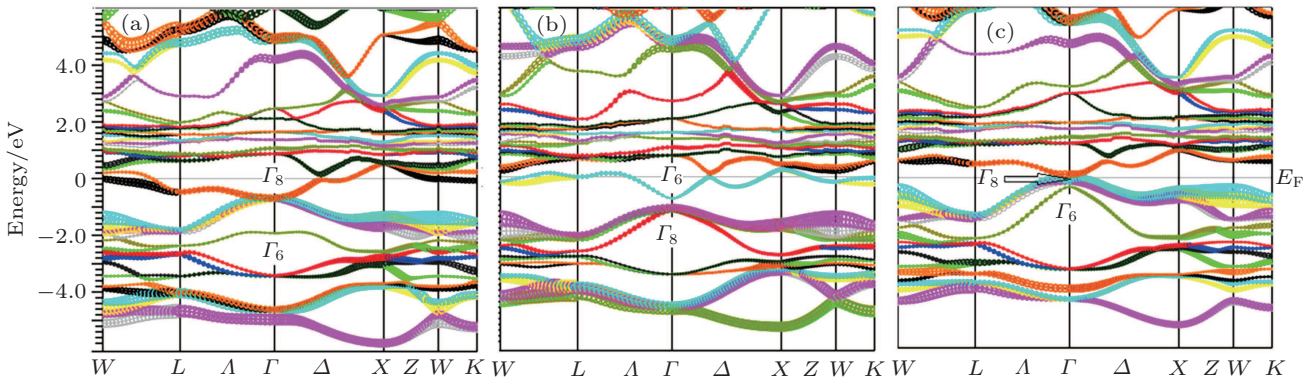


Fig. 3. (color online) The calculated band structures of ThPtBi (a), ThPdSb (b), and ThPtSn (c) compounds within GGA_EV approach.

Table 2. The calculated energy band gaps (eV) of ThPtSn and ThPdSn compounds within GGA and GGA_EV and experimental results.

	GGA	GGA_EV	Experimental
ThPtSn	0.16	0.249	0.32[4]
ThPdSn	0.036	0.39	–

3.2.3. Topological phases of ThXY compounds

Using the calculated band structure of ThXY compounds in the presence of spin–orbit coupling, we have studied the band order of these compounds. The energy bands of these compounds at the Γ point near the Fermi energy split, due to the spin–orbit coupling, into Γ_6 (s-like levels), Γ_7 (p-like levels, $j = 1/2$) with twofold degeneracies and Γ_8 (p-like levels, $j = 3/2$) with fourfold degeneracy. The band orders of ThPtSb and ThPdSb are from high to low energy Γ_8, Γ_6, Γ_7 and Γ_6, Γ_8, Γ_7, respectively. The ThPdSb has a normal band order (the Γ_6 state sits above the state), while the ThPtSb has an inverted band order (the Γ_6 state sits below the Γ_8 state).

The topological phases of these compounds can be characterized by band inversion between Γ_6 and Γ_8 at the Γ symmetry point in the first Brillouin zone. The band inversion strength (Δ) in compounds with cubic symmetry is defined as the energy difference between Γ_6 and Γ_8 states ($\Delta = E_{\Gamma_6} - E_{\Gamma_8}$). A negative Δ indicates that the compound is a topological nontrivial insulator, semimetal or metal, while that with a positive Δ is a topological trivial phase.

The band inversion strengths of ThXY compounds using the calculated band structures (Fig. 3) within GGA and GGA_EV approaches are calculated. The calculated results are shown in Fig. 4. The results indicate that: (i) The calculated band inversion strength of these compounds within GGA is smaller than the corresponding value within GGA_EV. In particular, if band inversion strength has a small magnitude within GGA calculation, it may change its magnitude and sign within GGA_EV approach. Because the sign of the band inversion strength shows a topological or normal phase of compounds, thus the type of the exchange correlation potential plays an important role in the investigation of topological phases, especially when the magnitude of band inversion strength is small. (ii) The main difference between the band order of these compounds is that ThPtSn, ThPtBi, ThPdBi, ThAuBi, and ThPtSb within GGA_EV and GGA possess an inverted band order, while ThAuSb, ThAuSn, ThPdSb, and ThPdSn compounds have a normal band order. ThPtSn is a candidate for topological insulators that is in agreement with other works.[2,3] ThPtBi, ThPdBi, ThAuBi, and ThPtSb are candidates for topo-

logical metals. To the best of our knowledge, there are no theoretical or experimental results for band order of these compounds (except ThPtSn) to compare with. We leave these results as references for future investigation.

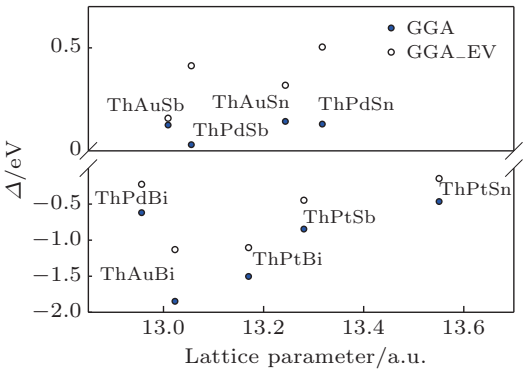


Fig. 4. The calculated band inversion strengths, Δ, of ThXY compounds within GGA and GGA_EV approaches.

3.3. Pressure dependence of the band order of ThXY compounds

To study the effect of pressure on the band order of ThXY compounds, the band structures of these compounds within GGA and GGA_EV at different pressure are calculated. The GGA_EV approach is not a good approximation for energy–volume curve and pressure calculations,[19] so the pressure (the lattice parameter) was calculated within GGA and applied to the band structure calculations within GGA and GGA_EV approaches. The calculated Δ as a function of pressure within GGA and GGA_EV are shown in Fig. 5. The Δ is sensitive to pressure and the variation of it with pressure is not linear in the considered pressure ranges. We have fitted the data by a second-order polynomial, $\Delta(P) = \Delta(0) + \alpha P + \beta P^2$, where $\Delta(0)$ is band inversion strength at zero pressure (shown in Fig. 4), P (GPa) is pressure, α and β are the first- and second-order pressure coefficients of band inversion strength. The calculated α and β for these compounds are given in Table 3. The magnitudes of α and β are very small with respect to the $\Delta(0)$. In addition, β is nearly two orders of magnitude smaller than α. Therefore, the band inversion strength has a small deviation from the linear law. To our knowledge, there are no experimental or theoretical results for the pressure derivative of the band inversion strength of ThXY compounds to compare with the calculated results.

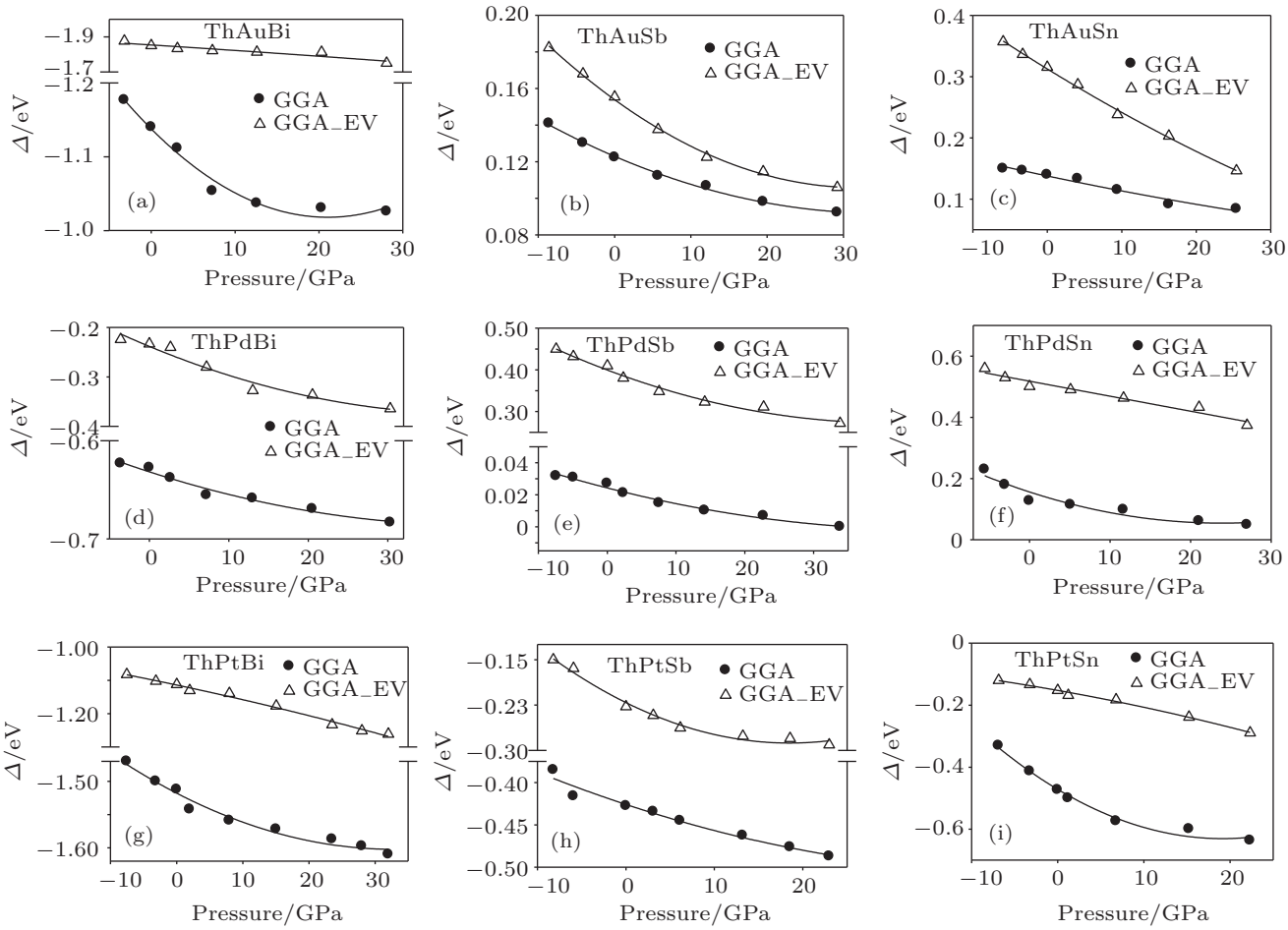


Fig. 5. The calculated band inversion strength (Δ) as a function of pressure for different compounds within GGA and GGA_EV. (a) ThAuBi, (b) ThAuSb, (c) ThAuSn, (d) ThPdBi, (e) ThPdSb, (f) ThPdSn, (g) ThPtBi, (h) ThPtSb, (i) ThPtSn.

Table 3. The calculated first-order (α) and second-order (β) pressure coefficients of band inversion strength within GGA and GGA_EV..

	$\alpha/10^{-2}$ eV·GPa^{-1}		$\beta/10^{-4}$ eV·GPa^{-2}	
	GGA	GGA_EV	GGA	GGA_EV
ThAuBi	1.138	0.3034	–2.703	0.08672
ThAuSb	–1.1783	–0.3012	0.2558	0.4723
ThAuSn	–0.2565	–0.747	0.1253	0.3668
ThPdBi	–0.2612	–0.6670	0.3123	0.8176
ThPdSb	–0.1098	–0.6207	0.1157	0.7597
ThPdSn	–0.8531	–0.4909	1.788	0.0034
ThPtBi	–0.513	–0.4219	0.7775	–0.1895
ThPtSb	–0.6890	–1.442	0.7352	3.895
ThPtSn	–1.661	–0.493	4.342	-0.5131

4. Conclusions

We have studied the band structures of ThXY compounds using GGA and GGA_EV approaches for the purpose of delineating their band order and topological phases. ThPtSn, ThPtSb, ThPtBi, ThPdBi, and ThAuBi compounds have an inverted band order, while ThPdSb, ThPdSn, ThAuSn, and ThAuSb compounds have a normal band order. ThPtSn is a candidate for the topological insulator and ThPtSb, ThPtBi, ThPdBi, and ThAuBi are candidates for topological metals.

The behavior of band inversion strength of these compounds with pressure shows that the variation of band inversion strength is not linear and changes with pressure by a second-order polynomial. The second-order pressure coefficients of these compounds are smaller than the first-order pressure coefficients.

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