

Structural properties of Sb- and Te-based binary compounds: Spin-orbit effect

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The band structure of AlSb, GaSb, ZnTe and CdTe is calculated using the empirical pseudopotential method (EPM) coupled with spin-orbit (SO) splitting. We applied our empirical model of bulk modulus with SO effect. It has been noticed that SO has a crucial effect on the band structure of these compounds but does not influence the structural phase transition. The calculated results are in good agreement with the experimental data.

Keywords: *binary compounds, spin-orbit, structural properties*

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1. Introduction

Semiconductors have received considerable attention for their possible use in double heterostructure (DH) blue laser diodes (LDs) [1–5]. Searching for suitable cladding layer material, having energy band gap 0.3 eV higher than that of the active layer such as ZnTe [6, 7], remains a problem. The electronic properties of zinc-blende compounds have been computed to provide a basis for understanding future device concepts and applications. The self-consistent pseudopotential method in the local density approximation underestimates the band gap and gives incorrect values for the effective mass [8, 9]. The quasiparticle method [9] is reliable but it is time consuming for the computation of semiconductor compounds. Therefore, the empirical pseudopotential method (EPM) [10] coupled with spin-orbit (SO) interaction is used. In this method, the actual atomic potential is replaced by pseudopotential and a set of atomic form factors is adjusted so as the calculation produced the energy bands as accurately as possible in overall comparison with the existing experimental data. EPM gives quick, reliable and valuable results for the assessment of material phenomena to study the optoelectronic devices.

Sazuki and Uenoyama [11] have calculated the electronic properties of binary semiconductors under spin-orbit effect theoretically. It seems very interesting to relate the SO splitting behavior of the compounds to the type of bonds between the nearest atoms. Reshak et al. [12–17] have used *ab initio* methods to elaborate the electronic, optical, first and second harmonic generation, linear and nonlinear optical response of Te- and Sb-based compounds. In addition, Al-Douri and Reshak [18] have calculated the optical properties of Sb-based compounds under hydrostatic pressure using full potential – linearized augmented plane wave (FP-LAPW) method. Khenata et al. [19] have calculated the elastic, electronic and optical properties of Te-based compound under pressure effect. Recently, Umar et al. [20] have investigated the photoluminescence and nonlinear optical properties of different colors of CdTe quantum dots experimentally. Their study was conducted at different laser light power densities and incident angles. The aim of this work is to link SO effect with the structural properties of bulk modulus to provide a possibly real picture of the structural phase transition from the fourfold coordinated crystal structure (ZB) to the six-fold one. Also, this procedure is used for testing the validity of our model [21] of bulk modulus. Section 2 presents a brief description of the method of calculation. In section 3, the spin-orbit interaction coupled

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with pseudopotential method is summarized to describe the spin-orbit splitting included in the band structure calculations. Finally, section 4 presents the calculated results and discussion.

2. Pseudopotential calculation

The calculation of the pseudopotential Hamiltonian is given by

$$H = - \left(\frac{\hbar^2}{2m} \right) \nabla^2 + V(r) \quad (1)$$

where $V(r)$ is the pseudopotential that can be expanded in reciprocal lattice vectors G . For the zinc-blende structure, this yields [10]

$$V(r) = \sum_G (V_G^S \cos G \cdot \tau + i V_G^A \sin G \cdot \tau) e^{-iG \cdot \tau} \quad (2)$$

where $\tau = \tau_1 = -\tau_2 = \frac{1}{2}a(1,1,1)$ and a is the lattice constant. V_G^S and V_G^A are the symmetric and antisymmetric pseudopotential form factors of an endpoint binary compound and can be written in terms of the atomic potentials as

$$\begin{aligned} V_G^S &= \frac{1}{2} [V_1(G) + V_2(G)], \\ V_G^A &= \frac{1}{2} [V_1(G) - V_2(G)]. \end{aligned} \quad (3)$$

The form factors in equation 3 are determined empirically by fitting the calculated band structure to experimental data. They depend on the magnitudes of G . In most of the EPM calculations, a cut-off value of $|G|^2 = 11(2\pi/a)^2$ is used. The contribution to the summation in equation 2 from the terms beyond this cut-off $|G|^2$ is small and can be neglected.

To fit the known discrete symmetric and antisymmetric form factors simultaneously, a least square method is used. The discrete form factors have been taken from Cohen and Bergstresser [10]. The discrete form factors of the endpoint binary compounds and the lattice constant a are given in Table 1.

3. Spin-orbit interaction

The pseudopotential form factors in equation 1 are stated to calculate the band structure coupled

with spin-orbit effect. The contribution of the spin-orbit matrix element to the pseudopotential Hamiltonian is added following the work of Weisz [22] and Chelikowsky and Cohen [23]:

$$H_{GG'}^{SO}(k) = (K \times K') \cdot \sigma_{ss'} (-i \lambda^S \cos[(G - G') \cdot \tau] + \lambda^A \sin[(G - G') \cdot \tau]) \quad (4)$$

where $K = k + G$, $K' = k + G'$ and $\sigma_{ss'}$ refers to the Pauli spin states. λ^S and λ^A are the symmetric and antisymmetric contributions to the spin-orbit Hamiltonian.

Also

$$\begin{aligned} \lambda_{ij}^S &= \frac{1}{2} \mu_{ij} [B_i^{nl}(K) B_i^{nl}(K') + \alpha_{ij} B_j^{nl}(K) B_j^{nl}], \\ \lambda_{ij}^A &= \frac{1}{2} \mu_{ij} [B_i^{nl}(K) B_i^{nl}(K') - \alpha_{ij} B_j^{nl}(K) B_j^{nl}]. \end{aligned} \quad (5)$$

where λ_{ij}^S and λ_{ij}^A are the symmetric and antisymmetric contributions of the endpoint binary compounds, $\mu_{i,j}$ is an adjustable parameter for the spin-orbit splitting Δ_{SO} , and $\alpha_{i,j}$ are the fixed ratios of the spin-orbit splitting of free anion and cation atoms [24]. The B^{nl} is defined as

$$B^{nl}(k) = \beta \int_0^\infty J_{nl}(kr) R_{nl} r^2 dr \quad (6)$$

where R_{nl} is the radial part of the outermost p-core wave function and β is a normalization constant as in reference [25].

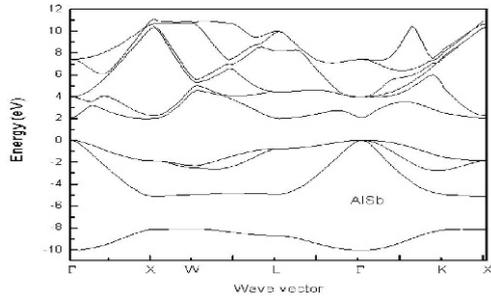
4. Results and discussion

Generally, the spin-orbit splitting occurs in the valence band and in the conduction band by the cation atomic spin-orbit splitting [26]. This work aims at calculating the electronic band structure of such binary compound with spin-orbit splitting. Empirical pseudopotential method enables calculation of the electronic structures in the valence and conduction bands of III-V and II-VI semiconductors such as AlSb, GaSb, ZnTe and CdTe.

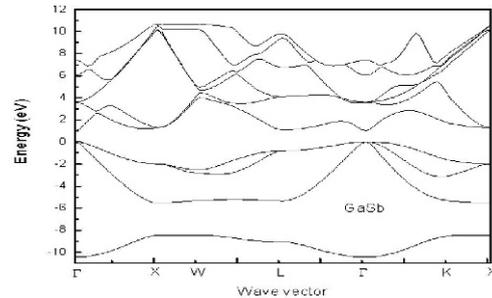
To determine the band structures of the binary materials with emphasis placed on accurate determination of the principal energy gaps [27], a pseudopotential method coupled with spin-orbit splitting is provided.

Table 1. The adjusted symmetric and antisymmetric form factors (in Rydberg) and the lattice constant a (in atomic units) for AlSb, GaSb, ZnTe and CdTe.

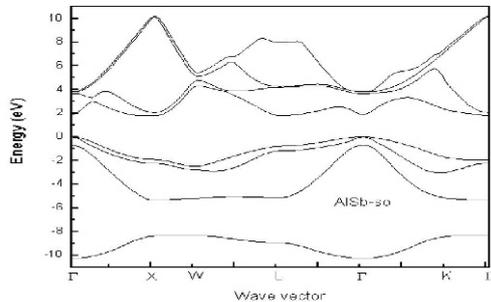
Compound	a	$V_s(3)$	$V_s(8)$	$V_s(11)$	$V_a(3)$	$V_a(4)$	$V_a(11)$
AlSb	11.5857	-0.20805	0.02117	0.06223	0.05966	0.03685	0.01820
GaSb	11.5668	-0.18991	-0.00016	0.05314	0.05316	0.03446	0.00216
ZnTe	11.4723	-0.22863	-0.01263	0.05947	0.10887	0.10582	-0.01284
CdTe	12.11491	-0.20	0.00	0.04	0.15	0.09	0.04



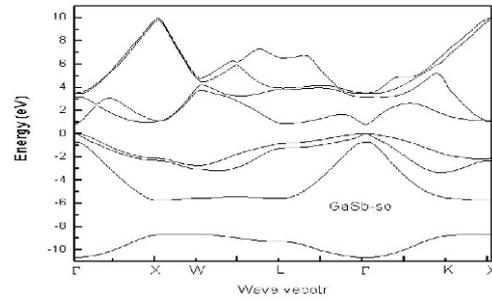
(a)



(a)



(b)



(b)

Fig. 1. Calculated band structure of AlSb (a) without SO and (b) with SO.

Fig. 2. Calculated band structure of GaSb (a) without SO and (b) with SO.

The parameters used in these calculations, together with the band gap energies are tabulated in Table 2, where good agreement is shown between the calculated and experimental spin-orbit splitting and energy gap values.

The spin-orbit splitting at Γ of zinc-blende (ZB) structure is determined by the anion atomic spin-orbit splitting in the valence band and by the cation atomic spin-orbit splitting in the conduction band [30]. Due to the fact that the anion components are the same and have near the same

values, it is reasonable to assess the Δ_{SO} data for Sb and Te based compounds.

The electronic band structures with spin-orbit splitting seem to have direct band gap. Since the values of band gaps at the main symmetry points Γ , X and L are adjusted, it can be assumed that the electronic band structures in Figs. 1, 2, 3, 4 are reasonable. Without spin-orbit splitting, the covalent semiconductors are fourfold coordinated. Also, the covalent bonding character is still strong with SO splitting effect. The reason

Table 2. Spin-orbit parameters, calculated spin-orbit splitting and principal energy gaps without and with spin-orbit (SO) for the endpoint binary compounds: AlSb, GaSb, ZnTe and CdTe.

			Δ_{SO} (eV)		E_g (eV)						Others				
	α	μ (a.u.)	Cal.	Exp.	without SO			with SO			$E_{\Gamma\Gamma}$	$E_{\Gamma X}$	$E_{\Gamma L}$		
AlSb	44.84	3.7×10^{-4}	0.74	0.75 ^a	2.1	1.99	1.99	1.85	1.75	1.76	2.1 ^c	1.9 ^c	1.17 ^j	2.0 ^c	
GaSb	5.69	2.3×10^{-3}	0.70	0.70 ^a	0.99	1.29	1.08	0.76	1.06	0.84	1.0 ^c	0.2 ^d	1.6 ^e	1.3 ^c	1.08 ^c
ZnTe	17.027	6.9×10^{-4}	0.93	0.91 ^b	2.52	3.89	3.75	2.21	3.58	3.44	2.6 ^c	1.4 ^f	1.28 ^g	4.0 ^c	3.8 ^c
CdTe	5.55	2.1×10^{-3}	0.95	0.95 ^b	1.75	3.90	3.26	1.43	3.59	2.95	1.8 ^c	1.31 ^h	0.76 ⁱ	4.0 ^c	3.5 ^c

a: ref. [24], b: ref. [28], c: ref. [29] exp., d: ref. [14] theo., e: ref. [18] theo., f: ref. [17] theo., g: ref. [19] theo., h: ref. [12] theo., i: ref. [15] theo., j: ref. [16] theo.

Table 3. The calculated bulk modulus without and with spin-orbit (SO) splitting effect compared with experimental and theoretical ones corresponding to the transition pressure.

	B_o (GPa)	B_o (GPa)	B_o (GPa)	B_o (GPa)	P_t (GPa)
	without SO	with SO	Exp.	Theo.	
AlSb	50.14	57.01	55.1 ^a	57 ^b , 56.4 ^c , 61 ^d	5.6 ^e
GaSb	60.40	67.01	57 ^b	58 ^b , 56.9 ^c , 59 ^d	7.65 ^a
ZnTe	63.20	68.67	61.2 ^c	59 ^b , 32.3 ^c , 54 ^d	8.5 ^a
CdTe	42.70	46.38	42 ^b	47 ^b , 27.5 ^c , 56 ^d	3.9 ^a

a: ref. [31], b: ref. [32], c: ref. [33], d: ref. [34], e: ref. [35].

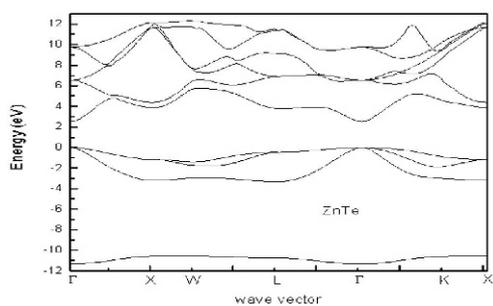
can be understood by energy consideration. We have evaluated the bulk modulus B_o from our model [21], which is based on the energy gap along Γ -X (in eV), $E_{g\Gamma X}$, according to the formula:

$$B_o = (30 + \lambda 10)[(P_t^{1/2} / E_{g\Gamma X})/3], \quad (7)$$

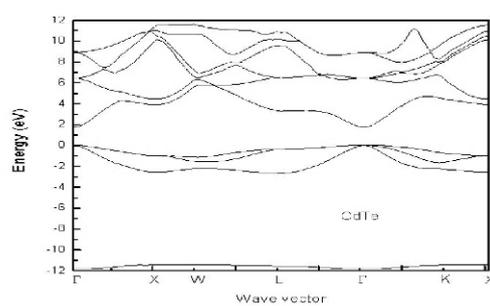
where P_t is the transition pressure (in GPa) and λ is an empirical parameter which accounts for $\lambda = 0, 1, 5$ for group IV, III-V, and II-VI semiconductors, respectively. The density is so low because the nearest neighbors are bound together, overlapping hybridized orbitals that are sp^3 hybrids with tetrahedral direction. The comparison of the calculated bulk modulus values with and without spin-orbit splitting effect is shown in Table 3. It can be noticed that the spin-orbit splitting effect separates the decrease and the increase of the bulk modulus values.

With the splitting effect, the bulk modulus varies up to the value which is characterized by a random behavior (Table 3). The ZB structure represents a more appropriate atomic arrangement.

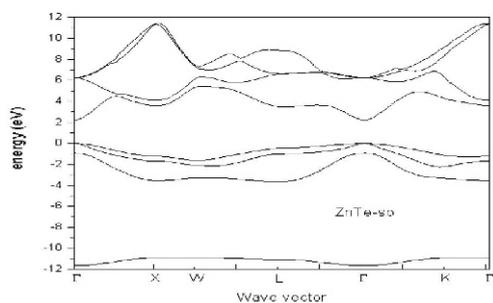
Therefore, a fluctuation of the bulk modulus is observed. As mentioned previously, there is an approach [35] that elucidates the correlation of the transition pressure with the optical band gap. This procedure gives a rough correlation but fails badly for some materials, such as AlSb, which have a larger band gap than Si, but have a lower transition pressure [36]. All the zinc-blende type compounds can be divided into two groups having small or large average energy gap ($E_g^2 = E_h^2 + C^2$). A likely origin for the above result is the increase of ionicity and the loss of covalency. It was noticed that the effect of ionicity reduces the amount of the bonding charge and hence, the bulk modulus. A comparison of the measured values of B_0 with the experimental ones leads to two possible improvements. One is to account the increasing covalency for such elements as Si, and the other is to include the effects of ionicity explicitly. The first effect was discussed earlier and it is possible to investigate the elements in the first three rows. Materials made from these elements have the largest bulk moduli and therefore



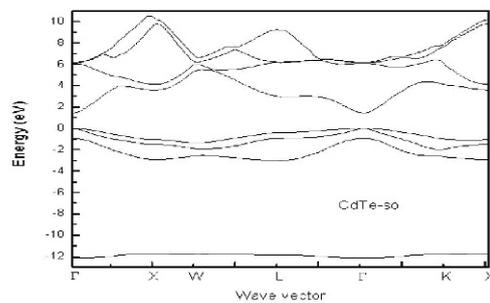
(a)



(a)



(b)



(b)

Fig. 3. Calculated band structure of ZnTe (a) without SO and (b) with SO.

Fig. 4. Calculated band structure of CdTe (a) without SO and (b) with SO.

are likely to be the hardest materials like B, C, N, Si and P. Alloys and more complex structures with tetrahedral bonding can be analyzed in an approximate way. It should be noted that in all of the above considerations and estimations, the ionicity factor has been ignored. The compounds with small E_g prefer the β -Sn structure while the NaCl structure is stabilized when the gap becomes larger [35]. From Eq. 7, a correlation can be found between the transition pressure and B_o ; e.g., the B_o for Si is 98 GPa and the transition pressure to β -Sn is 12.5 GPa, whereas for AlSb, B_o is 50.14 GPa and the transition pressure to β -Sn is 5.6 GPa. This correlation fails for a compound such as ZnTe, of large band gap, that has a smaller value of B_o and lower value of transition pressure than Si.

In conclusion, empirical pseudopotential method (EPM) method confirms the validity of our empirical model of bulk modulus for III–V and II–VI compounds. Also, it can be stated that SO effect is not the only factor responsible

for transforming these compounds from fourfold coordinated structure to a denser structure such as the β -Sn or NaCl phase.

Acknowledgements

This work has been achieved using FRGS grants numbered: 9003-00249 & 9003-00255. The author would like to acknowledge TWAS-Italy, for full support of his visit to JUST-Jordan under TWAS-UNESCO Associateship.

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Received: 2012-09-18

Accepted: 2012-12-13