Computational Materials Science 87 (2014) 187–197

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Phase transition of Nowotny–Juza NaZnX (X = P, As and Sb) compounds at high pressure: Theoretical investigation of structural, electronic and vibrational properties

Z. Charifi [a,*], H. Baaziz [a], S. Noui [b], Ş. Uğur [c], G. Uğur [c], A. İyigör [d], A. Candan [d], Y. Al-Douri [e]

[a] Department of Physics, Faculty of Science, University of M'sila, 28000 M'sila, Algeria
[b] Department of Physics, Faculty of Science, University of Batna, 05000 Batna, Algeria
[c] Department of Physics, Faculty of Science, Gazi University, 06500 Ankara, Turkey
[d] Central Research and Practice Laboratory (AHILAB), Ahi Evran University, 40100 Bağbaşı-Kırşehir, Turkey
[e] Institute of Nano Electronic Engineering, University Malaysia Perlis, 01000 Kangar, Perlis, Malaysia

ARTICLE INFO

Article history:
Received 30 November 2013
Received in revised form 6 February 2014
Accepted 11 February 2014
Available online 6 March 2014

Keywords:
Electronic materials
Ab initio calculations
Electronic structure
Phase transitions

ABSTRACT

A theoretical study of structural, electronic, elastic and phonon properties of NaZnX (X = P, As and Sb) compounds is presented by performing ab initio calculations based on density-functional theory using the full-potential linear augmented plane wave (FP-LAPW) and pseudopotential plane wave method. The generalized-gradient approximation (GGA) and the local density approximation (LDA) are chosen for the exchange–correlation energy. The Engel-Vosko (EVGGA) formalism is applied for electronic properties. The calculated structural parameters, such as the lattice constant, bulk modulus, second-order elastic constants, the electronic band structures and the related total density of states and charge density are presented. The high-pressure α *or* β phase of all compounds is investigated and phase transition pressure from tetragonal to high-pressure phase is determined. We have found that the Nowotny–Juza compounds NaZnP and NaZnAs are *direct* gap semiconductor at ambient pressure. Our calculations predict that NaZnSb is a metal in all phases. The bonding character and the phase stability of NaZnX (X = P, As and Sb) compounds are discussed. The nature and the size of the band gap of NaZnX (X = P, As and Sb) compounds are associated with the bonding character of two kinds of bonds, namely, Na–X and Zn–X bonds. The elastic constants were derived from the stress–strain relation. Phonon-dispersion curves were obtained using the first principles linear-response approach of the density functional perturbation theory. The influence of the pressure and X atomic number on the electronic structure, structural properties and phonon properties are investigated.

1. Introduction

The search of new semiconducting compounds for thermoelectric and photovoltaic applications becomes necessary. Therefore, filled tetrahedral Nowotny–Juza compounds have been studied extensively [1–8]. Zunger et al. [1,2,4] have studied the degree of the direct versus the indirect nature of the fundamental gap, by inserting of small atoms at tetrahedral interstitial states, of zinc blende semiconductors. Nowotny–Juza compounds of the form $A^IB^{II}C^V$ were predicted to be a new group of *direct* gap semiconductors [1,2] in the range of 1.3–2 eV. Many members of this interesting class of materials such as LiXY (X = Mg, Zn and Y = N, P, As), LiCdP, LiCdAs, and AgMgAs were prepared but just a few of them have been characterized. Band gaps are estimated to be 1.25 eV for LiZnAs, 1.3 eV for LiCdP, and 2,1 eV for LiZnP [3]. Electronic band structure calculations have predicted that LiZnP is a direct-band-gap semiconductor, despite the fact that its binary GaP is a strongly indirect-gap material [1,7]. The bonding and the phase stability of LiZnAs compound is studied and it is concluded that the bonding in $A^IB^{II}C^V$ can be remarkably characterized as half ionic and half covalent, with the A^I–C^V and B^{II}–C^V bonds being nearly pure ionic and covalent, respectively [4]. It is found that the cohesive energy of LiZnAs considerably exceeds that of GaAs. The optical band gap of the filled tetrahedral semiconductor LiZnAs is measured and it is found to be direct of 1.51 eV at 300 K and 1.61 eV at 77 K. This slightly larger band gap of LiZnAs, as compared to that of GaAs (1.42 at 300 K) is attributed to the higher ionicity in comparison with the ionicity of GaAs [5]. The band-gap nature of LiZnN predicted theoretically by the interstitial insertion rule of Zunger et al. [2] is confirmed

---

* Corresponding author. Tel./fax: +213 35556453.
E-mail address: charifizoulikha@gmail.com (Z. Charifi).

http://dx.doi.org/10.1016/j.commatsci.2014.02.018
0927-0256/

experimentally to be direct with a forbidden gap of 1.91 eV at room temperature [6]. While the observed band gap of LiZnN is smaller than that of GaN (3.36 eV at 300 K), the relatively small band gap of LiZnN may be attributed to the relatively high covalency of Zn–N bond exceeding the ionicity of Li–N bond, keeping a cubic phase without a phase transition to wurtzite structure. Very recently, Beleanu et al. have investigated experimentally the structural and electronic properties of LiMgZ (Z = P, As and Sb). The measurements show that all compounds exhibit semiconducting behavior with direct band gaps of 1.0–2.3 eV depending on the Z element [7]. With the increase of atomic number of the anion from P to Sb, the samples show higher conductivity [7]. So these compounds are predicted to be promising candidates for optoelectronics and anode materials for Lithium batteries. In order to discover new interesting materials for thermoelectric applications, the electronic structure of LiZnSb was analyzed in detail and has been suggested as a potential new thermoelectric material [8].

Although Lithium Nowotny–Juza compounds are studied elsewhere, to the best of our knowledge there has missed investigation of NaZnX (X = P, As and Sb) compounds in term of electronic, structural and vibrational properties [9]. NaZnX (X = P, As and Sb) compounds which belong to the same group but with tetragonal **Cu_2Sb** type structure (space group *P4/nmm)* [9] in contrast to cubic lithium semiconductors such as LiZnX (X = P, As and S) compounds. In the present work, using the DFT approach we studied the tetrahedral Nowotny–Juza compounds NaZnX (X = P, As and Sb). We derived electronic properties for these compounds, and we also investigated the influence of the pressure and X atomic number on the electronic structure. In Section 2, we report some details about the crystal structure and the numerical calculations. We concentrate on the equilibrium lattice constant, bulk modulus and the elastic properties in Section 3.1. We focus on the electronic properties in terms of band structures, density of states and charge density in Section 3.2 and we discuss the vibrational properties in Section 3.3. Finally, we draw conclusions in Section 4.

2. Calculation method

The space group of the majority of Lithium–Zinc based Nowotny–Juza compounds like LiZnN is F43m as well as a zincblende structure, NaZnX (X = P, As and Sb) compound crystallize at ambient pressure in the tetragonal structure with space group *P4/nmm.* The unit cell contains two molecules per formula unit. In the cubic (α, β, γ) phase under pressure, there are 3 atoms by unit cell.

The calculations presented in this work were performed using the full potential linearized augmented plane wave (FP-LAPW) method. We use the WIEN2K [10] implementation of the method which allows the inclusion of local orbitals in the basis, improving upon linearization and making possible a consistent treatment of the semicore and valence states in an energy window, hence ensuring proper orthogonality. The electron–electron interaction was treated within local density approximation (LDA) and generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) exchange–correlation potential [11]. In addition, and for the electronic properties we also applied the Engel-Vosko (EV-GGA) scheme [12]. Basis functions, electron density and potential were expanded in spherical harmonics trough ℓ=10 within non overlapping muffin-tin spheres, and plane waves in the interstitial region. In order to achieve energy eigenvalues convergence, the wave functions in interstitial region were expanded in plane waves with a cutoff of $K_{max} = 8/R_{MT}$–$8.5/R_{MT}$ where R_{MT} denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane-wave expansion. The R_{MT} is taken to be 1.8–2.2 atomic units (a.u) for Na, Zn and X (X = P, As and Sb) atoms for the four phases. Brillouin-zone (BZ) integrations within the self-consistency cycles were performed via a tetrahedron method [13,14] using 64–35 K points in the IBZ for tetragonal and cubic structure respectively. For calculating the electronic and the density of states (DOS), a denser sampling of uniformly distributed $\boldsymbol{k}$ points is required, Hence, the Brillouin zone integration was performed using 330 $\boldsymbol{k}$ point in the IBZ for tetragonal and 285 for cubic phase of NaZnX (X = P, As and Sb) compound. When the energy difference was less than 0.1 mRy, convergence was assumed.

Because of the lack of experimental and theoretical works regarding the compounds under study, and also the discrepancy between our results and those reported in Ref. [9], we have employed a pseudopotential method for further results. The plane wave pseudopotential scheme within density functional theory (DFT) is implemented in the Quantum-ESPRESSO package [15]. The electronic exchange–correlation potential was calculated by the generalized gradient approximation (GGA) using the scheme of Perdew–Burke–Ernzerhof (PBE) [11]. The wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off of 40 Ry. Brillouin-zone integrations were performed using a $10 \times 10 \times 10$ $\boldsymbol{k}$-points mesh. Having obtained self-consistent solutions of Kohn–Sham equations, the lattice-dynamical properties were calculated within the framework of the self-consistent density functional perturbation theory [16,17]. To obtain complete phonon dispersions and density of states, eight dynamical matrices were calculated on a $4 \times 4 \times 4$ $\boldsymbol{q}$-point mesh. The dynamical matrices at arbitrary wave vectors were evaluated using Fourier deconvolution on this mesh.

3. Results and discussions

3.1. Total energy calculations and phase transition

NaZnX (X = P, As and Sb) compounds belong to Nowotny–Juza compounds $A^IB^{II}C^V$ which based on three main group elements (A, B and C). They can be viewed as zinc-blende III–V compounds in which the III column has been disproportionated into $A^I + B^{II}$ atoms [1,2,4].The most stable phase of NaZnX (X = P, As and Sb) compounds is the tetragonal **(Cu_2Sb)** structure at ambient pressure in contrast to the most cubic Nowotny–Juza compounds which crystallize in α phase [1,2,5,6]. This fact is confirmed by Jaiganesh et al. [9] using the tight-binding linear muffin-tin orbital method within the local density approximation (LDA).

The **Cu_2Sb** structure exhibits *P4/nmm* symmetry with two internal parameters for the Na and X (X = P, As and Sb) atoms and contains six atoms in the unit cell. At a given volume, positions of Na and X (X = P, As and Sb) of each compound were determined by minimizing the forces on atoms. The calculated atomic position of As in the tetragonal phase are listed in Table 1. Under pressure this structure transforms to cubic phase α or β then γ with F43m space group. Also the atomic positions for each compound in each structure are listed in Table 1.

The structures of all compounds were optimized by calculating the total energy as a function of volume, which was followed by fitting the results with Murnaghan equation of state [18]. The calculated total energy versus volume using GGA approximation for NaZnX (X = P, As and Sb) compound is shown in Fig. 1. One can be clearly seen that the three phases tetragonal, α or β are very close to each other however there is a little difference in energy between them whereas the more stable phase at ambient pressure, is the tetragonal while β is a high pressure phase for NaZnX (X = P, As and Sb) compounds. In contrast to results reported in Ref. [9] in which it is predicted that α is a high pressure phase for NaZnP and NaZnAs, while that of NaZnSb is β phase.

Table 2 presents our calculated values obtained after optimization compared with the available experimental data and other

Table 1
The calculated atomic positions of NaZnX (X = P, As and Sb) for tetragonal (**Cu_2Sb**) and cubic (α, β, γ) phases.

Compound	Tetragonal	α-Phase	β-Phase	γ-Phase
NaZnP				
Na	(1/4, 1/4, 0.3578) (3/4, 3/4, 0.6422)	(1/2, 1/2, 1/2)	(3/4, 3/4, 3/4)	(0, 0, 0)
Zn	(1/4, 3/4, 0) (3/4, 1/4, 0)	(0, 0, 0)	(0, 0, 0)	(3/4, 3/4, 3/4)
X	(1/4, 1/4, 0.7865) (3/4, 3/4, 0.2135)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)
NaZnAs				
Na	(1/4, 1/4, 0.3596) (3/4, 3/4, 0.6404)	(1/2, 1/2, 1/2)	(3/4, 3/4, 3/4)	(0, 0, 0)
Zn	(1/4, 3/4, 0) (3/4, 1/4, 0)	(0, 0, 0)	(0, 0, 0)	(3/4, 3/4, 3/4)
X	(1/4, 1/4, 0.7807) (3/4, 3/4, 0.2193)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)
NaZnSb				
Na	(1/4, 1/4, 0.6546) (3/4, 3/4, 0.3454)	(1/2, 1/2, 1/2)	(3/4, 3/4, 3/4)	(0, 0, 0)
Zn	(1/4, 3/4, 0) (3/4, 1/4, 0)	(0, 0, 0)	(0, 0, 0)	(3/4, 3/4, 3/4)
X	(1/4, 1/4, 0.2245) (3/4, 3/4, 0.7755)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)	(1/4, 1/4, 1/4)

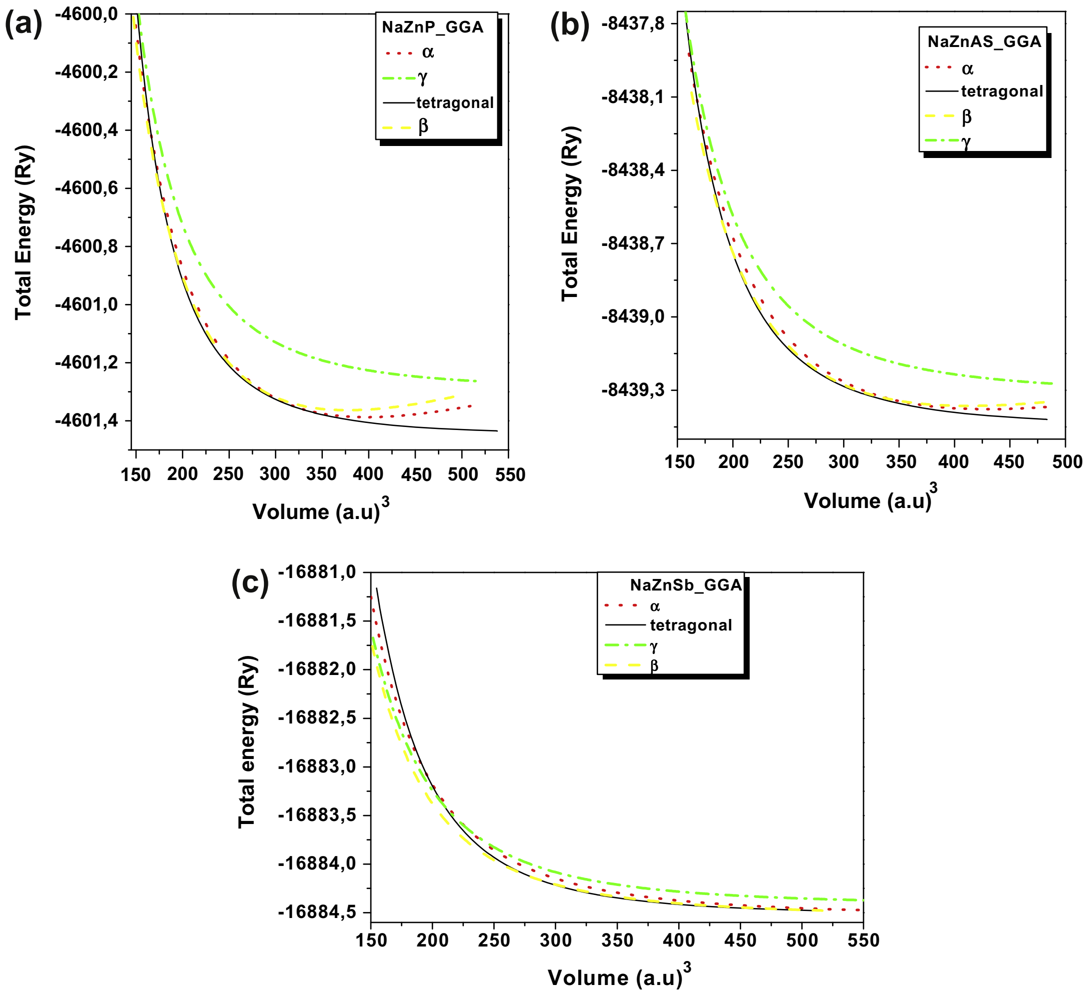

Fig. 1. Variation of total energies as a function of volume of unit cell for tetragonal phase (solid curve), α phase (dot curve) and β phase (dashed curve) and γ phase (dot–dashed curve) using GGA for: (a) NaZnP compound, (b) NaZnAs compound, (c) and NaZnSb compound.

theoretical results [9,19,20]. It is clearly seen that for all compounds the GGA overestimates the lattice parameter while the LDA underestimates it; these findings are consistent with the general trend of these approximations [21,22]. Generally speaking our lattice parameters are in good agreement with those found experimentally and theoretically reported in Refs. [9,19]. The lattice constant increases as we increase the X atomic number when substituting As for P and upon substituting Sb for As in the tetragonal phase and the cubic phases using GGA or LDA approximations.

Hardness measures a material's ability to resist deformation. Bulk modulus is the best indicator of hardness for materials. To

Table 2
Calculated lattice constants (a and c) in Å, bulk modulus (B_0) in GPa and pressure derivative (B_0') and elastic constant parameters at equilibrium volume using LDA and GGA compared to experimental and other works of NaZnX (X = P, As and Sb) for tetragonal (**Cu_2Sb**) and cubic (α, β, γ) phases.

Phase	NaZnP			NaZnAs			NaZnSb		
	Present work		Other works	Present work		Other works	Present work		Other works
	LDA	GGA		LDA	GGA		LDA	GGA	
Cu_2Sb									
a	3.965	4.076	4.066 [18]exp 4.012 [9]theo 4.0673 [19]	4.069	4.192	4.176 [18]exp 4.121 [9]theo	4.325 4.460		4.442 [18]exp 4.365 [9]theo
c/a	1.705	1.694	1.695 [18] exp 1.695 [9]theo	1.704	1.697	1.697 [18]exp 1.69721 [9]	1.681 1.679		1.686 [18] 1.6868 [9]
B_0	66.59	54.741	124.85 [9]theo	59.22	49.54	111.95 [9]theo	47.65	38.41	95.34 [9]
B_0'	4.76	4.39		4.59	3.87		4.64	4.78	
α-Phase									
a	5.962 6.144 [b]	6.148	5.750 [9]theo	6.140 6.338 [b]	6.350	5.916 [18] 5.7501 [9]	6.537 6.717 [b]	6.767	6.276 [9]
B_0	60.55 64.40 [a] 47.3 [b]	47.59 56.94 [a]	122.62 [9]	51.89 57.20 [a] 50.85[a] 41.9 [b]	39.93	107.11 [9]	42.02 33.8 [b]	31.69	86.91 [9]
B_0'	5.00 4.16 [b]	4.44		4.53 4.35 [b]	4.33		4.42 4.33 [b]	4.34	
C_{11} (GPa)	100.4331			81.0143			57.9957		
C_{12} (GPa)	22.2636			22.2836			22.2666		
C_{44} (GPa)	37.9071			31.7030			28.7287		
β-Phase									
a	5.89 6.063 [b]	6.07		6.05 6.251 [b]	6.26		6.39 6.568 [b]	6.61	
B_0	63.68 66.16 [a] 50.5 [b]	50.40 59.54 [a]		56.47 44.2 [b]	44.20		47.87 38.7 [b]	36.96	
B_0'	4.45 4.39 [b]	4.28		4.45 4.46 [b]	4.13		4.62 4.71 [b]	4.36	
C_{11} (GPa)	88.9317			76.4330			70.9		
C_{12} (GPa)	31.6935			28.1561			22.9069		
C_{44} (GPa)	47.8318			37.4525			31.2961		
γ-Phase									
a	6.074 6.284[b]	6.294		6.214 6.445[b]	6.454		6.538 6.753[b]	6.796	
B_0	45.95 35.1 [b]	35.06		42.19 31.9 [b]	32.11		36.18 27.5 [b]	27.03	
B_0'	4.21 4.26 [b]	4.02		4.28 4.39 [b]	4.01		4.31 4.66 [b]	4.09	
C_{11} (GPa	−1.7688			1.4835			3.1715		
C_{12} (GPa	53.6079			47.0418			39.914		
C_{44} (GPa)	48.6705			40.9198			33.3312		

[a] The calculated data by Eq. (1).
[b] The calculated data with pseudopotential method within GGA.

estimate the bulk modulus, we assumed uniform compression and expansion of the lattice and calculated total energy as a function of volume for each structure. Then the calculated total energies are fitted to the Murnaghan equation of state. Table 2 summarizes the values of the bulk moduli for the NaZnX (X = P, As and Sb) compounds. The bulk modulus decreases when we move from NaZnP to NaZnSb while the lattice parameter increases in all phases and also it decreases when the tetragonal phase become cubic under the effect of the pressure which is in a good agreement with the results of Ref. [9]. A big discrepancy was found in the values of the bulk moduli between the calculated values and those of Jaiganesh et al. [9], which is probably due to fact that they used the TB-LMTO method [9] within the LDA approximation. Because of the lack of the experimental results, we have used the ab initio pseudopotential method to found the bulk modulus of the compounds under consideration. Our results are listed in Table 1 and are found to be in excellent agreement with those calculated using LAPW method. To be more sure we have also used the model suggested in Ref. [23] to compute the bulk modulus B_0 of NaZnX (X = P and As) in the cubic phase α and β. The bulk modulus is given by:

$$B_0 = [3000 - \lambda 100]\left(\frac{a}{2}\right)^{-3.5} \tag{1}$$

where a is the lattice constant in (Å) and λ is an empirical parameter which accounts for the effect of ionicity; $\lambda = 0, 1, 2$ for group IV, III–V, and II–VI semiconductors, respectively, 2 in (Å) and the first term in (GPa). The calculated B_0 values are compared with other values. The comparison is given in Table 2. The results show that the calculated B_0 values exhibit the same trends, and are in reasonable agreement with our calculated values using LAPW and pseudopotential method. From Table 2, one can note that NaZnSb has the smallest bulk modulus among the studied compounds. This can be related to the larger atomic size and bond lengths of NaZnSb compound.

NaZnX (X = P, As and Sb) compounds transform from the initial tetragonal structure to the cubic structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs energy given by [24]:

$$G = E_{tot} + PV - TS \tag{2}$$

Since the theoretical calculations are performed at 0 K the free energy becomes equal to the enthalpy (H):

$$H = E_{tot} + PV \tag{3}$$

At a given pressure, a stable structure is one for which enthalpy has its lowest value and the transition pressure is calculated at which the enthalpies for the two phases are equal. It is predicted that the tetragonal phase of NaZnP and NaZnAs compounds transforms to α phase (which is not detected in Fig. 1) under very small value of pressure about 1 GPa using the two approximations LDA and GGA then it turns out to β phase. This suggests that there is a competition between the two phases tetragonal and α to occur, however for NaZnSb compound, the high pressure phase is directly β phase (see Fig. 2). We have found that the total energy differences between the tetragonal (**Cu_2Sb**) and cubic α-phases using LDA (GGA) are $-0.036(-0.035$ Ry), $-0.032(-0.036$ Ry) and $-0.029(-0.027$ Ry) for NaZnP, NaZnAs and NaZnSb respectively. For That reason, NaZnAs is also found to crystallize in α-phase (cited in Ref. [9]) at ambient pressure. The γ phase has high energy so it is considered to be unstable phase.

The transition pressure from tetragonal phase to the α *or* β phase for NaZnX (X = P, As and Sb) compounds are listed and compared with the previous calculations and experimental data [9] in Table 3. We note that a big disagreement is observed between our results and those of Ref. [9]. This is due to the fact that they have predicted the existence of tetragonal phase over a long range. However from our calculation we predict it over very short range about 1 GPa. This suggest that the NaZnX (X = P, As and Sb) compounds prefer to be in the α phase like the majority of Nowotny–Juza compounds. No experimental work has been reported for these compounds; hence more measurement is required to confirm our results.

Table 3
Calculated transition pressure values of NaZnX (X = P, As and Sb) compounds using LDA and GGA approximation.

		NaZnP	NaZnAs	NaZnSb
Transition pressure (P_t) GPa				
$Cu_2Sb \rightarrow \alpha$-phase	GGA	1.06	1.12	
	LDA	1.93	1.26	
		19.60 [9]	15.75 [9]	
$\alpha \rightarrow \beta$-Phase	GGA	29.15	14.04	
	LDA	6.92	11.42	
		90.50 [9]	72.40 [9]	
$Cu_2Sb \rightarrow \beta$-phase	GGA			0.73
	LDA			0.28
				51.6 [9]

In order to gain further information on pressure effect upon vibrational properties of NaZnX (X = P, As and Sb) compounds, we have calculated the elastic constants. To obtain the elastic constants of these compounds with cubic structure we have used numerical first principles pseudopotential method by computing the components of the stress tensor $\boldsymbol{e}$ for small strains, using the method reported in Ref. [25] and used in our previous works [26,27]. Our estimated elastic constants are presented in Table 1.

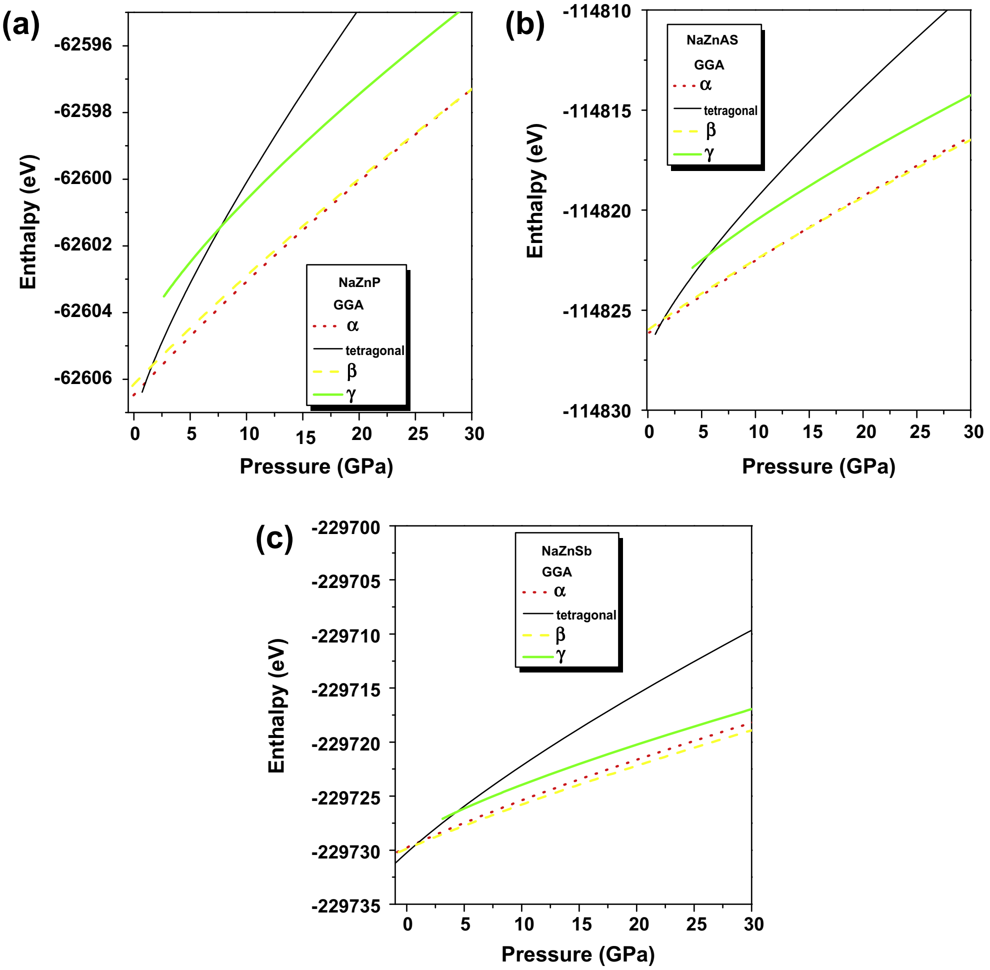

Fig. 2. Variation of total enthalpy as a function of pressure of unit cell for tetragonal phase (solid curve), α phase (dot curve) and β phase (dashed curve) and γ phase (dot–dashed curve) using GGA for: (a) NaZnP compound, (b) NaZnAs compound, (c) and NaZnSb compound.

Table 4
Band gaps of NaZnX (X = P, As and Sb) compounds within LDA, GGA and EVGGA calculated in all phases tetragonal, α, β and γ phases (all values are in eV).

E_g (eV)				
Compound	Tetragonal	α-Phase	β-Phase	γ-Phase
NaZnP				
LDA	0.79	0.73	0.71	0
	0.64 [9]	0.75 [9]	0.66 [9]	
GGA	0.77	0.45	0.35	0
EVGGA	1.30	1	0.850	0
NaZnAs				
LDA	0.44	0 [9]	0 [9]	0
	0.163 [9]			
GGA	0.39	0	0	0
EVGGA	0.79	0	0	0

To the best of our knowledge, there is no experimental value for the elastic constants of these compounds in the literature; our results for the cubic phase can serve as a prediction for future investigations. As one can see from Table 1, the value of C_{11} decreases from NaZnP to NaZnAs to NaZnSb, C_{12} and C_{44} increase in three phases α, β and γ phase. Otherside, in same phase, α or β the values of C_{11} and C_{44} decrease. We note also that the value of C_{11} increases and C_{44} and C_{12} decrease in γ phase. In phase α the C_{12} is constant and its value is around 22 GPa for all compounds.

3.2. Electronic band structure and density of states

The self-consistent scalar relativistic band structures of NaZnX (X = P, As and Sb) compounds along representative symmetrical

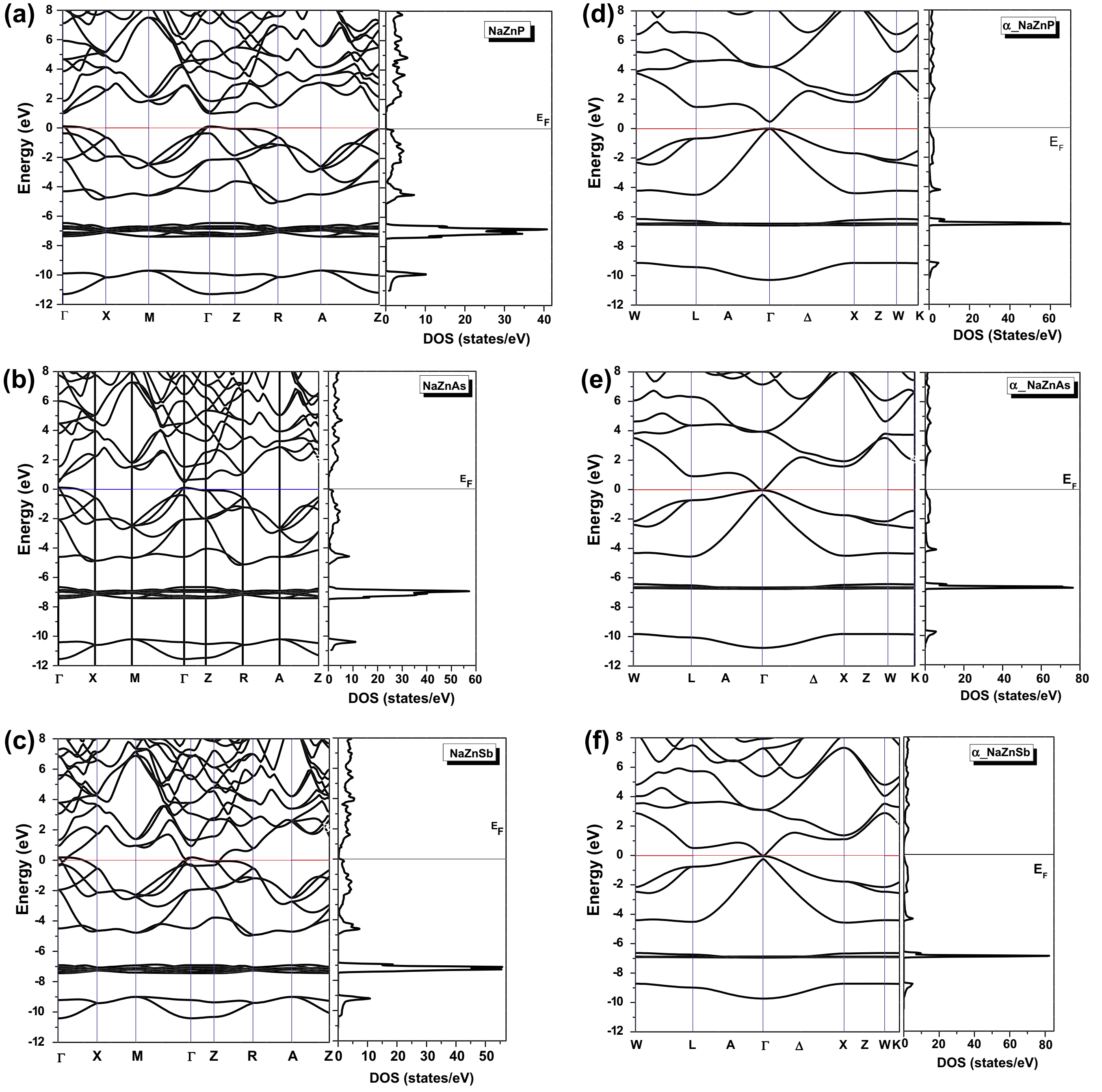

Fig. 3. Band structure along the symmetry lines of the Brillouin zone and total densities of states (states eV^{-1} unit cell) for NaZnX (X = P, As and Sb) using GGA approximation for tetragonal phase. The position of the Fermi level is shown by the horizontal line.

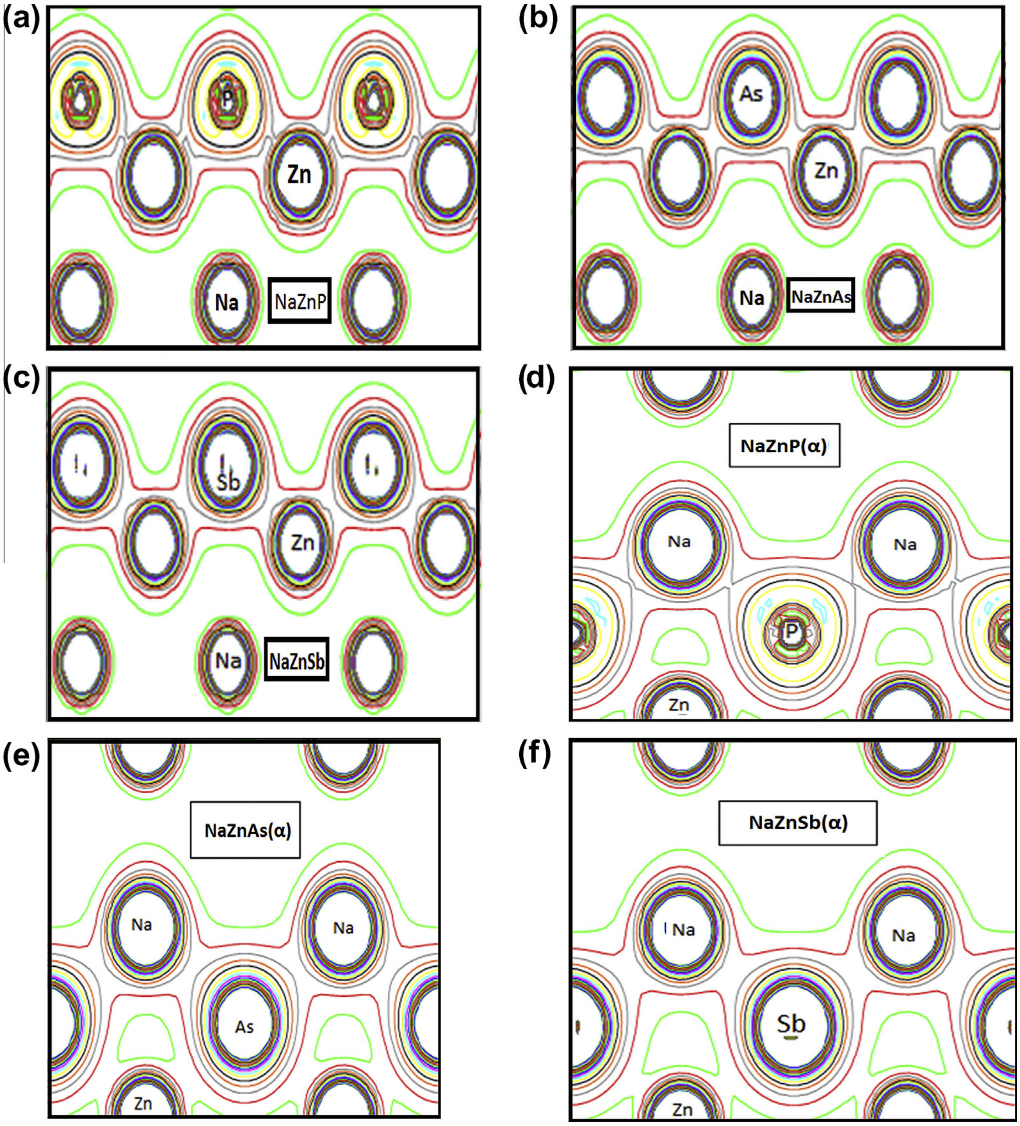

Fig. 4. Calculated electron charge density in the (010) plane for tetragonal phase (a, b, c) and (011) plane for α phase (d, e, f) of the NaZnX (X = P, As and Sb) compounds.

directions of the Brillouin zone were obtained in the tetragonal phase at equilibrium volume as well as at high pressure within the LDA, GGA and EV-GGA schemes. The Fermi level E_F is shown by a solide horizontal line. As a prototype we have shown the band structure and total density of states of NaZnX (X = P, As and Sb) using GGA approximation in the tetragonal and α phase in Fig. 3. Accordingly, the conduction band minimum appears to be at the zone center Γ. Hence, NaZnP and NaZnAs are direct gap semiconductors. Our calculations predict that NaZnSb is a metal. The calculated band gap $E_{\Gamma\Gamma}$ for NaZnP and NaZnAs are found to be 0.79 (0.77), 0.44 (0.39) eV using LDA (GGA), respectively in tetragonal phase. Our results are in agreement with the earlier first-principles [9] calculations for NaZnP, while we find a bigger value than that reported in [9] for NaZnAs.

It is well known that the LDA and the GGA usually underestimate the energy gap [28,29]. This is mainly because they have simple forms that are not sufficiently flexible for accurately reproducing both exchange–correlation energy (E_{xc}) and its charge derivative. The PBE-GGA is the standard parameter-free GGA, while the EV-GGA has been designed by optimizing the exchange potential rather than using (E_{xc}) [12].The reason for performing calculations using both GGA and EV-GGA is that the EV-GGA has been shown in several cases to give band gaps in good agreement with experiment [30,21]. The band structure calculated using the GGA and the EV-GGA for NaZnX (X = P, As and Sb) compounds were similar except for the value of their band gap which was higher within the EVGGA. The band gap values are given in Table 4, compared with available theoretical works. It is shown that the calculated energy gap values decrease with increasing the size of the pnictide atom (P, As and Sb). Under pressure NaZnP is predicted to be semiconductor in both phases α and β and became a metal in the third phase which is γ, with decreasing in the value of the band gap. However NaZnAs transforms to a metal under the effect of pressure.

The total density of states (DOS) for NaZnX (X = P, As and Sb) compounds at the equilibrium lattice constant is displayed at Fig. 3. It is shown that there are two regions of the valence band: the upper valence bands are dominated by X-*p* and Zn-*s*, *p* orbitals while the bottom valence band is dominated by the X-*s* and Zn-*d* orbitals. As shown in Fig. 3, the peaks are various according to the kind of structure. The height of the peak situated in −10 up to −5 eV increases as we substitute P by As and As by Sb in both phases tetragonal and α phase, and about 60 eV in β phase and in the range of 120–150 eV in γ phase. For Zn-*d* orbital is in the same

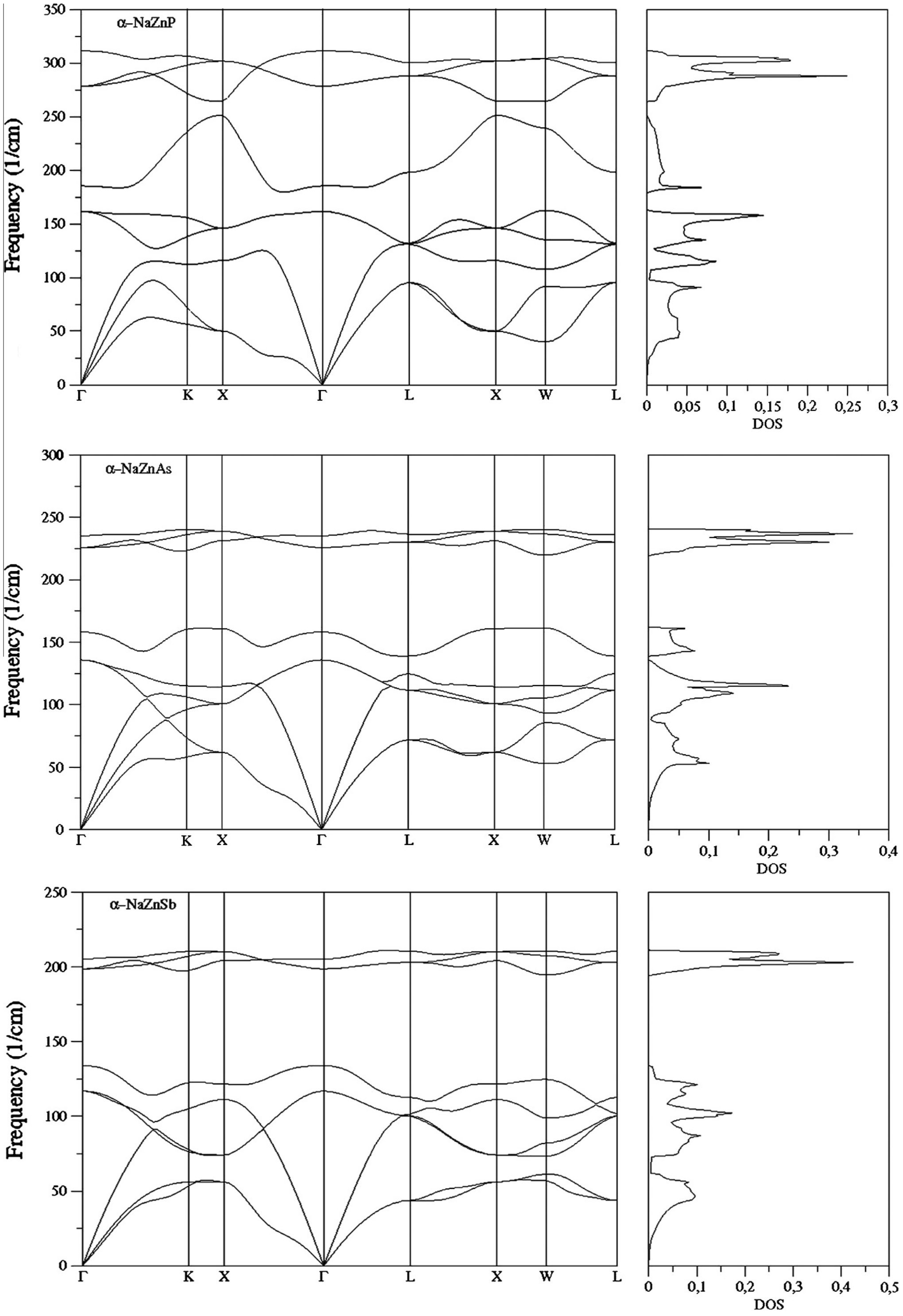

Fig. 5. Calculated phonon dispersion curves and phonon DOS for NaZnX (X = P, As and Sb) alloys along several lines of high symmetry in the Brillouin zone.

position with same height in all phases. For *s*-X orbital, its height is around 3 eV in tetragonal, α and β phases, however is around 5 eV in γ phase. Generally the density of states of NaZnX (X = P, As and Sb) compounds is in agreement with the previous work reported in [9]. Finally we mention that all compounds in γ phase are metals.

To obtain a deeper understanding of elastic properties of these compounds, we need to have a clear idea of the bonding nature. The charge density is an appropriate tool that permits us to better understand the bonding character. For this reason, we have studied the nature of the bond for NaZnX (X = P, As and Sb) compounds. We have calculated the total charge density of NaZnX (X = P, As and Sb) compounds, in different planes and for different Phases. Fig. 4 illustrates all the bonds in the (010) plane for tetragonal phase and (011) plane for α phase containing Na, Zn and X atoms. One can see clearly for the Na–P bond that the bonding charge is displaced strongly toward the P atom, due to the difference between the electronegativity values of the two atoms, and hence the Na–P bond is ionic, however the bond Zn–P is covalent (see

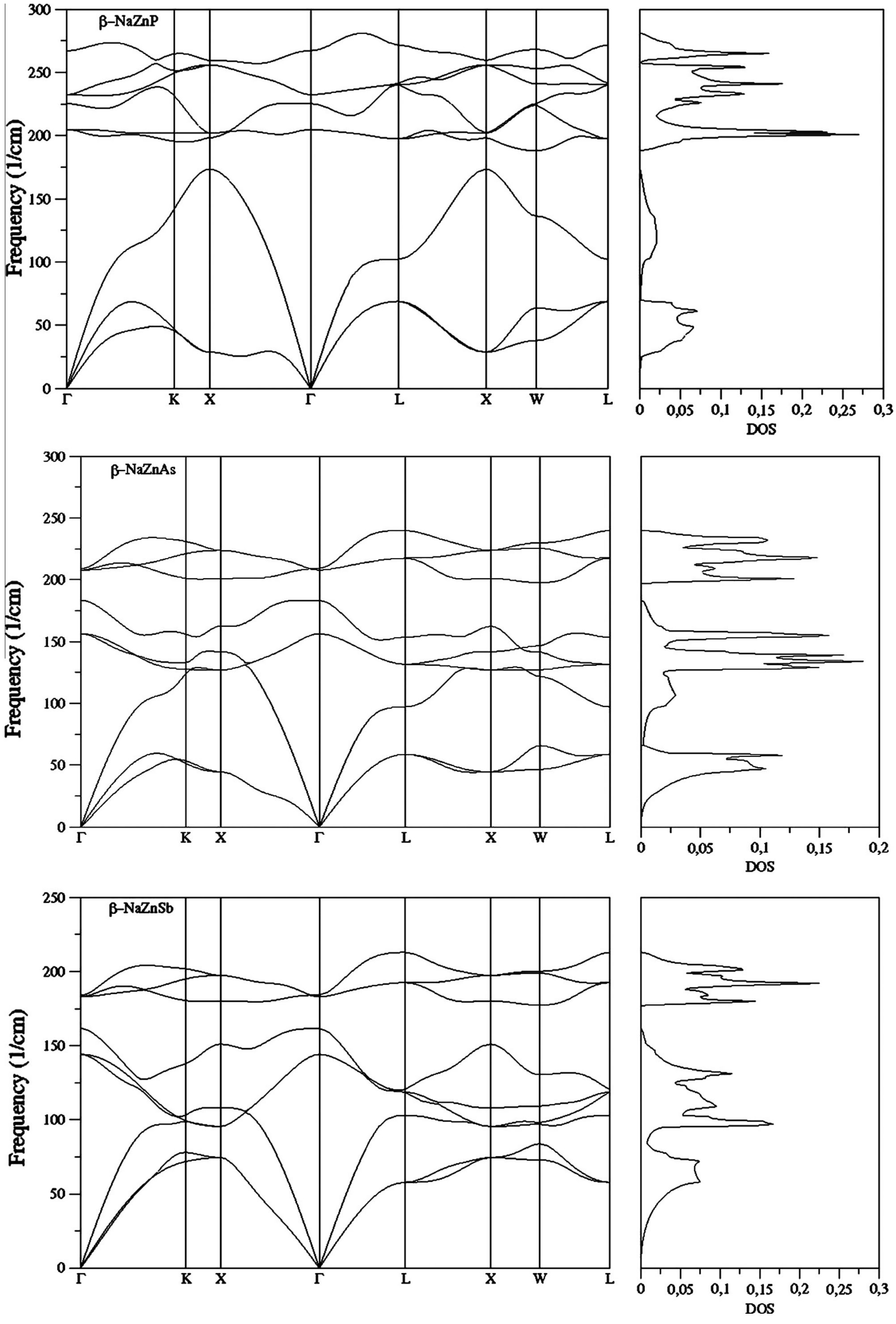

Fig. 5 (*continued*)

Fig. 4a), when we replace P by As and Sb the Na–X bond becomes less ionic, and Zn–X becomes covalent in tetragonal phase. Our results suggest the following ionicity order is NaZnP > NaZnAs > NaZnSb. This explains the fact that the energy gap decreases when we move from P to As to Sb in the compound NaZnX (X = P, As and Sb). Under pressure, the covalency character of the bonds exceeds the ionic character and hence NaZnAs and NaZnSb become metals at high pressure, while NaZnP still semiconductor with small gap.

3.3. Phonon properties

The knowledge of the phonon dispersion plays a significant role in determining various materials properties such as thermodynamic stability, phase transition, transport and thermal properties. To gain more insight about the elasic properties of the compounds under investigation, the calculated phonon dispersion curves along high-symmetry directions in the Brillouin zone together with the phonon density of states (DOS are displayed in Fig. 5 for α, β and

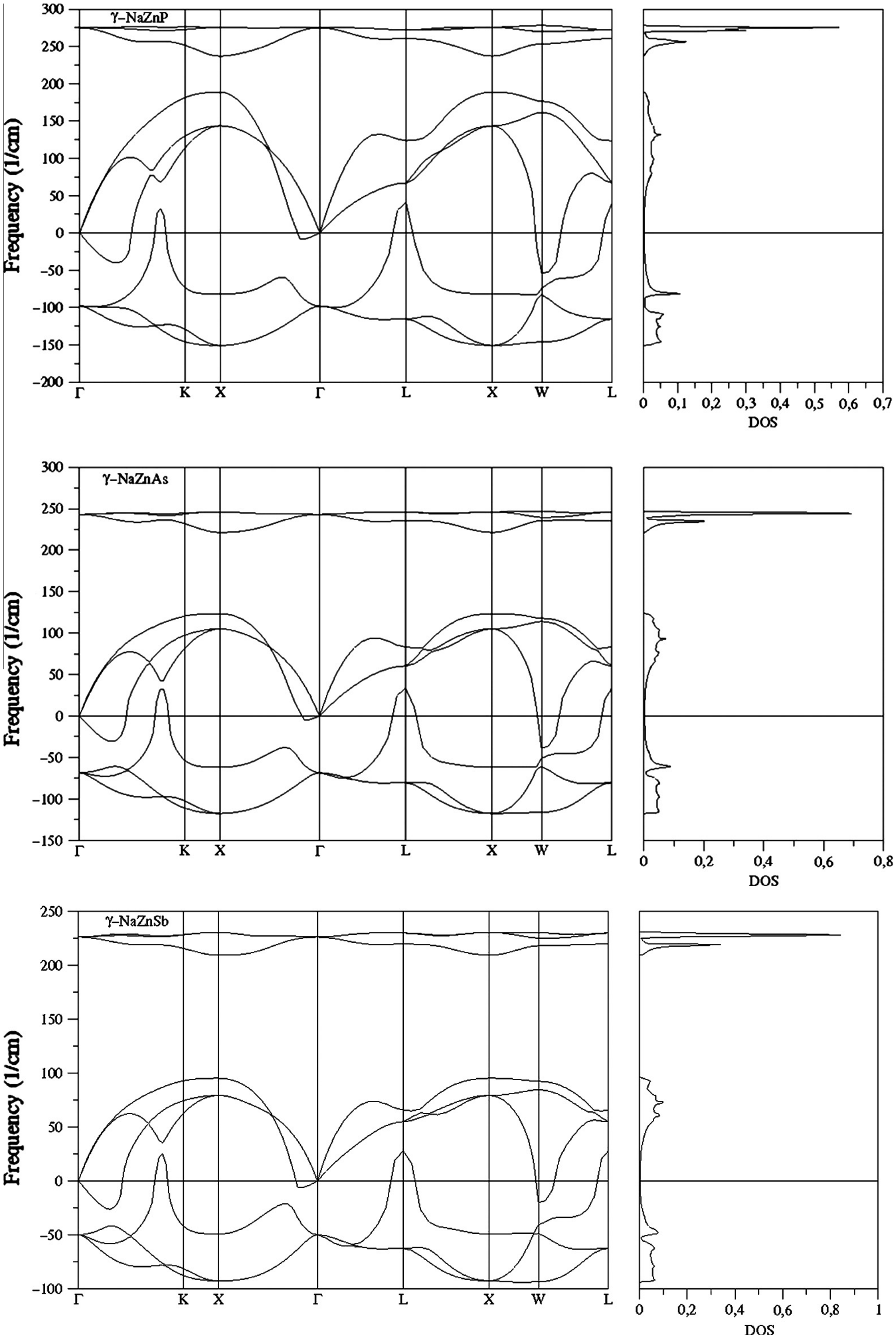

Fig. 5 (*continued*)

γ phases of NaZnX (X = P, As, Sb). Our results indicate that the α and β phases are dynamical stable, but the γ phase is dynamically unstable. The experimental data of the phonon spectrum for these materials are not yet available. For compound NaZnX (X = P, As and Sb), the total DOS at high frequencies mainly comes from the X states. The highest optical branch is separated from the rest of phonon branches except β-NaZnP. The band gap for α phase of NaZnP, NaZnAs and NaZnSb are around 16.7 cm^{-1}, 61.1 cm^{-1} and 63.2 cm^{-1}, respectively. The longitudinal acoustical (LA) branches do not overlap with transverse acoustical (TA) branches for NaZnP in α and β phase along all directions. The TA phonon branches of NaZnSb in α and β phase along the Γ–K directions are different from those of NaZnAs and NaZnP. The phonon branches (TA_1 and TA_2) for NaZnSb fairly close along this directions. We can conclude that the highest optical frequencies for all phases decrease with the increase of the mass of pnictide atoms.

4. Conclusions

The electronic, structural and phonon properties of NaZnX (X = P, As, Sb) Nowotny–Juza compounds have been studied using both methods, the self consistent full-potential linear augmented plane wave (FP-LAPW) and pseudopotential total energy method. The bonding and the phase stability of NaZnX (X = P, As and Sb) compound is studied and it is concluded that the more stable phase is the tetragonal phase under pressure this later transforms to α or β phase according to X element. The bulk modulus has been calculated using two different methods LAPW and pseudopotential method and gave excellent agreement with others. Basing on electronic band structure calculations, NaZnX (X = P and As) is a direct-band-gap semiconductor in the tetragonal phase with band gap of 1.30 and 0.79 eV respectively and NaZnSb is a metal using EVGGA approximation. The elastic constants C_{ij} are estimated from the energy variation as function of stress. Elastically, all the compounds have been found to be stable under pressure in α or β phase. The bonding in NaZnX (X = P, As and Sb) is characterized by the fact that Na–X and Zn–X bonds being nearly pure ionic and covalent, respectively in tetragonal phase. In α phase the small band gap of NaZnP is attributed to the relatively high covalency of Zn–P bond over the ionicity of Na–P bond. It is predicted that under high pressure, NaZnAs and NaZnSb are metals. The phonon frequencies and phonon densities of states in all phases in several lines of high symmetry of the Brillouin zone, were obtained and discussed using the density-functional perturbation theory.

Acknowledgments

This work is supported by the Algerian-National programs Research (NPR) under project No. 8/u28/5051 (2011). One of us Y.A. would like to acknowledge UniMAP for grant No. 9007-00062 and TWAS-Italy, for full support of his visit to JUST, Jordan under TWAS-UNESCO Associateship.

References

[1] D.M. Wood, A. Zunger, R. de Groot, Phys. Rev. B 31 (1985) 2570.
[2] A.E. Carlsson, A. Zunger, D.M. Wood, Phys. Rev. B 32 (1985) 1386.
[3] R. Bacewicz, T.F. Ciszek, Appl. Phys. Lett. 52 (1988) 1150.
[4] Su-Huai Wei, A. Zunger, Phys. Rev. Lett. 56 (1986) 528.
[5] K. Kuriyama, T. Kato, K. Kawada, Phys. Rev. B 49 (1994) 11452.
[6] K. Kuriyama, T. Kato, T. Tanaka, Phys. Rev. B 49 (1994) 4511.
[7] A. Beleanu, M. Mondeshki, Q. Juan, F. Casper, C. Felser, F. Porcher, J. Phys. D: Appl. Phys. 44 (2011) 475302.
[8] G.K.H. Madsen, J. Am. Chem. Soc. 128 (2006) 12140.
[9] G. Jaiganesh, T. Merita, J. Phys.: Condens. Matter 20 (2008) 085220.
[10] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Universitat, Wien, Austria, ISBN 3-9501031-1-1-2, 2001.
[11] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[12] E. Engel, S.H. Vosko, Phys. Rev. B 47 (1993) 13164.
[13] O. Jepson, O.K. Anderson, Solid State Commun. 9 (1971) 1763.
[14] J.A. Wilson, A.D. Yoffe, Adv. Phys. 18 (1969) 193.
[15] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal, J. Phys.: Condens. Matter 21 (2009) 395502.
[16] S. Baroni, P. Giannozzi, A. Testa, Phys. Rev. Lett. 58 (1987) 1861.
[17] S. Baroni, S. de Gironcoli, A. Dal, Rev. Mod. Phys. 73 (2001) 515.
[18] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 30 (1944) 244.
[19] P. Villars, L.D. Calverts, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, second ed., vols. 1 and 4, ASM International, The Materials International Society, Materials Park, OH, 1991, p. 1188, 4508 & 4520.
[20] H. Kabbour, L. Cario, F. Boucher, J. Mater. Chem. 15 (2005) 3525.
[21] Z. Charifi, H. Baaziz, F. El Haj, J. Phys.: Condens. Matter 17 (2005) 4083.
[22] A. Mokhtari, H. Akbarzadeh, Physica B 324 (2002) 305.
[23] Y. Al-Douri, H. Abid, H. Aourag, Mater. Chem. Phys. 87 (2004) 14.
[24] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Clarendon, Oxford, 1954.
[25] S.Q. Wang, H.Q. Ye, Phys. Status Solidi B 240 (2003) 45.
[26] Ş. Uğur, A. İyigör, Z. Charifi, H. Baaziz, M.R. Ellialtıoğlu, Philos. Mag. 93 (2013) 3260.
[27] A. Candan, G. Uğur, Z. Charifi, H. Baaziz, M.R. Ellialtıoğlu, J. Alloys Compd. 560 (2013) 215.
[28] P. Dufek, P. Blaha, K. Schwarz, Phys. Rev. B 50 (1994) 7279.
[29] G.B. Bachelet, N.E. Christensen, Phys. Rev. B 31 (1985) 879.
[30] A.H. Reshak, Z. Charifi, H. Baaziz, Eur. Phys. J. B 60 (2007) 463.