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Structural and Electronic Properties of Ternary $Al_xIn_{1-x}P$ Alloys

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III–V based alloys and heterostructures have much attention due to their great device applications as well as for the development of electronic, optic and optoelectronic devices. Because of this reason, the present study reports an investigation of the structural optimization of ternary alloys $Al_xIn_{1-x}P$. Method of WIEN2k code is applied considering Wu–Cohen correlation energy functional based on density functional theory. We have constructed $1\times1\times1$ supercell containing 8 atoms in zinc-blende structure. For all studied alloys structure, we have implemented geometric optimization before the volume optimization calculations. In this work, the structural and electronic properties of ternary alloys $Al_xIn_{1-x}P$ are presented. The obtained equilibrium lattice constants of studied binary compounds are more compatible with experimental data compared to standard semilocal (LDA–PBE) calculations.

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1. Introduction

The alloys of III–V zinc-blende semiconductor compounds are of vital importance because these materials are potentially good for application of optoelectronic and high-speed electronics [1]. Among these semiconductor compounds AlP has attracted particular attention due to its incorporation in the AlAs/AlP and GaP/AlP based alloys [2]. One another semiconductor compound InP has en energy band gap changing from 920 nm to 1650 nm and this characteristic makes it convenient to application in laser and photo-detectors as an active optical material. The binary compound InP is also a natural substrate widely used for both optoelectronic and high speed device applications. In the last years, ternary $Al_xIn_{1-x}P$ alloys is the alloy of two binaries AlP and InP, has been studied by several theoretical [2–4] and experimental [5–7] research group because of its potential for the applications such as GaInP/GaAs solar cell [8, 9] and visible lasers and modulators [10]. The aim of this work is to investigate the structural properties, such as the equilibrium lattice constants (a_0) and bulk modulus (B_0), and electronic properties of binary compounds, AlP and InP, and ternary alloys $Al_xIn_{1-x}P$ by employing the density functional theory. The obtained results are compared with previous theoretical calculations and experimental results. By means of this work, electronic band structure of considered ternary alloys was also represented for the first time in the literature.

2. Method of calculation

In the current study, all calculations are implemented into WIEN2k [11] software package which is based on the full-potential (linearized) augmented plane wave and local-orbitals method (FP-(L)APW+lo) to solve the Kohn–Sham equations. The Wu–Cohen (WC)-generalized gradient approximation (GGA) [12] exchange-correlation functional is used for electron–electron interactions. For comparison, the local density approximation (LDA) [13] and the GGA [14] were also used as a correlation potential.

We use an energy cut-off parameter $RK_{\max}$ (R is the average radius of the muffin-tin (MT) spheres and $K_{\max}$ is the cut-off for the wave function basis) of value 6. The cut-off energy is set to -6 Ry for separating core from valence states. Inside the MT spheres, the angular momentum expansion is expanded up to $l_{\max} = 10$. Magnitude of the largest vector G is equal to 12 $\mathrm{Ry}^{1/2}$ in charge density Fourier expansion. For a well force, charge convergence of crystal system is stable within less than $0.001e$. The total energy between self-consistency cycles (SCF) was $< 10^{-4}$ Ry. In the considered alloy structure, free coordinates of atoms were relaxed using the quantum-mechanical forces so residual forces on the ions were < 1 mRy/bohr.

For accurate Brillouin zone (BZ) integrations, the standard special k-points technique of Monkhorst and Pack (MP) [15] was used. The k-mesh sizes was $3\times3\times3$ MP special points (14 special k-points in the irreducible wedge of the BZ) for each considered 8-atom $1\times1\times1$ supercell. The k-meshes and basis sets are chosen to be good enough such that the obtained results are well converged.

3. Results and discussions

In this study, the binary InP and AlP compounds and ternary alloys $Al_{0.25}In_{0.75}P$, $Al_{0.5}In_{0.5}P$ and $Al_{0.75}In_{0.25}P$ are investigated in the zinc-blende (ZnS) structure at zero pressure. We use equations of state proposed by Murnaghan [16] in order to get the equilibrium lattice constants (a_0) and the static bulk modulus (B_0). The calculated equilibrium lattice parameters of the considered

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binary and ternary structures are presented and compared with available experimental and other theoretical results in Table I. For binary compounds, InP and AlP, our calculated lattice parameter results within the WC potential are in more agreement with experimental results [5, 17, 18] than the semilocal LDA, GGA and other theoretical results [2, 3] listed in Table I. Our calculated a_0 value within the WC potential for InP (5.8933 Å) and AlP (5.4748 Å) are 0.4% and 0.1% smaller than the experimental value [17] of 5.867 Å and 5.467 Å, respectively. Our calculated GGA and LDA results are within typical limits of numerical accuracy within the application of the DFT. In particular, compared with the experimental results [5, 17, 18], we find that LDA 0.5% underestimates, while GGA 0.9–1.8% overestimates for the lattice constant of the studied binary compounds. On the other hand, two different approaches namely plane-wave pseudo-potential (PW-PP) and full-potential linear muffin-tin-orbital (FP-LMTO) are respectively 0.9–2.4% underestimated and 1.2–2.5% overestimated compared with the experimental results [5, 17, 18] for the considered binary structures.

TABLE I

The equilibrium lattice parameter of binary InP, AlP compounds and ternary $Al_xIn_{1-x}P$ alloys. The present results are compared with previous experimental and theoretical calculations.

Material	WC	GGA	LDA	Exp.	Other
	(this work)				
InP	5.893	5.972	5.84	5.867 [17] 5.869 [5] 5.869 [18]	5.729 (PW-PP) [3] 6.014 (FP-LMTO) [2]
$Al_{0.25}In_{0.75}P$	5.788	5.856	5.74	–	5.909 (FP-LMTO) [2]
$Al_{0.50}In_{0.50}P$	5.683	5.740	5.64	–	5.792 (FP-LMTO) [2]
$Al_{0.75}In_{0.25}P$	5.582	5.628	5.54	–	5.664 (FP-LMTO) [2]
AlP	5.475	5.514	5.44	5.467 [17] 5.464 [5]	5.417 (PW-PP) [3] 5.534 (FP-LMTO) [2]

We have also presented our calculated bulk modulus, B_0, and comparison with theoretical [2] and experimental [17] results in Table II. As a result of the overestimation within the WC potential of the equilibrium lattice constants of the considered binary compounds, our calculations within the WC potential underestimate the bulk modulus of binary InP and AlP compounds compared to their experimental value of 71 [17] and 86 GPa [17], respectively. One can see that our calculated bulk modulus within the WC potential of binary InP and AlP are 5–13% larger and 3–8% smaller than our used GGA and LDA methods, respectively, due to lattice constant differences between these approaches. The value of B_0 within the WC potential of InP is 3.5% smaller than the value of 71 GPa obtained within experimental study [17] whereas for AlP compound the B_0 value within the WC potential is 1.4% larger than the experimental value of 86 GPa [17]. The B_0 values of both binary compounds from our WC, GGA and LDA calculations are presented in Table II with previous theoretical results [2] and available experimental data [17]. It is clearly seen from Table II, in particular, compared with other theoretical approach, GGA, LDA and FP-LMTO [2] the results of InP and AlP within the WC potential have the smallest error rate according to the experimental works [17]. To the best of our knowledge, there are no experimental results for bulk modulus for ternary $Al_xIn_{1-x}P$ alloys. However, our calculated bulk modulus results of ternary $Al_xIn_{1-x}P$ alloys within the WC, GGA and LDA method are larger than the FP-LMTO method value of 14–16% as shown in Table II as expected from underestimation of the lattice constants results.

TABLE II

The calculated bulk modulus of binary InP, AlP compounds and ternary $Al_xIn_{1-x}P$ alloys. The present results are compared with previous experimental and theoretical calculations (all results are in GPa).

Material	WC	GGA	LDA	Exp.	Other
	(this work)				
InP	68.474	59.697	73.701	71 [17]	60.250 (FP-LMTO) [2]
$Al_{0.25}In_{0.75}P$	73.378	66.033	75.726	–	61.458 (FP-LMTO) [2]
$Al_{0.50}In_{0.50}P$	76.378	71.632	80.033	–	65.575 (FP-LMTO) [2]
$Al_{0.75}In_{0.25}P$	84.627	79.200	84.760	–	72.485 (FP-LMTO) [2]
AlP	87.181	82.962	89.880	86 [17]	81.890 (FP-LMTO) [2]

TABLE III

The calculated high symmetry point energies of binary InP, AlP compounds and ternary $Al_xIn_{1-x}P$ alloys. The present results are compared with previous experimental and theoretical calculations (all energies are in eV).

Material	InP	$Al_{0.25}In_{0.75}P$	$Al_{0.50}In_{0.50}P$	$Al_{0.75}In_{0.25}P$	AlP
This work (WC)	0.48063				
Γ–Γ	1.6443	1.08004	1.47435	1.61989	3.1077
Γ–X		2.36529	2.46569	2.54229	1.45953
Other					
Γ–Γ (LDA) [4]	0.5647	1.0099	1.5819	1.578	3.3666
Γ–X (LDA) [4]	1.6479	2.3836	2.3997	2.5961	1.4658
Γ–Γ (GGA) [4]	0.2674	0.8315	1.4578	1.742	3.0881
Γ–X (GGA) [4]	1.8804	2.7014	2.5271	2.7014	1.6386
Exp.					
Γ–Γ	1.39[19], 1.35[20], 1.424[21], 1.35[3]	–	–	–	3.63 [22], 2.45 [20]
Γ–X	–				2.50 [22], 2.52 [23], 2.50 [21]

On the other hand, the electronic band structures for considered structures along the high symmetry directions in the BZ are obtained by using their equilibrium lattice parameters calculated with WC calculations. The energy level differences at different high symmetry points (Γ–Γ and Γ–X) are also listed in Table III. Our obtained results are consistent with the previous LDA and GGA results [4]. It is clearly seen that the obtained band gaps for studied binary compounds are smaller than experimental results [3, 19–23] for AlP and InP. This underestimation of the band gaps is mainly due to the fact that the simple form of GGA does not take into account the quasiparticle self-energy correctly [24] which makes them not sufficiently flexible to accurately reproduce both exchange and correlation energy and its charge derivative [4].

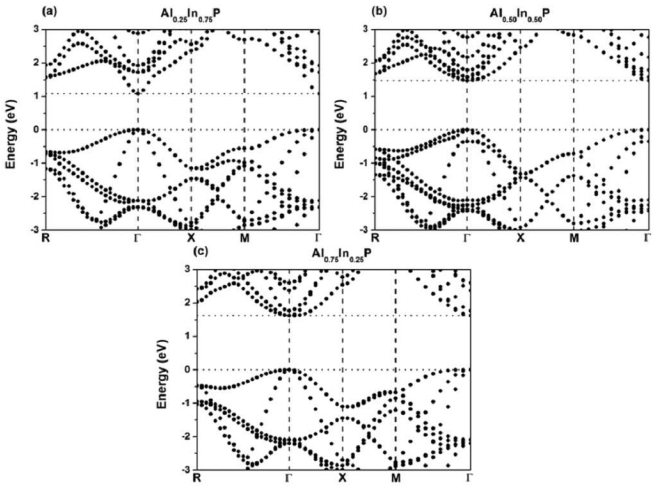

Fig. 1. The calculated electronic structure along several high-symmetry directions for ternary alloys (a) $Al_{0.25}In_{0.75}P$, (b) $Al_{0.50}In_{0.50}P$, (c) $Al_{0.75}In_{0.25}P$.

The calculated electronic structure along several high-symmetry directions for ternary alloys $Al_xIn_{1-x}P$ is displayed in Fig. 1 for the first time in the literature. In this figure, the Fermi level is set to 0 eV. The valence band maximum and the conduction band minimum occur at the Γ point indicating that these ternary materials have a direct band gap.

4. Conclusion

In this study, the structural and electronic properties of binary InP and AlP compounds and ternary alloys $Al_xIn_{1-x}P$ have been studied using Wu–Cohen GGA within the density functional theory as implemented in the WIEN2k. The obtained structural results of binary compounds are in good agreement with experimental and available theoretical studies. For ternary alloys $Al_xIn_{1-x}P$, the valence band maximum and the conduction band minimum occur at the Γ point indicating that these ternary materials have a direct band gap.

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