

## STUDY THE ELECTRONIC PROPERTIES OF $AlAs_xP_{1-x}$ NANOCRYSTAL ALLOYING COMPOSITION, USING DENSITY FUNCTIONAL THEORY

M. T. HUSSEIN<sup>a</sup>, A. RAMIZY<sup>b\*</sup>, B. K. AHMED<sup>b</sup>, H. A.FAYYADH<sup>a</sup>

<sup>a</sup>*Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq*

<sup>b</sup>*Department of Physics, College of Science, Al-Anbar University, Al-Anbar, Iraq*

The structural and the electronic properties of III-V zinc-blende AIP, AlAs semiconductors nanostructure and their alloying composition  $AlAs_xP_{1-x}$  have been studied in details using Ab-initio density functional theory (Ab-initio DFT) at the generalized gradient approximation (GGA) level. This has been coupled with large unit cell (LUC) approximation with STO-3G basis set. These calculations for 8 core atoms with concentration of ( $x=0, 0.25, 0.5, 0.75$  and  $1$ ) with 3D periodic boundary condition (PBC) effect on electronic properties such as energy gap valance and conduction band width and density of states were included. Gaussian 03 program are prepared to perform computation. Position and properties of atoms which compose these crystals has been used as input data. The final modified LUC-DFT equations are embodied in these computer routines and solved by iterative methods. Results show that the lattice constant and energy gap are increased with increasing the arsenide alloy concentration. The total energy, cohesive energy, electron affinity, ionization potential and ionicity has been reported for these concentrations.

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### 1.Introduction

Recently, III–V zinc-blende semiconductors compounds have become an area of great technological activity. The reason for this is the possibility of producing novel materials with adjustable electronic and magnetic properties. Among them, the aluminum compounds AlAs and their alloy  $AlAs_xP_{1-x}$  are concerned in this paper. AlAs is one of the most important electronic and optoelectronic materials because of its frequent incorporation into GaAs-based hetero structures [1,2]. Aluminum arsenide, with the largest direct gap of the III–V compound semiconductors, is undoubtedly the most “exotic” and least studied[1]. However, in recent years, it is attracted special attention to its incorporation in the AlAs/AIP and GaP/AIP based hetero structures. AlAs/AIP super lattices are attractive due to their potential applications in optoelectronic devices because they are expected to become direct band gap materials [3]. GaP/AIP-based hetero structures are attractive in their characteristics for the development of optoelectronic devices operating in the yellow-green spectral region [4,5] and are considered as an alternative to a GaN/AlGaIn system for the development of infrared semiconductor lasers and detectors [6]. Many research groups were used FP-LAPW method within local density approximation (LDA) of the exchange – correlation energy to calculate the electronic and optical properties respectively [6-9]. Briki et al, were studied the effects of relativistic on the structural and transport properties of III–V compounds utilizing LDA and PBE-GGA for the exchange– correlation energy [10, 11].

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\*Corresponding author: [asmat\\_hadithi@yahoo.com](mailto:asmat_hadithi@yahoo.com)

The objective of this work is to combine AlP and AlAs compounds which having different structural and electronic properties to obtain new materials. This could open a new and promising field if it transforms the material's properties by making them similar to the ternary  $AlAs_xP_{1-x}$  alloys with intermediate properties.

## 2. Theory and calculations

The basic idea of large unit cell (LUC) is in computing the electronic structure of the unit cell extended in a special manner at  $k=0$  in the reduced Brillion Zone. This equivalent to a band structure calculation at those  $k$ -point, which transform to Brillion Zone center on extending the unit cell. Using linear combination of atomic orbitals (LCAO), the crystal wave function uses the density functional theory at the generalized gradient approximation method level [11, 12].

Kohn-Sham density theory [11, 13] is widely used for self consistent – field electronic structure calculations of the ground state properties of atoms, molecules, and solids. In this theory, only exchange – correlation energy  $E_{XC} = E_X + E_C$  as a functional of the electron spin densities  $n_\uparrow(r)$  and  $n_\downarrow(r)$  must be approximated. The local spin density (LSD) approximation:

$$E_{XC}^{LSD}[n_\uparrow, n_\downarrow] = \int d^3r n \epsilon_{XC}^{unif}(n_\uparrow, n_\downarrow) \quad (1)$$

Where  $n = n_\uparrow + n_\downarrow$ , and the generalized gradient approximation (GGA) [14,15, 16].

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \quad (2)$$

In comparison with LSD and GGA's tend to improve total energy, atomization energies, energy barriers and structural energy differences.

To simplify particle calculations,  $\epsilon_{XC}^{unif}$  and  $f$  must be parameterized analytic functions. The exchange-correlation energy per particle of a uniform electron gas,  $E_{XC}^{LSD}(n_\uparrow, n_\downarrow)$ , is well established [17,18] but the best choice for  $f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$  is still a matter of debate.

Figs. 1 and 2 show the crystal structure of AlP and AlAs using 8 core atoms per LUC (cubic Bravais cell multiple).

The geometrical optimization calculations are performed with simultaneous optimization and complete convergence of maximum displacements, root mean square (RMS) displacements, maximum forces and RMS forces of all atoms in the nanocrystal. For example, RMS forces are optimized to less than 0.0003 Hartree/Bohr which is the standard convergence limit of Gaussian 03 program [19].

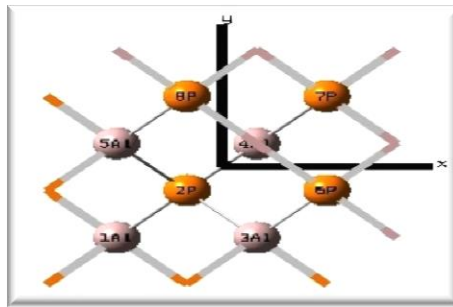


Fig.1 Structure of AlP using 8 core atoms per LUC by Gauss.View3.0w (cubic Bravais cell multiple)

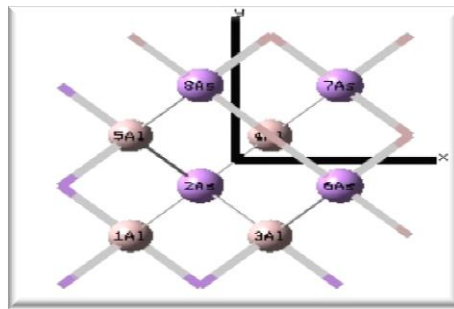


Fig.2 Structure of AlAs using 8 core atoms per LUC by Gauss.View3.0w (cubic Bravais cell multipl)

### 3. Results and discussion

Figs. 3 and 4 show the total energy as a function of the lattice constant optimization of 8 core atoms per LUC for AlP and AlAs respectively, while for  $\text{AlAs}_{0.5}\text{P}_{0.5}$  is shown in Fig.5. It is clear from these figures that the Stability of the nanocrystal is at equilibrium when lattice constant is equal to (0.53, 0.56) nm of AlP and AlAs , while it is equal ( 0.54) nm for  $\text{AlAs}_{0.5}\text{P}_{0.5}$  , and these indicate that the attraction and repulsion forces between atoms are equal [20-22].

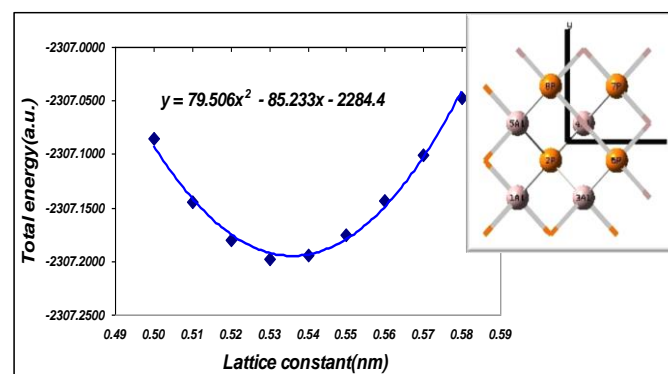


Fig. 3 Total energy as a function of lattice constant of AlP for 8 core atoms per LUC.

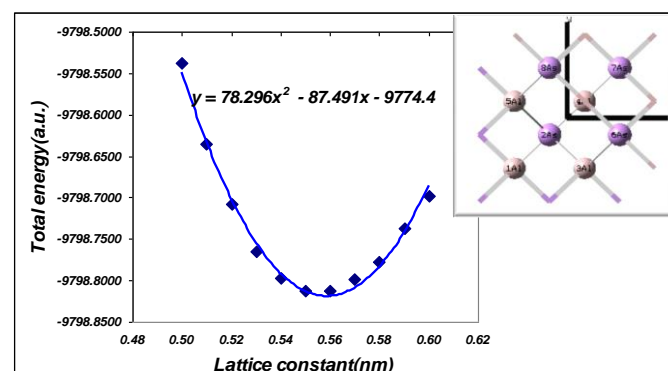


Fig . 4 Total energy as a function of lattice constant of AlAs for 8 core atoms per LUC.

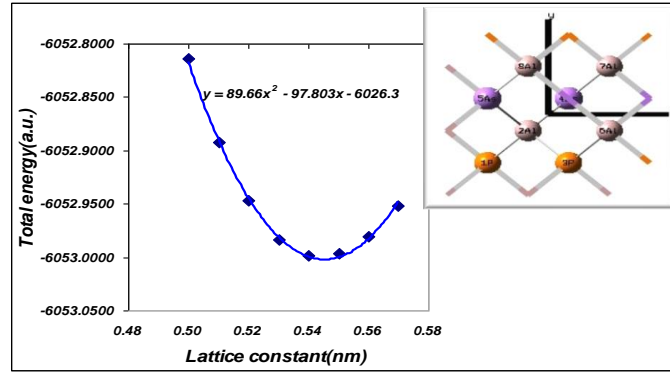


Fig. 5 Total energy as a function of lattice constant of  $AlAs_{0.5}P_{0.5}$  for 8 core atoms per LUC.

Fig. 6 shows the total energy of LUC increase (decreases with the negative sign) as concentrations of As atoms increased. This is reasonable case since the number of atoms increases the number of mutual interactions and this resulting in an increase in total energy. Arsenide atom is the heaviest atom in present ternary alloy that contains largest number of electrons. As a result the total energy increases with higher fractions of arsenide.

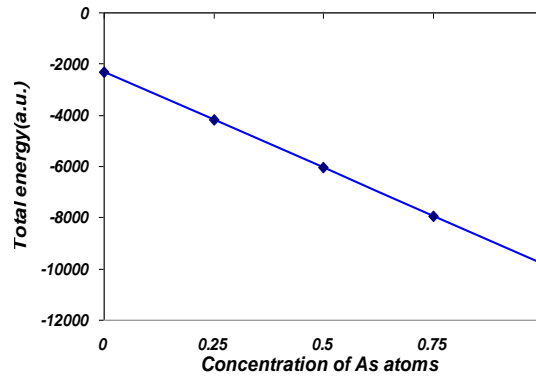


Fig.6 Total energy of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC.

Fig. 7 shows The cohesive energy increment as a function of concentrations of As atoms increased in the same behavior of the total energy. This can be understood by comparing experimental and theoretical cohesive energy of group V elements in periodic table [21,22,23]. The cohesive energy is given by:

$$E_{coh.} = E_T/n - E_{free} - E_0$$

Where  $E_T$  is the Total energy, while  $E_{free}$  is the free atom  $SP$  orbital shell energy [24]. The cohesive energy showed be corrected to the zero-point motion of the nuclei [25], but in this work we neglect  $E_0$  due to its small rate of correction compared with the total energy value.

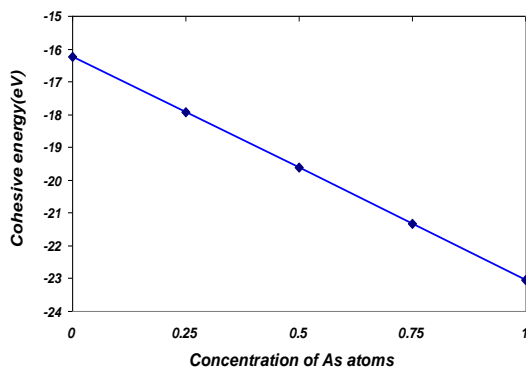


Fig . 7 Cohesive energy of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC.

Fig. 8 shows last HOMO (Ionization potential (I.P)) and first LUMO (electron affinity (E.A)) of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC which indicate that the energy value of ( E.A) is greater than (I.P) , while the energy of both AlP and AlAs are greater than other alloying composition .

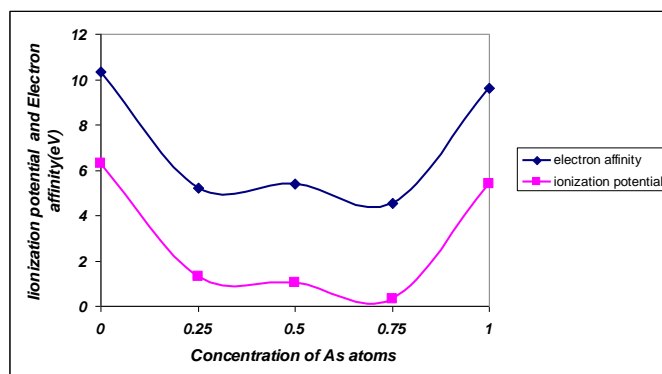


Fig . 8 Ionization potential and electron affinity of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC.

Fig. 9 shows the energy gap of the alloy composition of  $AlAs_xP_{1-x}$  which has been calculated using the following equation:  $E_g = | \text{LUMO} - \text{HOMO} |$  [26]. It is clear from this figure that the values of the energy are equal AlP (4.041eV ),  $AlAs_{0.25}P_{0.75}$  (3.896 eV),  $AlAs_{0.5}P_{0.5}$  (4.375 eV),  $AlAs_{0.75}P_{0.25}$  (4.234 eV) and AlAs (4.234 eV).

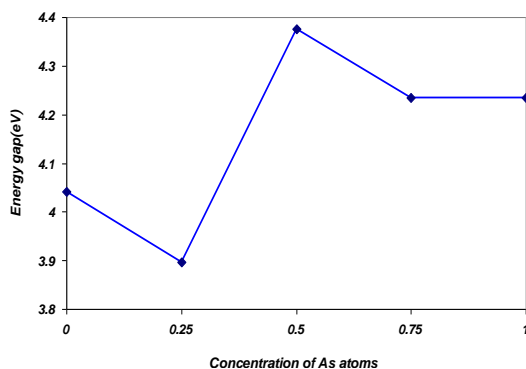


Fig . 9 Energy gap of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC.

The relation between the valence and conduction bands width as a function of concentrations of As atoms were calculated it's shown in Fig. 10. It is appear that the bands width decreased with increasing the concentrations of arsenide atoms. While, the valence band generally higher than conduction band and this are in a good agreement from the obtained results by [ 20,27,28,29].

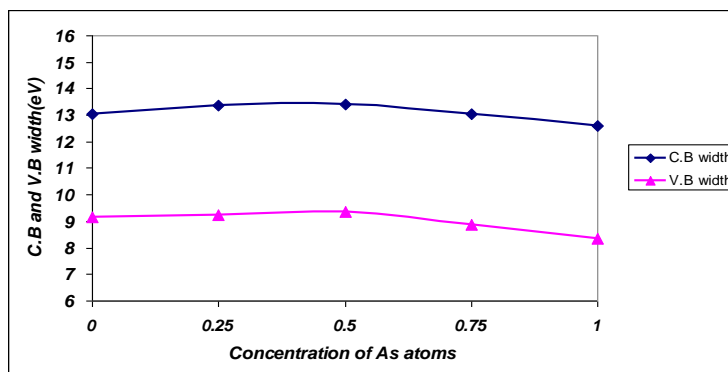


Fig . 10 Valence and conduction band widths of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC

Fig. 11 shows increment of lattice constant with fraction of arsenide. It is found that when  $x = 0$ , the lattice constant is about 0.53nm corresponds to AlP whereas, it is equal 0.56 nm for AlAs when  $x = 1$ . These results are corresponding to experimental bulk value of 0.545 and 0.565 nm for AlP and AlAs respectively [30,31]. The obtained value of lattice constant is acceptable taking into consideration the usual systematic error inhibited in molecular orbital calculations [32, 33] that underestimates this property especially for high atomic number elements such as germanium [34].

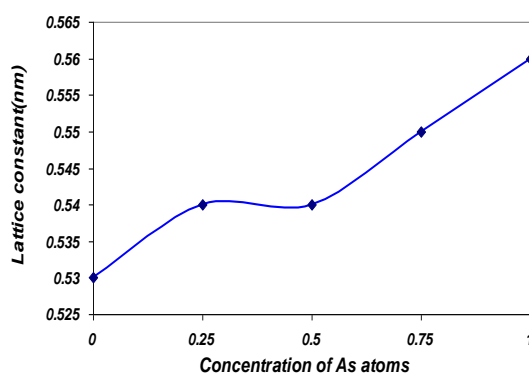


Fig . 11 Lattice constant of  $AlAs_xP_{1-x}$  alloying composition as a function of concentration of As for 8 core atoms per LUC.

Fig. 12 (a, b, c, d ,e) shows the Density of states as a function of orbital energy of the concentrations of As atoms. The density of states has maximum of (6, 5, 7, 9, 17) with concentration for ( $x=0, 0.25, 0.5, 0.75$  and 1) respectively for considered nanocrystals.

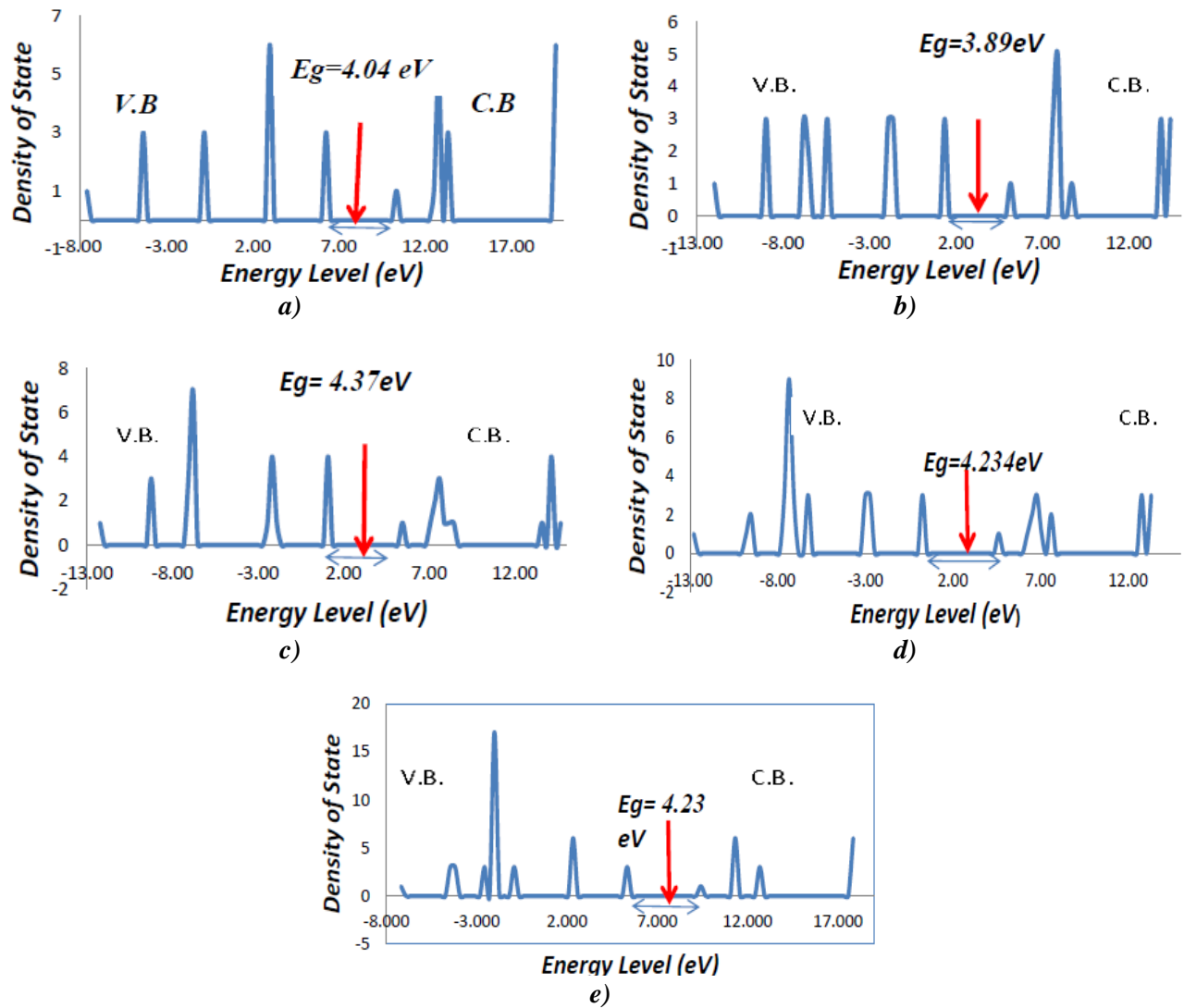


Fig. 12[a, b, c, d, e] Density of states of AlAs<sub>x</sub>P<sub>1-x</sub> alloying composition as a function of concentration of As for 8 core atoms per LUC. For AlP, (b) AlAs<sub>0.25</sub>P<sub>0.75</sub>, (c) AlAs<sub>0.5</sub>P<sub>0.5</sub>, (d) AlAs<sub>0.25</sub>P<sub>0.75</sub> (e) AlAs

Fig. 13 shows increment of maximum density of states with fraction of arsenide. It is clear from this figure that the density of state increases with increasing Arsenide atoms.

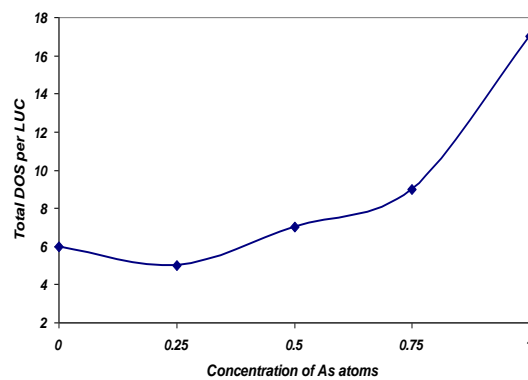


Fig. 13 Total DOS of AlAs<sub>x</sub>P<sub>1-x</sub> alloying composition as a function of concentration of As for 8 core atoms per LUC.

#### 4. Conclusions

The above results show that many properties of  $AlAs_xP_{1-x}$  nanocrystals change abruptly at the nanoscale. The obtained results show that the total energy and cohesive energy increase with increasing the arsenide concentration in  $AlAs_xP_{1-x}$  alloy. The energy gap varies a fluctuated value with respect to increasing the arsenide concentration. It is found that the equilibrium lattice constant and cohesive energy are in reasonable agreement with experimental result. The density of state increases with increasing the As concentration, While the valence and conduction bands decrease with increasing the arsenide concentration in  $AlAs_xP_{1-x}$  alloy Composition.

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