First principles calculations of Al As_xP_{1-x} ternary nanocrystal alloying composition

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Abstract

III-V zinc-blende AlP, AlAs semiconductors and their alloy Aluminum Arsenide phosphide Al As_xP_{1-x} ternary nanocrystals have been investigated using Ab- initio density functional theory (Ab-initio-DFT) at the generalized-gradient approximation (GGA) level with STO-3G basis set coupled with large unit cell method (LUC). The dimension of crystal is found around (1.56 – 2.24) nm at a function of increasing the sizes (8, 16, 54, 64) with different concentration of arsenide (x=0, 0.25, 0.5, 0.75 and 1) respectively. Gaussian 03 code program has been used throughout this study to calculate some of the physical properties such as the electronic properties energy gap, lattice constant, valence and conduction band as well as density of state. Results show that the lattice constant increases with the increasing in the arsenide concentration in the alloy. The total energy, cohesive energy, electron affinity and ionization potential as well as ionicity for these concentrations have been reported.

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حسابات المبادئ الاساسية لسبيكة ثلاثية المركب $AlAs_xP_{1-x}$ النانوية

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الخلاصة

تم في هذا البحث دراسة اشباه الموصلات AlP و AlAs وسبيكتهما النانوية $AlAs_xP_{1-x}$ والتي تمثل بالتركيب Zinc-blende المكعب والمجموعة V-III والتي تتحقق من خلال استخدام طريقة Ab-intio ونظرية دالية الكثافة وتقريب الانحدار المعمم ولاحجام مختلفة باستخدام الدالة الموجية STO-3G بالارتباط مع طريقة خلية الوحدة الكبيرة. وحيث وجد ان طول البلورة النانوية يتراوح بين nm (2.24 - 1.56) كدالة لزيادة الاحجام (8, 16, 54, 64) ولتراكيز مختلفة للارسنايد (1 ,0.75 ,0.5 ,0.25 ,0) على التوالي. وباستخدام برنامج Gaussian03 والذي يستخدم لدراسة بعض الخصائص الفيزيائية. حيث تم دراسة بعض الخصائص الالكترونية ومنها فجوة الطاقة، ثابت الشبيكة، حزمتي التكافؤ والتوصيل وكثافة الحالة. اظهرت النتائج زيادة في ثابت الشبيكة بزيادة التركيز للارسنايد. اما بالنسبة لكل من الطاقة الكلية وطاقة الترابط والالفة الالكترونية وطاقة التاين بالاضافة للتاينية فقد تم دراستها مع تغيير التركيز.

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Introduction

Aluminum arsenide (AlAs) is one of the most important electronic and optoelectronic materials because of its frequent incorporation into GaAs-based heterostructures [1, 2]. AlAs is a wide-gap semiconductor with a band structure and crystallize in the zinc-blende. The two semiconductors AlAs and AlP form a continuous series of

alloys denoted by Al $As_{1-x} P_x$, where x is the mole fraction of AlAs in the alloy, AlAs/AlP super lattices are attractive due to their potential applications in optoelectronic devices because they are expected to become direct band gap materials [3].

AlAs is a subject of extensive theoretical studies ranging from the semiempirical to the first principles methods [4], within the density functional theory framework using both pseudo potential [5], and all electron approaches. For the bulk properties of AlAs, theoretical calculations based on, the Hartree-Fock, and potential model have obtained a very good description of its structural and electronic properties [6, 7].

Recently, Annane et al. [8] investigated the structural and electronic properties of AlAs and AlP compounds using the full potential linearized augmented plane wave plus local orbitals method based on density functional theory.

In the present work, the electronic structure of Al As_xP_{1-x}NCs core part with different sizes(8, 16, 54and 64) and concentrations using an ab-initio density functional theory(DFT) method coupled with large unit cell method (LUC-DFT). LUC method was formulated and used for several kinds of bulk materials including diamond and zinc-blende structured materials [9, 10].

Theory

The central equation that describes the interaction of the electrons and the nuclei of a many-body system is the time-independent, non-relativistic form of the Schrödinger equation. In the most common formulation of quantum mechanics, solving this problem means solving the N-electron Schrödinger equation:

$$\hat{H}\,\psi = E\,\psi \tag{1}$$

This equation involving the Hamiltonian operator $\hat{H}$, Ψ the wave function, and the Eigen value E. Here, we will focus on finding the ground state of the system; that is, the Eigen function Ψ that gives the lowest energy E.

Several theories gave approximate solutions to calculate the electronic structure properties for Al As_xP_{1-x}nanocrystal for core atoms 8, 16, 54 and 64, one of these powerful theories is the density functional theory (DFT). It gives a superior accuracy to Hartree-Fock theory, Ab-initio and the semi-empirical approaches. The Slater Type Orbitals (STO-3G) basis set is used in the calculation. These calculations were carried out using the Gaussian 03 software package [11]. The central quantity in DFT is the electron density $\rho(r)$. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables (x=r,s):

$$\rho(\mathbf{r}) = N \int \cdots \int \left| \psi(x_1, x_2, ..., x_N) \right|^2 ds_1 \, dx_2 \, dx_3 \cdots dx_N \tag{2}$$

where $\rho(r)$ is the probability of finding any of the N electrons within a volume element dr. Because $\rho(r)$ represents the probability, this means that $\rho(r)$ is a non-negative function and vanishes at infinity and integrates to the total number of electrons N.

Kohn-Sham density theory 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 [12]. The local spin density (LSD) approximation:

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

where $n = n_\uparrow + n_\downarrow$, and the generalized gradient approximation (GGA) [13,14].

$$E_{XC}^{.GGA}[n_\uparrow, n_\downarrow] = \int d^3r \; f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) (4)$$

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

To simplify particle calculations, $\in_{XC}^{unif}$ 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 [15] but the best choice for $f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$ is still a matter of debate.

Results and discussion

Figs. 1 and 2 show total energy for 54 and 64 atoms respectively for Al As$_x$P$_{1-x}$ nanocrystal as a function of lattice constant, from which the equilibrium lattice constant is obtained.
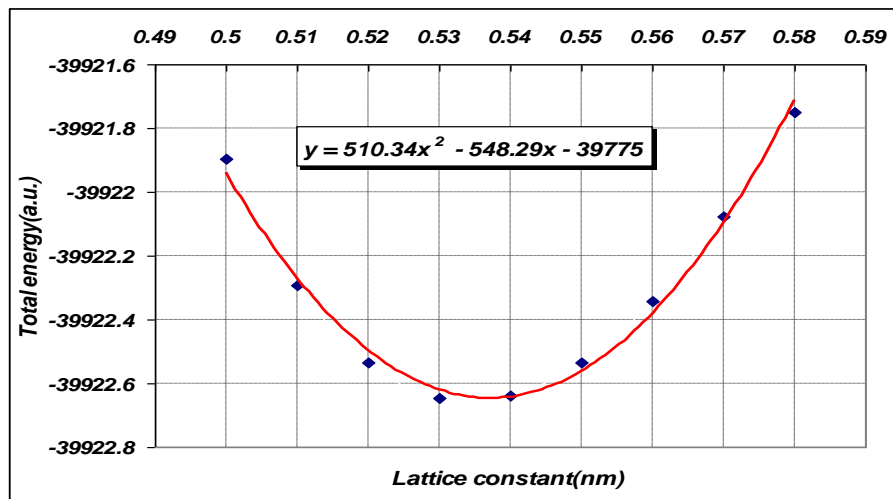

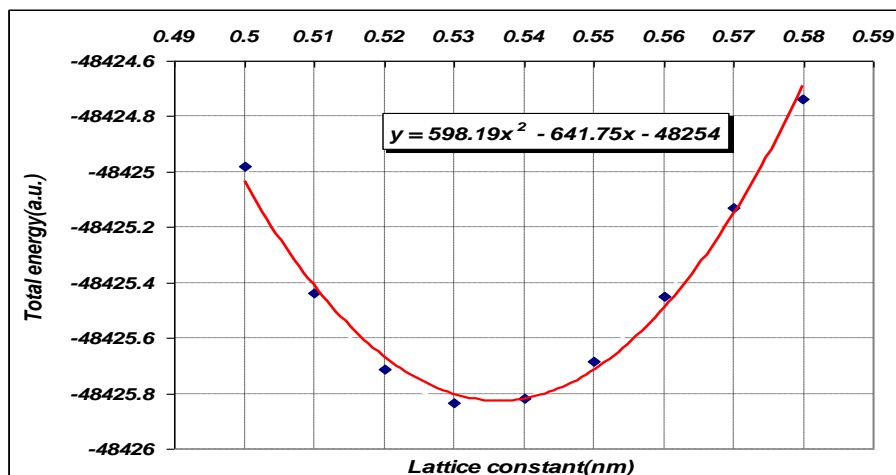Fig. 1: Total energy of 54 atoms of Al As$_{0.5}$P$_{0.5}$nanocrystal core as a function of lattice constant.

$y = 510.34x^2 - 548.29x - 39775$

Fig. 2: Total energy of 64 atoms of Al As$_{0.5}$P$_{0.5}$nanocrystal core as a function of lattice constant.

$y = 598.19x^2 - 641.75x - 48254$

In order to simulate zinc-blende nanocrystals electronic structure using LUC method two kinds of cells are available: primitive and Bravais cell multiplets. The main difference between these two kinds of cells is the shape and its associated surfaces. Primitive cells are parallelograms while Bravais cells are cubic in shape [16].

As shown in Fig. 3, the total energy of LUC increases (decreases with the negative sign) as the total number of atoms as well as the number of arsenide atoms increases. The obtained results appear to be reasonable as well as the number of atoms increases beside to that the number of mutual interactions resulting in an increase in total energy.
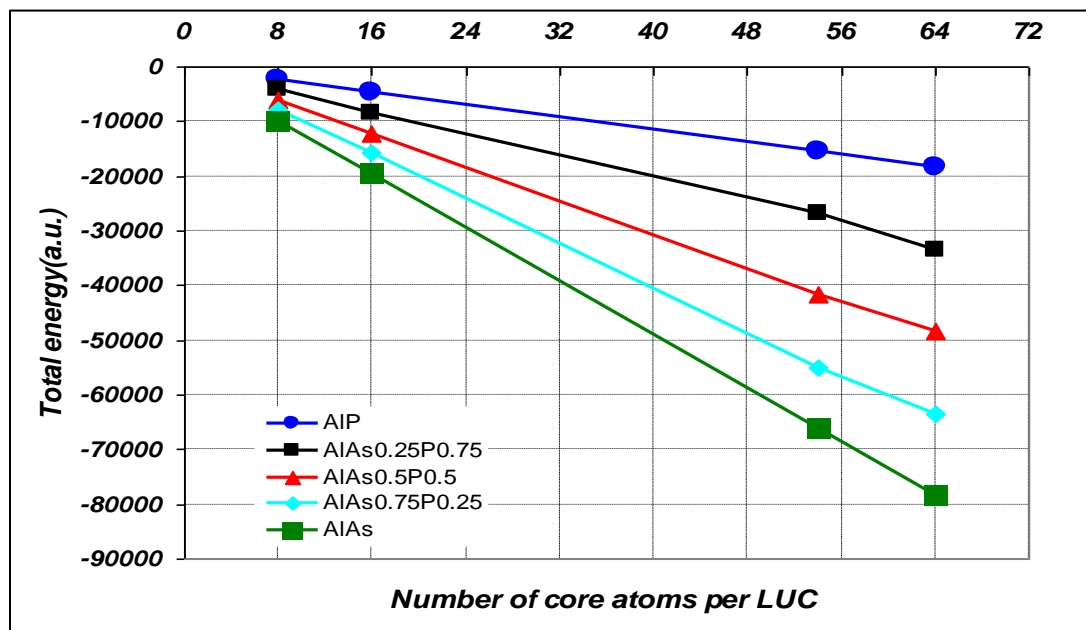

Fig.3: Total energy of Al As_xP_{1-x} alloying composition as a function of number of core atoms per LUC.

These results reflect the strong contribution of kind and number of atoms. The cohesive energy increment shown in Fig. 4as a function of number of atoms also holds for the same reason of total energy. However, the cohesive energy increases as a function of *as*

fraction instead of *P*, this arise from the fact that the elements of the same column tend to have greater affinity as they become lighter. This can be understood by comparing experimental and theoretical cohesive energy of group IV and V elements [10, 13, 17].
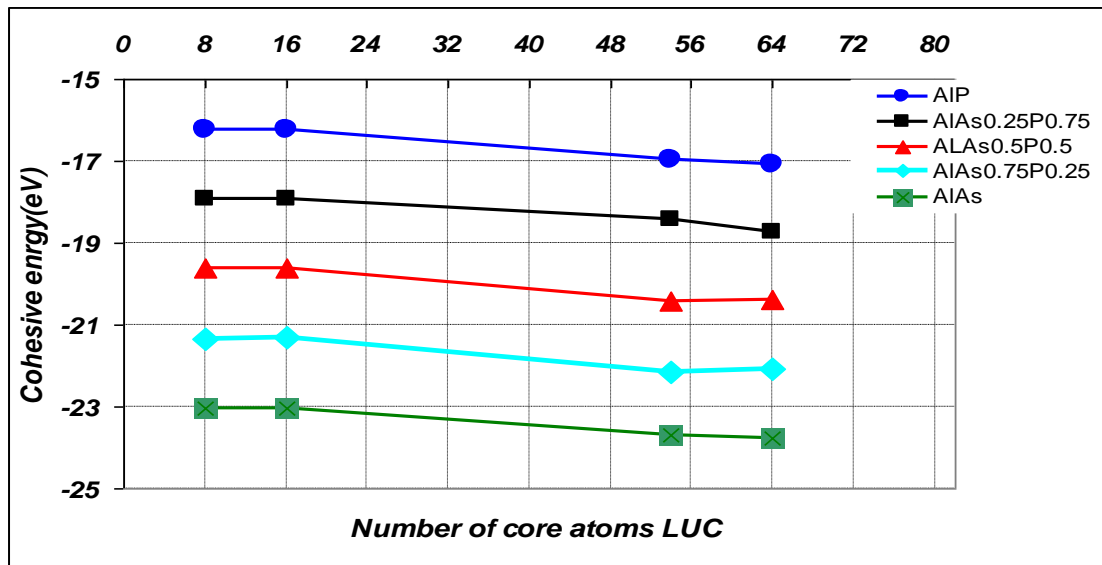
Fig.4: Cohesive energy of Al As$_x$P$_{1-x}$ alloying composition as a function of number of core atoms per LUC.

Fig. 5 shows increment of lattice constant with fraction of Arsenide. It is appear that the lattice constant decreases with increasing number of core atoms. This behavior has been found in several previous LUC results and also found experimentally for diamond [13, 18-20].
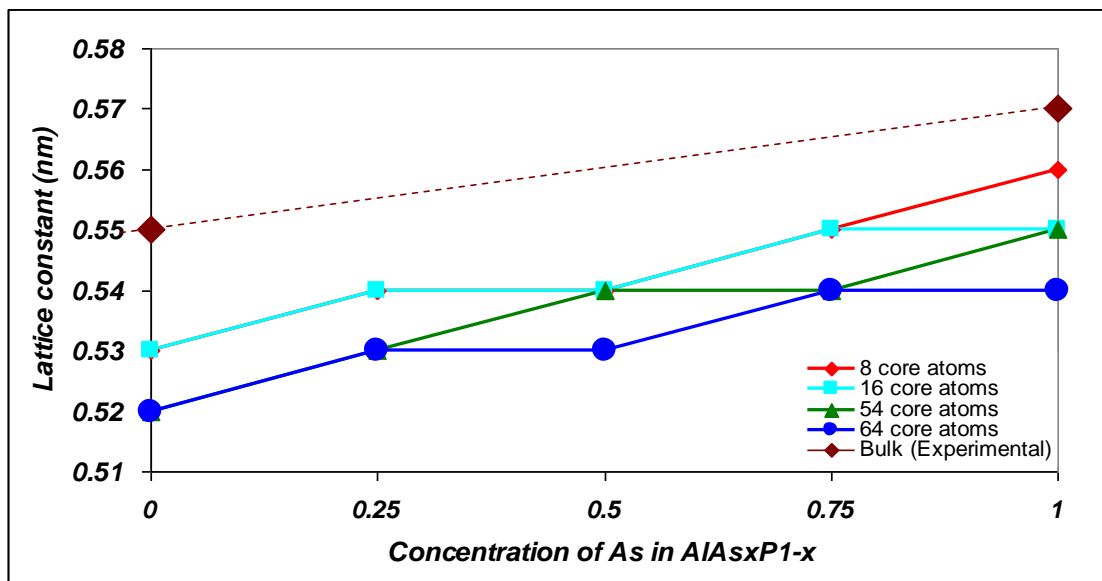

Fig.5: Lattice constant of Al As$_x$P$_{1-x}$ alloying composition as a function of concentration of As.

Fig. 6 shows the energy gap of 16 core atoms primitive parallelepiped cell multiple is greater than 64 core atoms cubic Bravais cell multiple with different concentration of Arsenide.
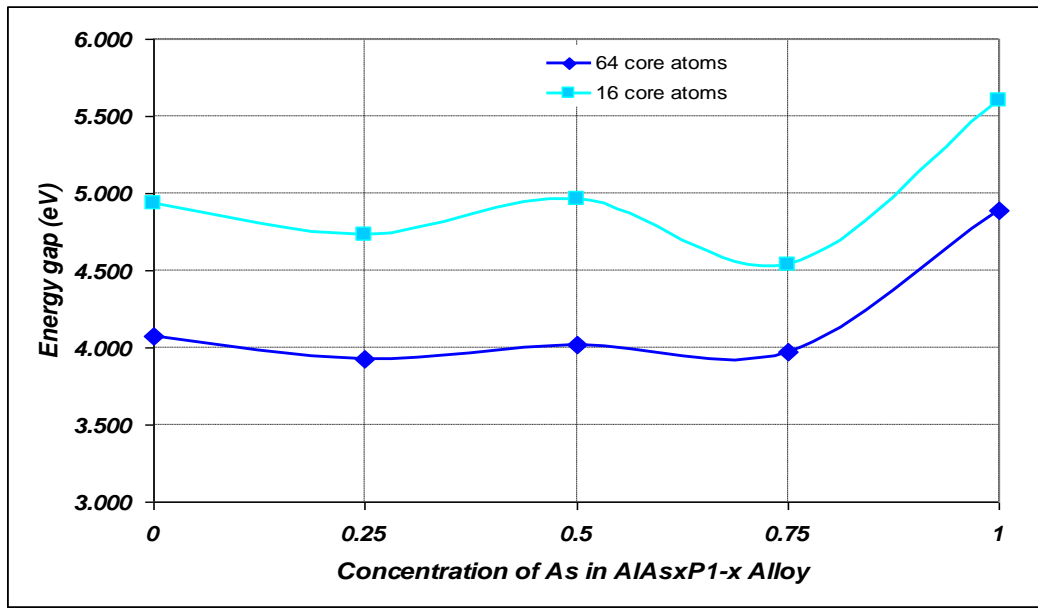
Fig. 6: Energy gap of Al As$_x$P$_{1-x}$ alloying composition as a function of concentration of As for 16 and 64 core atoms per LUC.

Fig. 7 shows the iconicity of Al As$_x$P$_{1-x}$ as a function of core atoms. It is clear from figure that the shape effect not found and this in agreement with previous results LUC calculations for other Nano crystals [15, 21]. However, some fluctuations for 8 atoms LUC in present work show that small number of atoms is associated with small number of basis state expansion might have errors that change expected results for some quantities such as present atomic charge.
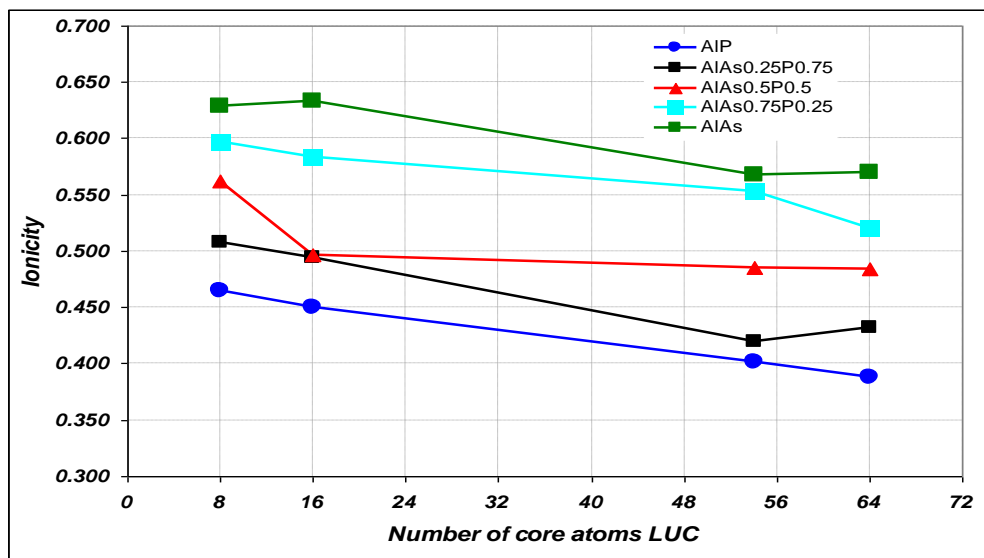

Fig.7: Ionicity of Al As$_x$P$_{1-x}$ alloying composition as a function of number of core atoms per LUC.

Fig.8 shows the density of states as a function of orbital energy. The degeneracy of states has been maximum values of (63 and 58) for 54 and 64 core atoms per LUC respectively. The high degenerate states seen in the core reflects the high symmetry.
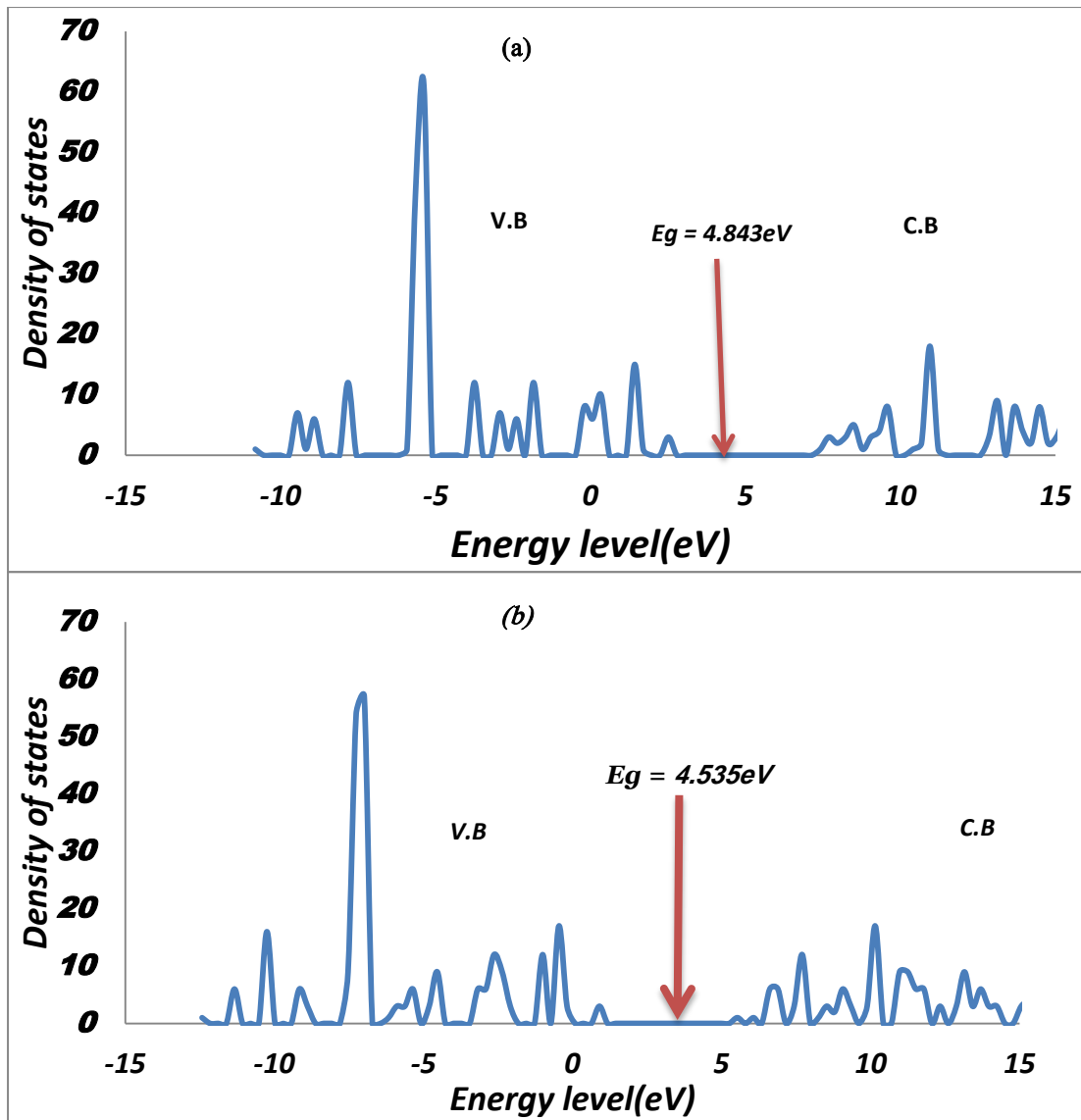
Fig. 8: Density of states of (a) 54 and (b) 64 atoms of core part of AlAs$_{0.75}$P$_{0.25}$ Nano crystals. The energy gap is shown between the conduction and valence bands.

Fig. 9 displays maximum density of states as a function of number of core atoms for various size and concentrations. This figure is very similar to that of the band gap. Low symmetry causes the split of equal energy (degenerate) states [22, 23]. However, this is not the only factor that affects energy gap it has also found that the concentration of Arsenide increases the energy gap.
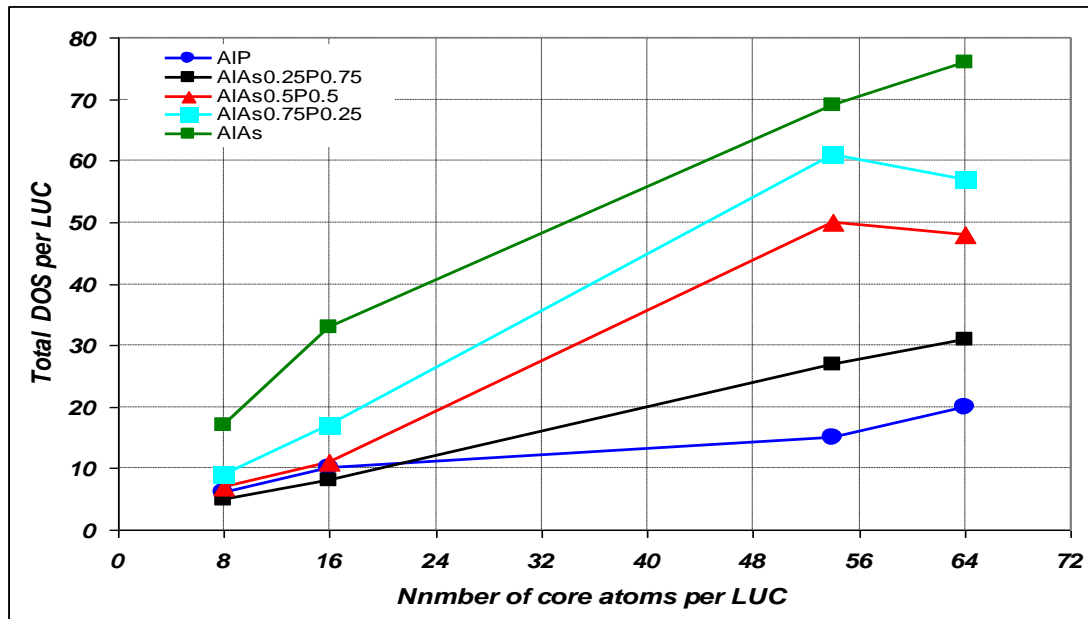
Fig .9: Density of state of AlAs$_x$P$_{1-x}$ alloy composition as a function of the number of core atoms per LUC.

Fig. 10 shows variation between arsenide concentration and wavelengths of 16 and 64 core atoms that corresponds to minimum energy gap. It's appear that the wavelength for AlAs$_{0.5}$P$_{0.5}$is between the values of the wavelength of AlP and AlAs while other concentrations (x = 0.25 and 0.75) are of higher value of wavelength, these results are in agreement with nanocrystals extended to bulk properties [24].
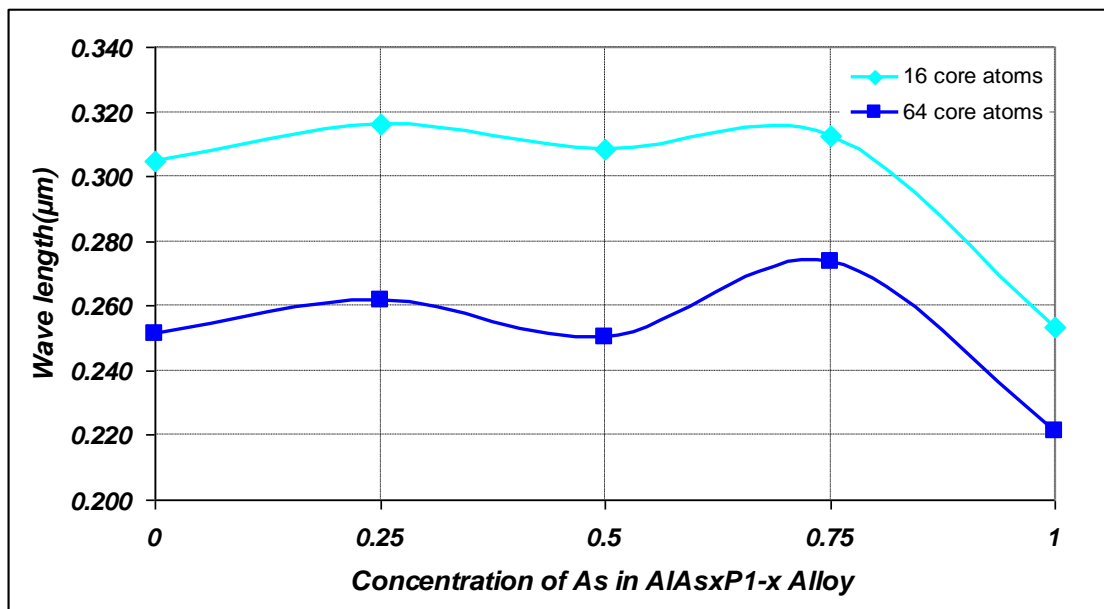

Fig.10: Variation of threshold absorption wavelength of AlAs$_x$P$_{1-x}$ alloying composition as a function of concentration of As for 16 and 64 core atoms per LUC.

Conclusions

In this study, the structural and electronic properties of binary AlP and AlAs compounds and ternary $AlAs_xP_{1-x}$ alloys as a function of the core size and concentration are presented using density-functional theory with in different approximations of exchange-correlation energy. It was found that some properties are only affected by the size and alloying percentage such as total energy, cohesive energy and ionicity. Other quantities are affected by shape such as lattice constant in addition to size and concentration. Density of stats shows highest degeneracy of states of Arsenide concentration (X=1 and 0), which corresponding to AlP and AlAs respectively. Other concentrations have lower degenercey of states and symmetry.

References

[1] I. Vurgaftman, J. R. Meyer, L. R. Ram-Mohan, Journal of Applied Physics, 89, 11 (2001) 5815-5875.

[2] S. Adachi, GaAs and Related Materials: Bulk Semiconducting and Superlattice Properties, World Scientific, Singapore (1994).

[3] T. Ohnuma, M. Nagano, Jpn. J. Appl. Phys. 39, L972 (2000) 154-162.

[4] A. Mujica, A. Rubio, A. Munoz, R. Needs, Reviews of Modern Physics, 75, 3 (2003) 863-912.

[5] A. Mujica, P. Rodr´ıguez-Hern´andez, S. Radescu, R. J. Needs, A. Mu˜noz, Physica Status Solidi B, 211, 1 (1999) 39-43.

[6] S. Froyen and M. Cohen, Physical Review *B*, 28, 6 (1983) 3258–3265.

[7] A. Jivani, H. Trivedi, P. N. Gajjar, A. Jani, Pramana, 64, 1 (2005) 153-158.

[8] F. Annane, H.Meradji, S. Ghemid, F. El Haj Hassan, Computational Materials Science, 50, 2 (2010) 274-278.

[9] M. A. Abdulsattar and K. H. Al-Bayati, Phys. Rev. *B*75, 24 (2007) 5201.

[10] M. A. Abdulsattar, Physica *E*41, (2009) 1679.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian 03, Revision B.01, Gaussian, Inc., Pittsburgh, PA, (2003).

[12] S.J. Sque, R. Jones, P.R. Briddon, Phys. Rev. B 73, 085313 (2006).

[13] R. Evarestov, M. Petrashen, E. Lodovskaya, Phys. Status Solidi(B), 68 (1975) 453-461.

[14] A. Harker, F. Larkins, J. Phys. C 12 (1979) 2487-2495.

[15] N. H. Aysa, M. A. Abdulsattar, A.M. Abdul-Lettif, Micro & Nano Letters 6 (2011) 137-140.

[16] O.IbtesamRadi, Mudar A. Abdulsattar, Ahmed M. Abdul-Lettif, Phys. Status Solidi (B) 244 (2007) 1304-1317.

[17] Mohammed T. Hussein, Bushra A. Hassan, Thekra K. Abdul Raheam, Hassan B. Jasim, IJAIEM, 2, 5 (2013) 2319-4847.

[18] Ali Bentouaf, Mohammed Ameri, Rezki Mebsout, Djelloul Hachemane, American Journal of Condensed Matter Physics, 2, 5 (2012) 126-134.

[19] Mohammed T. Hussein, T. K. Abdul Raheam, Askandar K. Kaka, International Journal of Thermal Technologies, 5, 1 (2015) 18-22.

[20] M. T. Hussein, T. Kasim, M. A. Abdulsattar, Indian J. Phys., 87, 11 (2013) 1079-1085.

[21] M. Abdualsattar Electronic Materials Lettters, Vol 6, 3 (2010).

[22] H.M. Abduljalil, M.A. Abdulsattar, S.R. Al-Mansoury, Micro & Nano Lett., 6 (2011) p 386.

[23] Mohammed T. Hussein, Akram H. Taha, Thekra Kasim, Iraqi Journal of Physics, 10, 17 (2012) 23-28.

[24] A. R.Degheidy, A. M. Elabsy, H. G.Abdelwahed, E. B.Elkenany Indian J. Phys., 86 (2012) p. 363.