

Ab-initio Density Functional Theory Core and Concentration of Al As_x P_{1-x} Nanocrystal Alloying Composition

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Abstract— Ab-initio Density function theory (DFT) method which coupled with Large Unit Cell (LUC) approximation have been used to simulate electronic structure properties. III-V zinc-blende AIP, AlAs semiconductors and their alloy Aluminum Arsenide phosphide Nano crystals structure of dimensions (1.62 – 2.12)nm which has been calculated as a function of concentration of arsenide (x=0, 0.25, 0.5, 0.75 and 1) and sizes(8, 16, 54 and 64) nanocrystals core atoms respectively. Gaussian 03 code program has been used throughout this study to calculate a physical properties such as energy gap, lattice constant, valence and conduction band as well as density of state (DOS). 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.

Index Terms— Ab-initio, DFT, Al As_x P_{1-x} alloying composition.

1 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 AIP 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/AIP superlattices 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 pseudopotential [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 AIP 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_x P_{1-x} NCs core part with different sizes(8, 16, 54 and 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].

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2 THEORY

The large unit cell method is a super cell method that is restricted to the $k=0$ point in the wave vector space. This method gets benefit from the fact that after some critical size (usually 1 nm in diameter) of the nano crystal, a core with ideal bulk structure is formed that has high symmetry and does not need to go through the geometrical optimization routine usually done in computing molecular or nanoscale electronic properties. On the other hand, the nanocrystal surface still needs to be geometrically optimized. The $k=0$ restriction is an essential part of the theory of LUC since quantum dots are restricted to one point in space and does not need to sum contributions from other points in real or reciprocal space as is usually done in bulk calculations[9-17].

Semiempirical methods were usually the choice in the older calculations of LUC method because of computational time consumed in repeating the central cell in three dimensional space. At the present time most calculations are reported with ab initio Hartree-Fock method [9-15]. Correlation corrections are rarely added because of computational time needed using quantum chemistry programs such as the present Gaussian 03 code program [18,19]. The present LUC-DFT is an exception from the previous literature. Note that the difference between super cell methods for bulk electronic structure calculations and the present nanocrystal core electronic structure calculations is the restricted periodicity to the size of the core part of the nanocrystal [15, 16, 20, 21].

In order to simulate zinc-blende nanocrystals electronic structure using LUC method two kinds of cells are available: primitive and Bravais cell multiplets (Fig. 1 and 2 respective-

ly). 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 [17]. This difference in shape results in many fluctuations in the electronic structure of diamond or zinc-blende structured materials [10-16]. Three primitive cell multiplet cores are investigated namely 16, 54 and 128 atoms. Two Bravais cell multiplet cores are investigated namely 8 and 64 atoms. The next Bravais large unit cell (216 atoms) is out of the Gaussian 03 program memory capabilities [19]. For details on the properties of these cells we can refer particularly to reference [20] in addition to the previously mentioned LUC references.

The generalized gradient approximation (GGA) coupled with large unit cell method is used to evaluate the electronic structure of $AlAs_xP_{1-x}$.

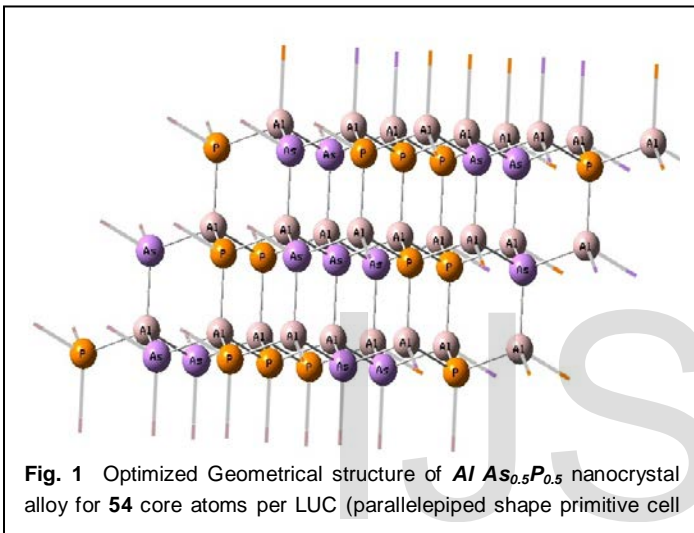


Fig. 1 Optimized Geometrical structure of $AlAs_{0.5}P_{0.5}$ nanocrystal alloy for 54 core atoms per LUC (parallelepiped shape primitive cell)

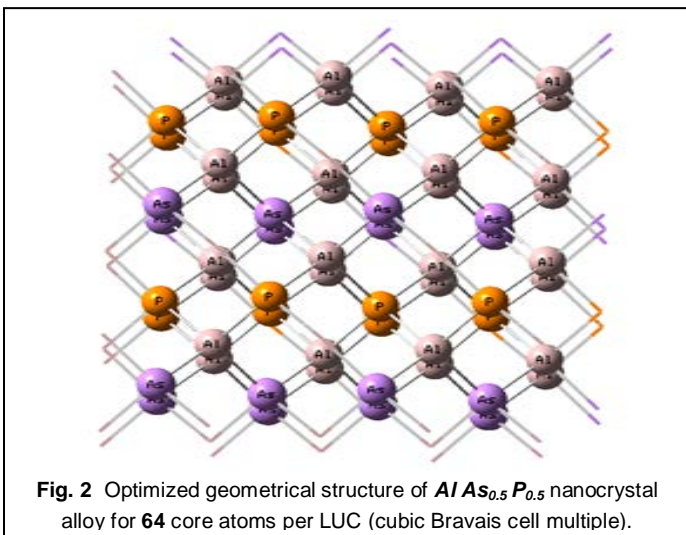


Fig. 2 Optimized geometrical structure of $AlAs_{0.5}P_{0.5}$ nanocrystal alloy for 64 core atoms per LUC (cubic Bravais cell multiple).

3 Results and discussion

Figures 3 and 4 show total energy for 54 and 64 atoms respectively for $AlAs_xP_{1-x}$ nanocrystal as a function of lattice constant, from which the equilibrium lattice constant is obtained.

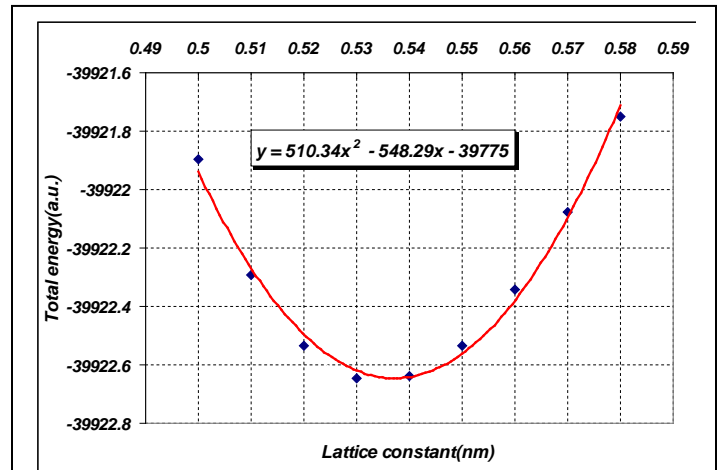


Fig. 3 Total energy of 54 atoms of $AlAs_{0.5}P_{0.5}$ nanocrystal core as a function of lattice constant.

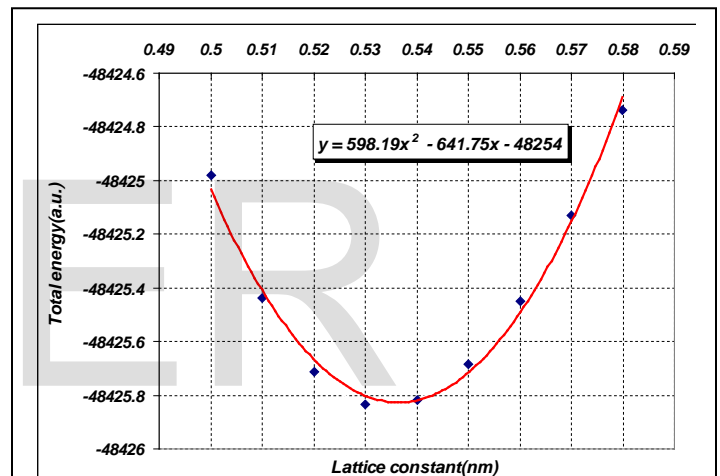


Fig. 4 Total energy of 64 atoms of $AlAs_{0.5}P_{0.5}$ nanocrystal core as a function of lattice constant.

As shown in Fig. 5, 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.

These results reflect the strong contribution of kind and number of atoms. The cohesive energy increment shown in Fig. 6 as 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 [10,11,22].

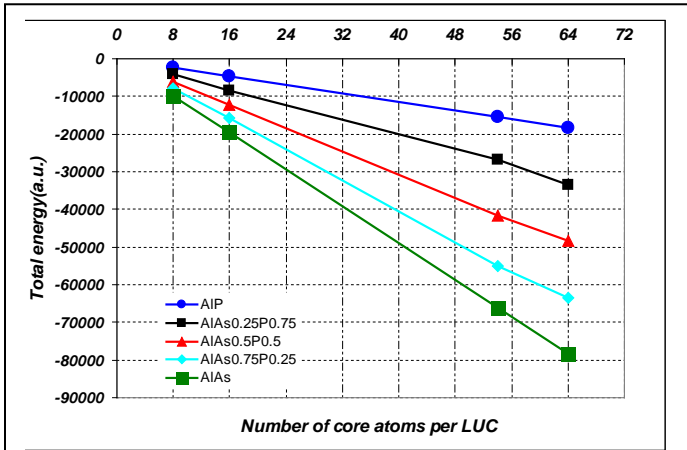


Fig. 5 Total energy of $AlAs_xP_{1-x}$ alloying composition as a function of number of core atoms per LUC.

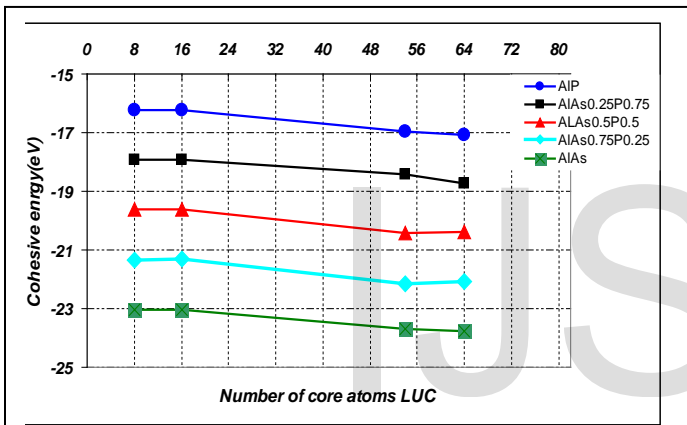


Fig. 6 Cohesive energy of $AlAs_xP_{1-x}$ alloying composition as a function of number of core atoms per LUC.

Fig. 7 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 [11,23-25].

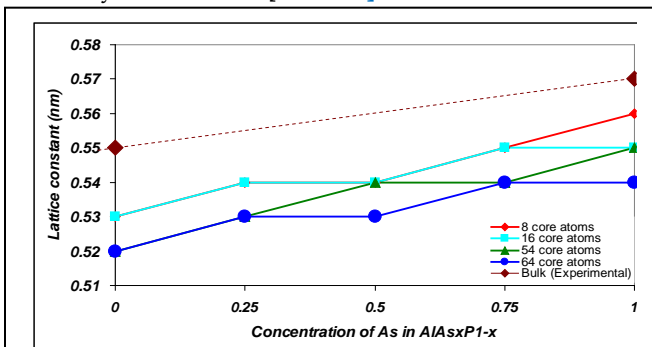


Fig. 7 Lattice constant of $AlAs_xP_{1-x}$ alloying composition as a function of concentration of As.

Fig. 8 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.

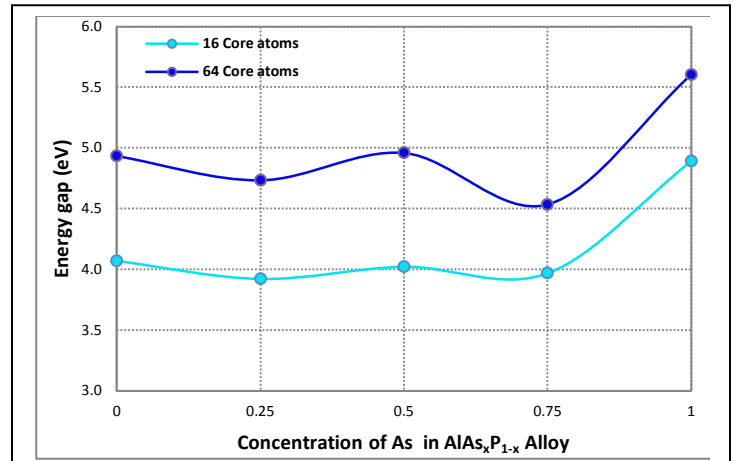


Fig. 8 Energy gap of $AlAs_xP_{1-x}$ alloying composition as a function of concentration of As for 16 and 64 core atoms per LUC.

Fig. 9. Shows the ionicity of $AlAs_xP_{1-x}$ 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 [16,26]. 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.

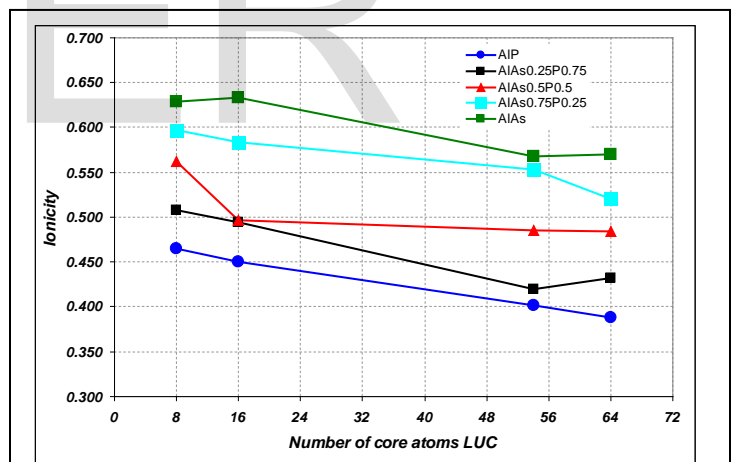


Fig. 9 Ionicity of $AlAs_xP_{1-x}$ alloying composition as a function of number of core atoms per LUC.

Fig. 10 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.

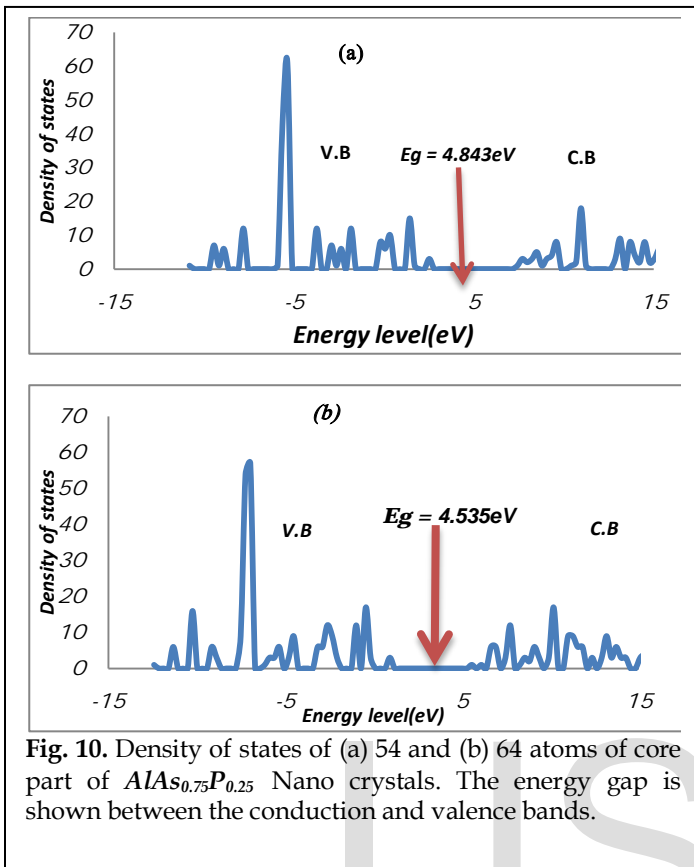


Fig. 10. Density of states of (a) 54 and (b) 64 atoms of core part of $AlAs_{0.75}P_{0.25}$ Nano crystals. The energy gap is shown between the conduction and valence bands.

Fig. 11 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 [27,28].

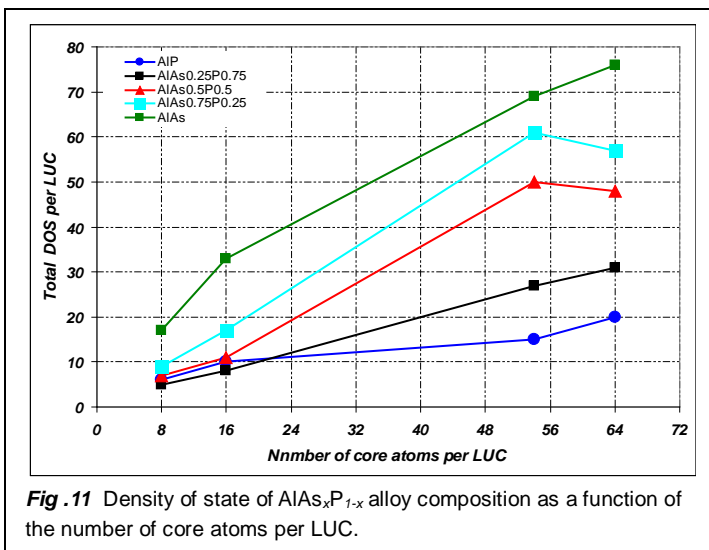


Fig. 11 Density of state of $AlAs_xP_{1-x}$ alloy composition as a function of the number of core atoms per LUC.

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. 12 shows variation between arsenide concentration and wavelengths of 16 and 64 core atoms that corresponds to minimum energy gap. It appears 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 Nano crystals extended to bulk properties [29].

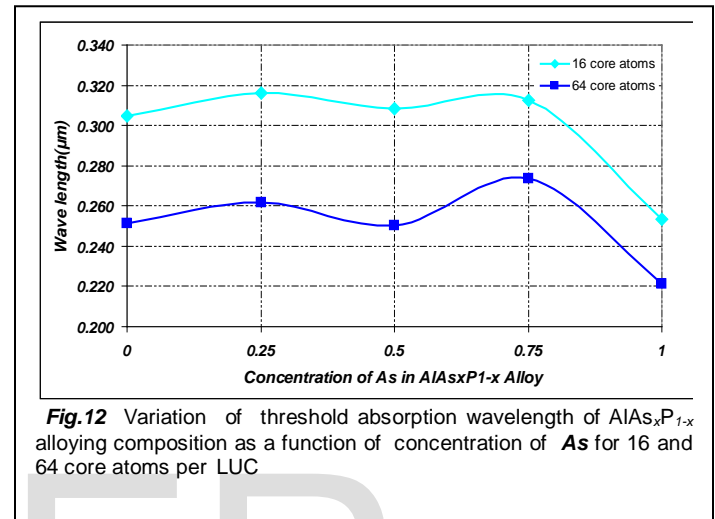


Fig. 12 Variation of threshold absorption wavelength of $AlAs_xP_{1-x}$ alloying composition as a function of concentration of **As** for 16 and 64 core atoms per LUC

4 CONCLUSION

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 within 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 degeneracy of states and symmetry.

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