Simulation of Electronic Structure of Gallium Phosphide Nanocrystals Using Ab Initio Density Functional Theory/3-21

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Abstract

Ab initio (Ab –initio is the Latin term for "from first principles", or "from scratch this name is given to computations which are derived directly from theoretical principles, with no inclusion of experimental data.) restricted Hartree-Fock method coupled based methods as well as Density functional theory is used to determine the electronic structure and physical properties of Gallium phosphide (GaP) nanocrystals with used diamondoids structure begin Diamantane, Tetramantane and Hexamantane with different sizes are investigated. Investigated properties include cohesive energy, dihedral angle, bond length, tetrahedral angle, and degeneracy of energy levels. Results revealed that electronic properties converge to some limit as the size of the Gallium phosphide material in several properties. Increasing nanocrystals size also resulted in a decrease in cohesive energy (absolute value) decreased with increased NO. of atoms, the dihedral angle and tetrahedral are nearest of the ideal value. Bond length was very close of the experiment value.

1. Introduction

Semiconductor nanostructures have been of particular interest because confinement effects lead to large increase in the band gap and efficient light emission [1]. Nano particles are of wide interest due to their potential use diverse commercial applications [2, 3]. Gallium phosphide (GaP), a phosphide of gallium, is a compound semiconductor material with an indirect band gap. Nanocrystals are excellent materials in many electronic devices. Gives it superiority in light-emitting devices

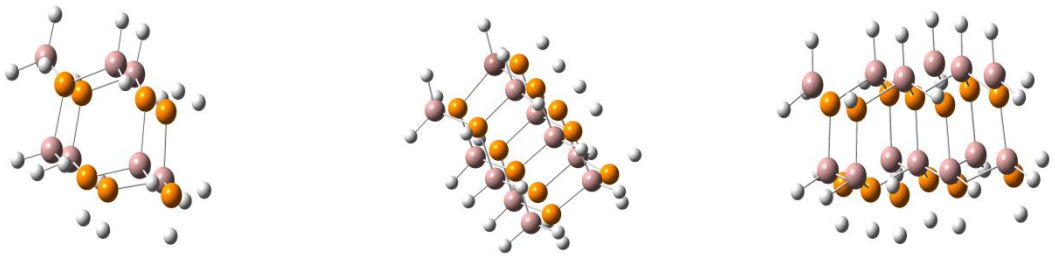
[4, 5] Diamondoids have been of great interest in recent years due to their role in nanotechnology. In this review paper we introduce at several the

cages nature of diamondoid molecules like as Diamantane, Tetramantane and Hexamantane [6, 7].

At normal conditions, GaP crystallizes in the zinc blende (zb) structure [8, 9]. In the present work, we study the electronic structure and physical properties of GaP nanocrystals. We shall investigate some properties of GaP nanocrystals using density function theory. This method is also the most computationally expensive both in time and resources. Have obtained a very good description of its structural and electronic properties. Recently, Annan et al [10].

2. Theory

Geometrical optimization method is used in the present work to obtain the electronic structure of GaP molecules and nanocrystals (Figure 1.) These include the following: GaP-diamantane, GaP-tetramantane and GaP-hexamantane. Density functional theory (DFT) is used in the present work at the generalized gradient approximation level of Perdew, Burke and Ernzerhof (PBE). STO-3G and 3-21G bases sets are used as the basis functions of DFT calculations. Gaussian 09 program which is used in the present work [11]. The present suggested GaP-diamondoids and (DFT) method are applied for the first time to GaP nanostructures. These methods can be compared with experiment and ideal value start from molecular sizes building up structures to reach the nanoscale region (bottom up methods) whereas the previous methods are essentially solid state methods reapplied to nanoscale sizes (top-down methods).



a b c

Figure (1): Shape of geometrically optimized (a) Diamantane (b) Tetramantane and (c) Hexamantane. PBE/3-21G method is used for the present figure.

3. Results and Discussion

Figure (2) shows (DFT) calculated bond length using (DFT) methods. These bond lengths are compared with bulk value. The bond lengths from nearly 2.36 A^0 in GaP molecules it is very close to the experimental value 2.37A^0. In this Figure we can note the bond length at left between (P-H), (Ga-H) in the surface and the right (Ga-p) in the core.

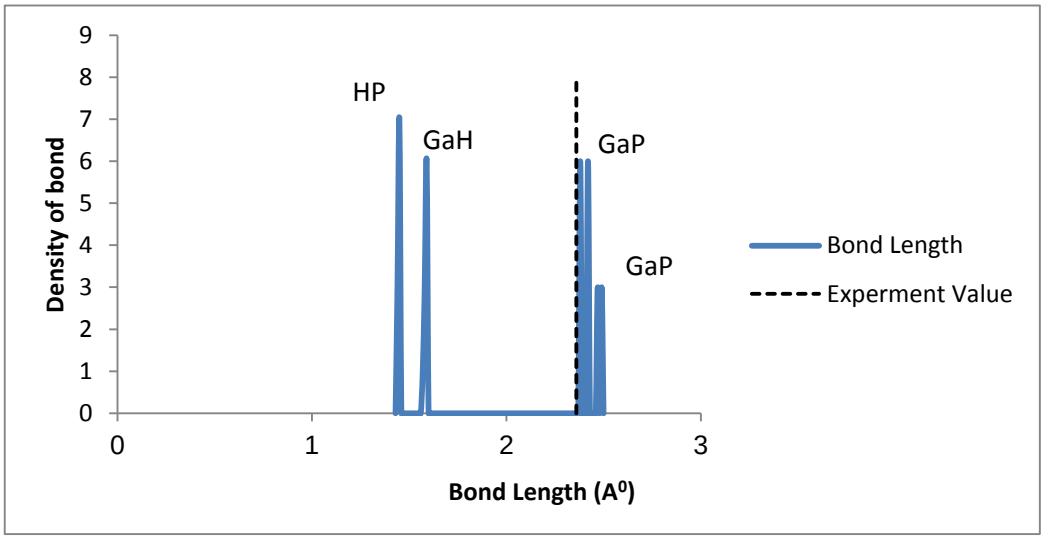


Figure (2): shows DFT calculated bond length using (DFT) methods of Diamantane GaP and comparator with experimental value.

In figure (3) illustrate a sample of density of states and energy levels of the Tetramantane of Gap from these figures one can determine the energy gap, width of conduction bands, position of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), energy gap intruder states valence and while.

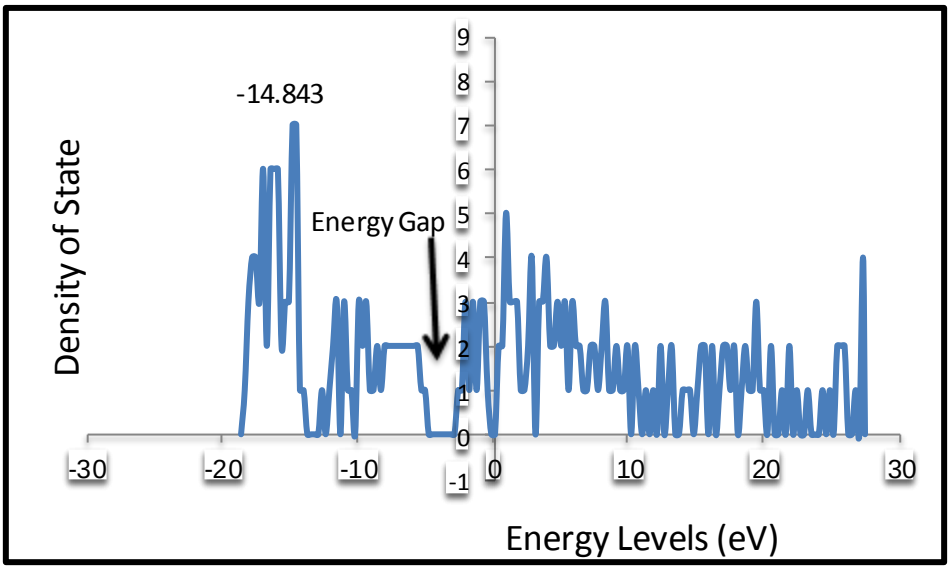


Figure (3): illustrate a sample of density of states of Gap Tetramantane

Arrow indicates the energy gap to his left is valance band and to his right is conduction band. For comparison purposes we kept the energy range in these figures from (−30 to 30 eV). The highest density of states in DFT is nearly (-14.843eV) of GaP-Tetramantane molecule. Figure (4) illustrate a sample of tetrahedral angle of Gap Hexamantane nanocrystal. It cans comparison calculation of DFT 109 degree is very identical with ideal value (109.47) degree.

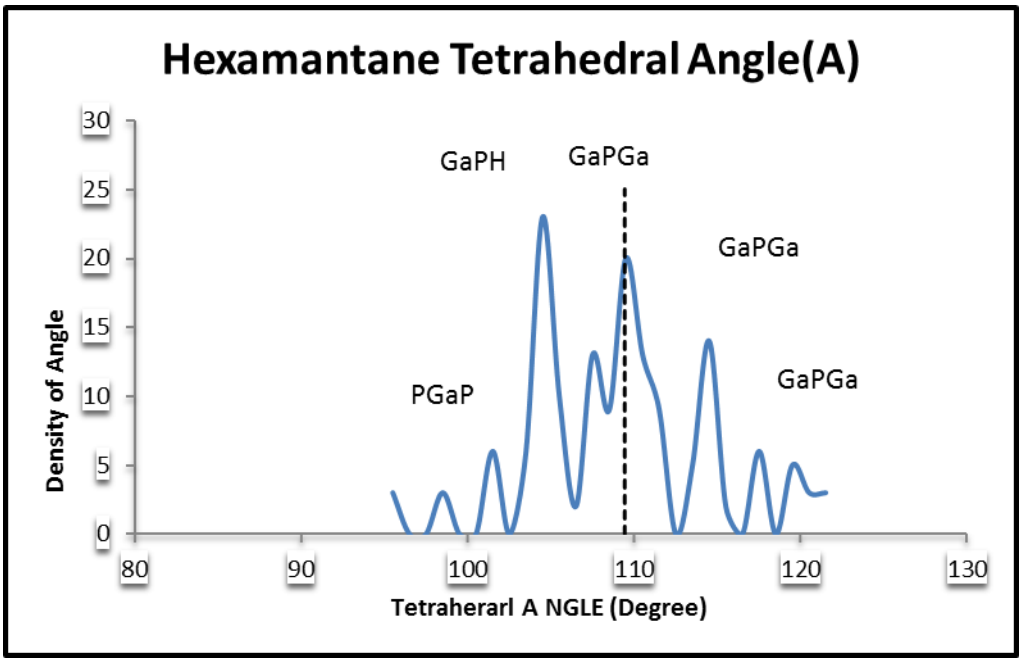


Figure (4): shows density of angle as a function of tetrahedral angle (degree) for Gap molecules and nanocrystals. The dashed line represents the ideal bulk value of tetrahedral angle.

At figure (5) shows dihedral angle (degree) of GaP Hexamantane as a function of density of angle. The result of DFT is very nearest of bulk ideal value is between (-180,-60, 60 and 180) degree.

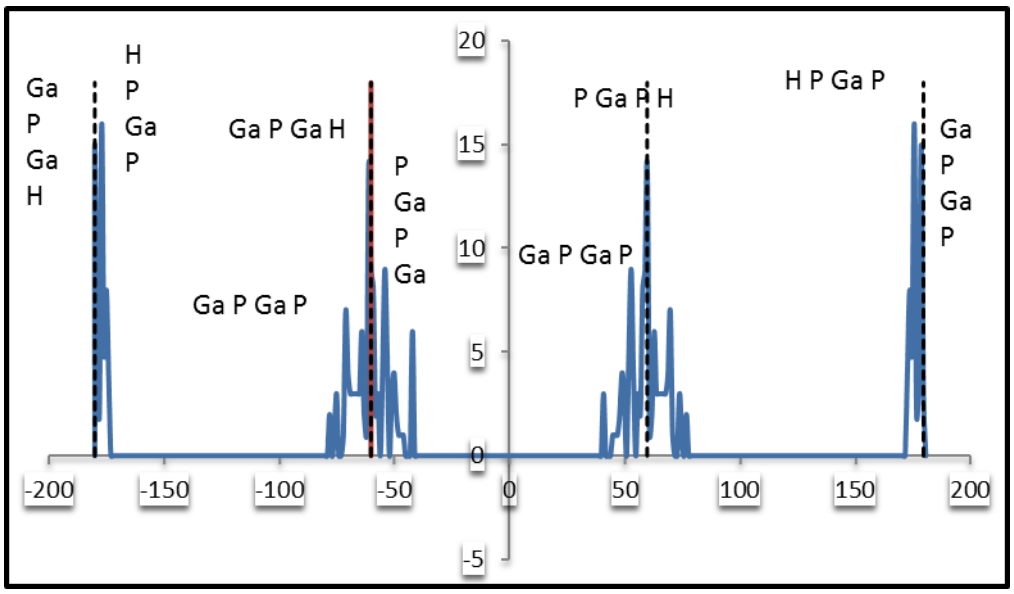


Figure (5): shows dihedral angle (degree) of GaP Hexamantane as a function of density of angle for Gap molecules and nanocrystals. The dashed line represents the ideal bulk value of tetrahedral angle.

Table (1) shows Stoichiometry No. of atoms in every state Diamantane, Tetramantane and Hexamantane

Diamantane	Ga7H20P7
Tetramantane	Ga11H28P11
Hexamantane	Ga13H30P13

Table (2) illustrates a sample of Cohesive Energy calculated by DFT method. It cans founded by calculated total energy of every states Diamantane, Tetramantane and Hexamantane and Find the energy of each individual atom for hydrogen atom (H) Gallium (Ga) atom and Phosphide (P) and multiply by No. of atoms of each state . Cohesive Energy can get from equation (1) with unit (atomic unit) can find by electron volte unit multiply by (27.211)

Cohesive Energy= [total energy (SCF) – {(Energy (H)*(No.atom of (H)) + (Energy (Ga)*No.atom of (Ga)) + (Energy (P)*(No. atom of (P)}..... (1)

Cohesive Energy decreased with increased No. of atoms

3 – 21g (OPT)	**Total Energy (Ga)**	**Total Energy (H)**	**Total Energy (P)**	**Cohesive Energy**
Diamantane	SCF= -1915.03*7 = -13405.2667 AU	SCF= -0.49438*20 = -9.88709844 AU	SCF= -339.2925134 *7= -2375.04759 AU	-15794.2608-(-15790.1977= -4.0631 *27.211= -110.561eV
Tetramantane	SCF= -1915.03811*11 = - 21065.41921 AU	SCF= -0.49438549*28 =-13.84279372 AU	SCF= -339.2925134 *11= -3732.217647	24811.47965-(-24817.61690- = - 6.13725*27.211 = -167.0007 eV
Hexamantane	SCF= -1915.03811*13 =-24895.4954 AU	SCF= -0.49438549*30 = -14.831564 AU	SCF= -339.2925134 *13=-4410.80267 AU	-29328.2438 -(-29321.12963= -7.11417*27.211= -193.583679 ev

Table (2): shows Cohesive Energy as a function of No. of atoms the result of DFT for Gap molecule the Cohesive Energy decreased with increased No.of atoms.

4. Conclusions

GaP diamondoids are suggested in the present work as building blocks of Gap nanocrystals. Shape and size dependence of electronic properties of these blocks in comparison with DFT method results is investigated. Results show that shape and size investigated structures play important role in their electronic properties. General reduction of energy gap and Ga-P bond lengths are seen with increasing particle size. By shape affects Density of states shows that electrons inside the core of GaP nanocrystals have more positive HOMO, LUMO, and with respect to diamondoid molecules. Tetrahedral and dihedral angle degree are very nearest of bulk ideal value. And the result of DFT for Gap molecule the Cohesive Energy decreased with increased No.of atoms.

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الخلاصة

استخدام نظرية كثافة الحالات وطريقة (Ab initio) المرتبطة بطريقة هارتري – فوك لتحديد التركيب الإلكتروني والخصائص الفيزيائية للالغاليوم فوسفيد (GAP) البلورات النانوية بأسخدام تركيب (diamondoids) وبتدا من اصغر تركيب هيكل تبد أDiamantane ، Tetramantaneو Hexamantane

وباحجام مختلفة. ويتم تحقيق الخصائص التي تتضمن طاقة الربط، وزاوية ثنائي السطح وطول الاصرة, زاوية رباعي السطوح والتعددية لمستويات الطاقة. وكشفت النتائج أن الخصائص الإلكترونية تتقارب إلى حد من حجم المواد الغاليوم فوسفيد فان زيادة حجم البلورات النانوية أدى أيضا إلى انخفاض في الطاقة الربط (القيمة المطلقة) انخفضت مع زيادة عدد الذرات، زاوية ثنائي السطح ورباعي السطوح هي أقرب من قيمة مثالية. كان طول الاصرة قريبة جدا من قيمة التجريبية.