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# Determination of Electronic Properties of Gallium Nitride Structure Using Density Functional Theory

*In this work, the density functional theory was used to determine the electronic and related properties of gallium nitride. The results of this work include electronic energy band gap at room temperature as the energy band gap increases with size. It was found that the bond length is within the distribution range. Tetrahedral and dihedral angles approach values of bulk gallium nitride up to higher structural configurations. The density of energy states was varied from approximately single levels to band structure.*

**Keywords:** Gallium nitride; Crystal structure; Density functional theory; Electronic properties

## 1. Introduction

The study of various Heusler alloys decades ago resulted in the serendipitous discovery of half-metallic (HM) magnetism [1,2]. Next, HM Ferromagnets aroused interest for its applicability as a spintronic material because they possess one electron spin channel at the Fermi energy level. This results in 100% polarization of the spin carriers [3-5]. Based on the properties of HM compounds, several studies have been carried out to understand their magnetic mechanistic and implications on the physics properties of materials [6-11].

Half-metallic ferromagnets (HMF) such as the alkaline earth pnictides [12], carbides [13,14] and nitrides [15-17] contains no transition metals and rare earth ions exhibits different mechanism for their magnetism compared with those that contain those ions [18]. The magnetism in these compounds is related to the *s* and *p* atomic orbitals and not *d* or *f* atomic orbitals. The ferromagnetic coupling mechanism varies from the *p-d* and double exchange which are vital in *3d* magnetic systems [19,20].

Gallium nitride (GaN) is a promising material in the development of short-wavelength light emitting devices [21]. The density functional theory is used with the local density approximation as implemented in the O(N) pseudopotential LCAO OpenMX package to calculate the band structure and electronic properties of wurtzite GaN nanowires (GaN NWs) and hydrogen-passivated GaN nanowires [22-24].

Most nitride structures consist of a diamond-like carbon cage, where all atoms are  $sp^3$  hybridised, and dangling bonds at the edges of the systems are terminated with hydrogen atoms. They have the shape of cages that are added together to form nanocrystals and bulk. Present trend in molecular electronics is to manufacture single molecules that should be the ultimate smallest possible electronic component. These molecules should have exceptional stability that can endure applied electrical or magnetic fields

that are applied due to electronic signals [25]. In general, they are strong, cage-like structures that differ from other molecules in the bonding of their surface atoms by one or two hydrogen atoms. This structure results in the bonding of these surface atoms to the core of the molecular nanocrystal by at least two bonds, which enhances their stability [26]. Boron phosphide is an indirect gap semiconductor. Under ambient conditions, it crystallizes in the zinc-blende (zb) structure [27]. Gallium nitride (GaN) has a very high thermal conductivity, a significant hardness, and an indirect band-gap [28]. Because of these properties, gallium nitride is useful in high temperature electronics applications and electro-optical devices in the short-wavelength range of the visible spectrum [29].

The density functional theory (DFT) at generalized gradient approximation level of Perdew, Burke, and Ernzerhof (PBE) is used. 6-31G(d) basis set that contains polarization functions are incorporated in present calculations. All calculations are performed using Gaussian 09 program. Density functional theory (DFT) for its successful handling of many properties especially the electronic structure however knowing that Kohn-sham DFT is insufficient method for its deficiencies concerning the gap issue and the long rang interactions approximations. Half-magnetic materials are cage shaped structures discovered in petroleum. These cages are stable and strong since all the constituting atoms (except hydrogen atoms) are connected to bulk of molecule by two or more bonds. Nomenclature of half-magnetic materials follows the number of cages in each half-magnetic material. As an example, diamantane contains two cages while octamantane contains eight cages [30] as shown in Fig. (1).

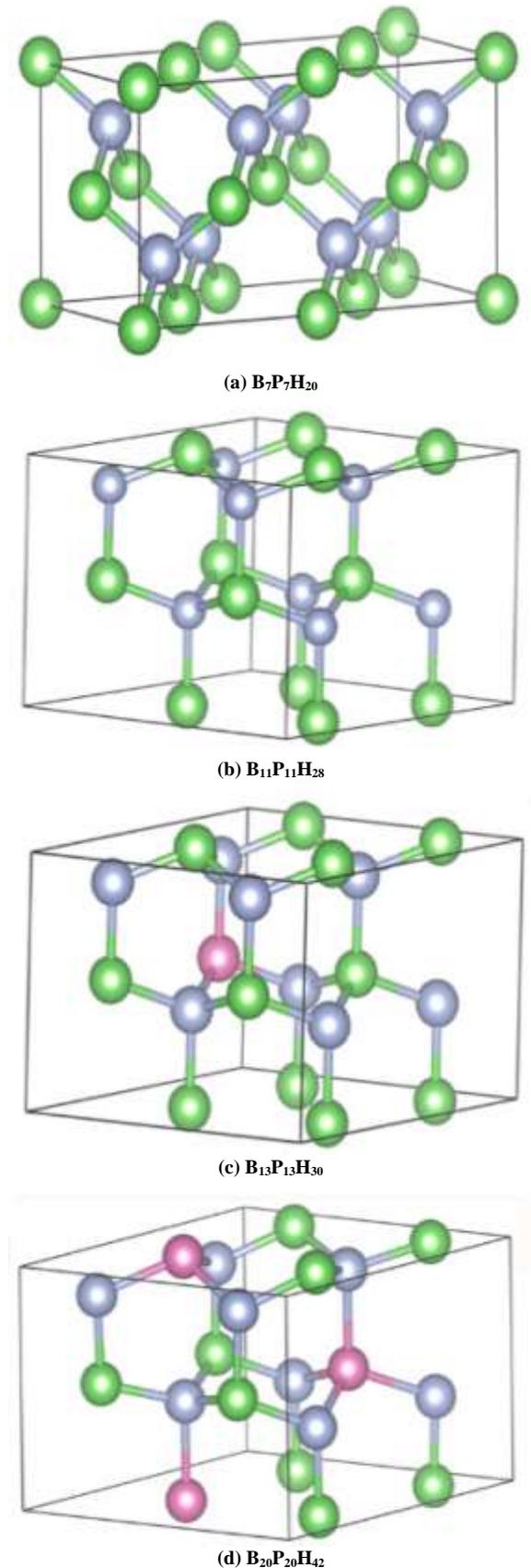


Fig. (1) Instrumentation of geometry of (a) GaN-diamantane, (b) GaN-tetramantane, (c) GaN-hexamantane, (d) GaN-octamantane molecules

## 2. Results and Discussion

The differences between the energy gap of the smallest half-magnetic materials were considered herein. GaN-diamantane and GaN-octamantane. Energy levels are nearly discrete in GaN-diamantane. As the number of energy levels increases, discrete behavior in GaN-diamantane turns to nearly continuous band in GaN-octamantane. Energy gap reduces from 3.4 eV in GaN-diamantane to 1.7 eV in GaN-octamantane. This reduction is in compliance with confinement effects that require size reduction of energy gap as manifested in Fig. (3) [31]. As in Fig. (2), the smallest gap recorded in our calculations is 1.7 eV for GaN-octamantane. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have all negative values (Fig. 3). HOMO and LUMO levels are sometimes used as approximations of ionization energy and electron affinity respectively [32,33], these values show that extraction of an electron or addition of an external electron requires an external energy.

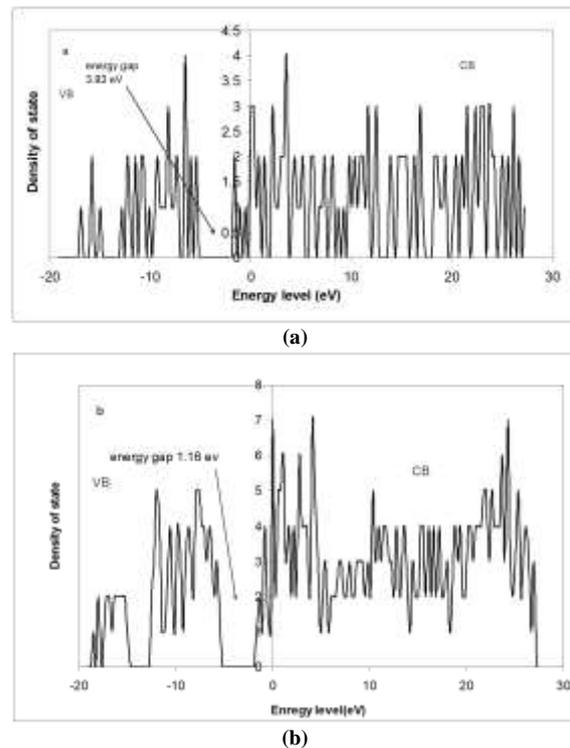


Fig. (2) Density of state of (a) GaN-diamantane and (b) GaN-octamantane

Bond lengths of GaN-diamantane and GaN-octamantane. Shortest bonds are P-H and B-H respectively. Small number of bonds in GaN-diamantane does not allow the true statistical features of these bonds. In GaN-octamantane B-H bond is a sharp high peak while P-H is a wide base and low height peak. The reason for this is that P is a nonmetal that strongly localize electrons in its bonds. On the contrary B is a semiconductor that has relatively more delocalized electrons in its bonds. The B-P bond has

several peaks depending on number of hydrogen atoms attached to B and P atoms. In B-P-diamantane the smallest value of this bond is when both B and P are connected to single hydrogen atom. These have the value 1.92Å that corresponds to the highest peak for diamantane. The longest bond is at 1.98Å near the far ends of diamantane molecule in which one of the core atoms (Ga or N) is connected to two hydrogen atoms. The location of the bond in the molecule affects its value that explains the several peaks for GaN-diamantane, GaN-octamantane on the other hand have a different situation that spectrum of bonds in case of GaN-octamantane has the range 1.93-2Å, with the highest peak at 1.97Å. Experimental bond length of bulk GaN (1.96Å) is within GaN-diamantane and GaN-octamantane bond distribution (Fig. 4).

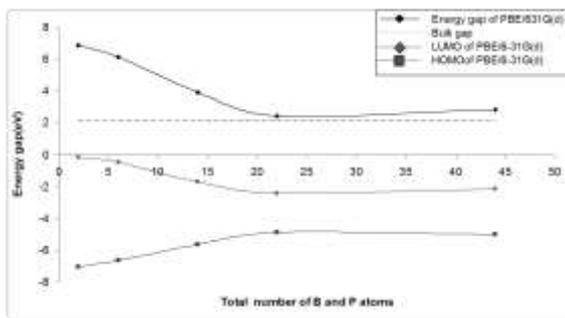
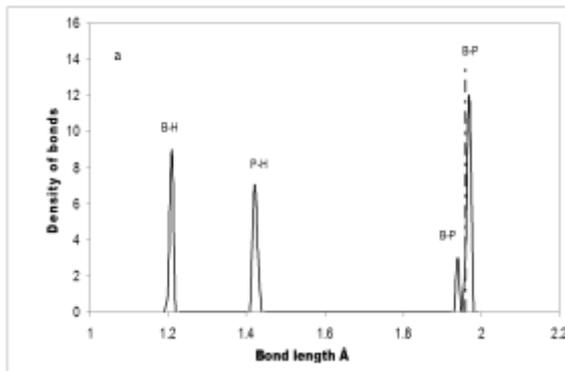
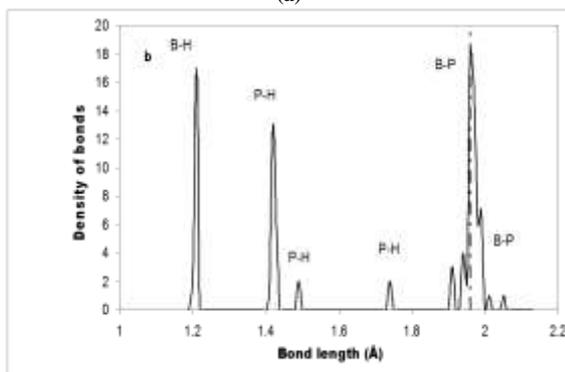


Fig. (3) Energy gap, HOMO and LUMO levels as a function of total number of gallium and nitrogen atoms in gallium nitride structure using PBE/6-31G (d)



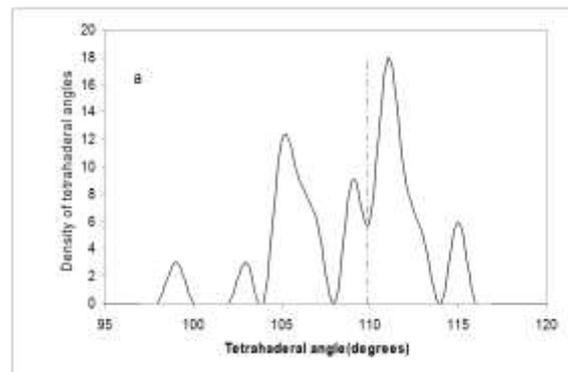
(a)



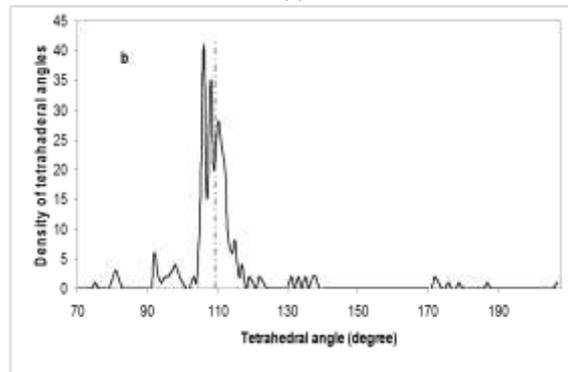
(b)

Fig. (4) Density of bonds in GaN-diamantane and density of bonds GaN-octamantane. Dashed line represents the experimental GaN bond length at 1.96Å

Figure (5) shows a comparison between density of tetrahedral angles in GaN-diamantane and density of tetrahedral angles in GaN-octamantane. In a piece of bulk far from surface all tetrahedral angles should have the value 108.57° [11]. As we can see from Fig. (5), the highest peak of GaN-diamantane is at 110.9°, while that of GaN-octamantane is at 105.47°. Tetrahedral angles of diamantane are much closer to the ideal value 108.57° than that of octamantane. This is due to the effect of surface reconstruction that has an effect on all atoms in GaN-diamantane and GaN-octamantane (all the atoms are bonded to surface hydrogen atoms).



(a)



(b)

Fig. (5) Density of tetrahedral angles in (a) GaN-diamantane (b) GaN-octamantane. The dashed line represents the ideal value of zinc-blende structure at 108.57°

Similarly, all dihedral angles should have a value of the following: -180°, -60°, 60° and 180° in bulk zinc-blende structure [34,35]. This may be correct for the angle values of ±180° in GaN-diamantane, GaN-octamantane. It is not totally correct for the angle values of -60° and 60°. For GaN-octamantane, the situation improves for the angles near -60° and 60° that become closer to their ideal values in Fig. (6).

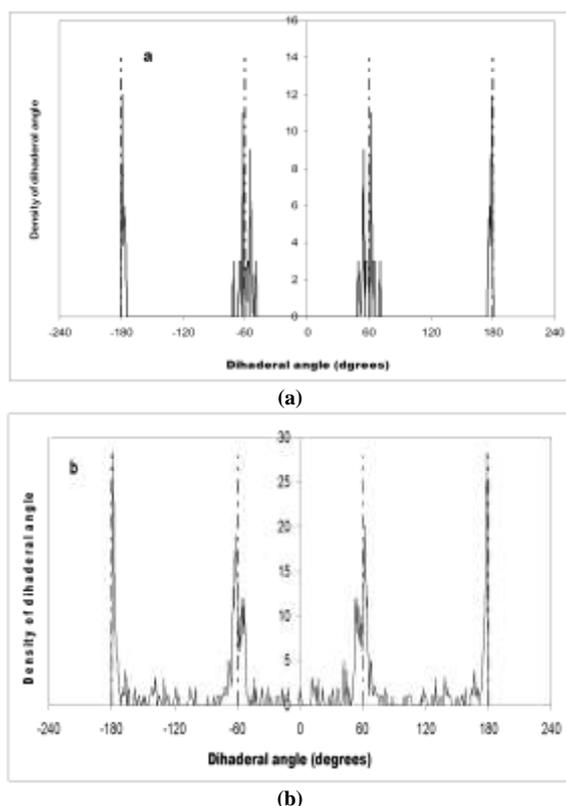


Fig. (6) Density of dihedral angles in (a) GaN-diamantane (b) GaN-octamantane, PBE/6-31G (d) basis sets is used. Dashed lines show the ideal value of this angle in bulk zinc-blende crystals, i.e.,  $\pm 60^\circ$  or  $\pm 180^\circ$

### 3. Conclusions

Half-magnetic materials are suggested to be building blocks of GaN nanocrystals and bulk. We can benefit from these structures to monitor how GaN nanocrystals and bulk properties are reached from their corresponding molecular properties. Half-magnetic materials show minimal surface relaxation effects, which can be deduced from their bond lengths, tetrahedral angles and dihedral angles, Energy gap, bond length. B-P bond lengths are affected by surface reconstruction. The shortest B-P bond is between the atoms that are not connected to surface hydrogen atoms. Tetrahedral and dihedral angles converge to their ideal zinc-blende values as we reach higher size structures. Density of energy states show the transition from single energy levels to band structure as we reach higher size structures.

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