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First-principles calculation of the band gap of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$

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Ab-initio calculations of the band gap variation of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ ternary compounds were carried out using the Full-Potential Linearized Augmented Plane Waves (FLAPW) method, within the Density Functional Theory (DFT). These nitrides were modeled in their wurtzite structure using the supercell method, for concentrations x = 0, 0.25, 0.50, 0.75 and 1.0. To optimize the cell parameters of the binary compounds we used the PBE96 (Perdew *et al.*, *Phys. Rev. Lett.* **77** (1996) 3865) exchange-correlation functional. For the band structure calculations, we used both PBE96 and EV93 (Engel *et al.*, *Phys. Rev. B* **47** (1993) 13164) exchange-correlation functionals. We considered experimental and calculated (with PBE96) lattice parameters to work out the electronic properties. We found that the fundamental gap is direct in all compounds. The calculation with EV93 functional gives a better band gap estimation for binary nitrides. The bowing parameter was also estimated obtaining the values b = 0.74 eV for $Al_xGa_{1-x}N$ and b = 2.12 eV for $In_xGa_{1-x}N$.

Keywords: Ab-initio calculations; band structure; bowing parameter; FLAPW; nitrides.

En este trabajo se realizaron cálculos de primeros principios de la variación del ancho de banda prohibido en los compuestos ternarios $Al_xGa_{1-x}N$ e $In_xGa_{1-x}N$, utilizando el Método Linealizado de Ondas Planas Aumentadas con Potencial Completo (FLAPW), dentro del marco de la Teoría del Funcional de la Densidad (DFT). Los nitruros fueron modelados en una estructura tipo wurzita utilizando el método de supercelda, y considerando las concentraciones x = 0, 0.25, 0.50, 0.75 y 1.0. Para la optimización de los parámetros de red se utilizó el potencial de correlación-intercambio PBE96 (Perdew *et al.*, *Phys. Rev. Lett.* **77** (1996) 3865). Para el cálculo de la estructura de bandas de energía se utilizaron los funcionales PBE96 y EV93 (Engel *et al.*, *Phys. Rev. B* **47** (1993) 13164). Se consideraron parámetros de red experimentales y calculados (con PBE96) para los cálculos de las propiedades electrónicas. Nuestros cálculos indican que la banda prohibida fundamental es directa en estos compuestos. Los cálculos con el funcional EV93 dan como resultado una mejor estimación de los anchos de las bandas prohibidas de los compuestos binarios. Calculamos el parámetro de curvatura, obteniendo los valores b = 0.74 eV para $Al_xGa_{1-x}N$ y b = 2.12 eV para $In_xGa_{1-x}N$.

Descriptores: Cálculos *Ab-initio;* estructura de bandas; parámetro de curvatura; FLAPW; nitruros.

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1. Introduction

In the last few years, the nitrogen-based III-V semiconductor compounds AlN, GaN and InN have attracted considerable attention, because these compounds can be used for developing short wavelength light emitting diodes (LED's), laser diodes, optical detectors and other devices of great technological importance. These devices can operate at high temperature and harsh environments since these semiconductors present low compressibility, good thermal stability and chemical and radiation inertness [1]. In addition, AlN and GaN present properties like high melting point, high thermal conductivity and large bulk modulus [2], all of them closely related to their wide band gap and strong bonding. At room temperature, AlN, GaN and InN crystallize in the wurtzite type structure, with corresponding direct energy band gaps of 6.28 eV, ∼3.5 eV and 1.9 eV [3]. Consequently, the fabrication of a new generation of devices operable from the ultraviolet (UV) to the visible region of the electromagnetic spectrum are now possible. However, in recent works [4,5], the band gap of InN is reported to be 0.7-0.8 eV and with this, the infrared region is at hand.

As the binary compounds, the optoelectronic properties of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys are of considerable importance, because of their potential use in the fabrication of devices like LED's, laser diodes, optical detectors, etc., For

an in-depth understanding of the physical mechanism that underlies the operation of these devices, the properties of these ternary alloys need to be extensively studied. Many of these properties, such as the energy band gap, are dependent of the atomic composition. The behavior of this optical property is the main reason why $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys are potentially fabricated into optical devices, which are active at wavelengths ranging from the infrared to the ultraviolet region. Accordingly, the study of optical properties like the band gap variation as a function of the atomic composition, are very important. A large number of experimental and theoretical studies have reported the band gap variation of these alloys; nevertheless the values are very scattered. Similarly to the binary nitrides, the ternary alloys grow also in the wurtzite structure, independently of the deposition technique [6-8].

In the present work we carried out ab initio calculation of band gap variation of ternary compound $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ in their wurtzite structure. In addition, structural optimization and energy band structure of binary nitrides AlN, GaN and InN were also performed. The ternary compounds are random alloys, and the cation should be treated statistically for an $A_xB_{1-x}C$ alloy. We have not examined the complete problem of alloy formation; instead we have considered particular cases that give us a clear physical view on the electronic properties of these compounds, gaining insight on the ternary compounds problem by means of ordered crystal models.

The supercell method is used here to study the ternary compounds, implemented on ordered structures to model concentrations of x = 0, x = 0.25, x = 0.50, x = 0.75 and x = 1.0, in an 8 atoms supercell. The lattice parameters of the supercells are calculated from Vegard's law, using experimental and calculated lattice parameters of binary nitrides. The band gap of the studied nitrides was determined and, in the case of ternary compounds, the concentration dependence of the band gap, by calculating the band gap bowing (deviation from linearity) parameter. For nitrides, we used experimental and calculated lattice parameters to obtain the electronic structure.

The calculations were performed within the framework of DFT [9], using the FLAPW method [10] as implemented in the computer code WIEN97 [11]. It is known that a major source of uncertainty in first principles calculations of electronic structure, within DFT, is the choice of the exchange-correlation functional, whose exact form is not known and hence cannot be handled accurately in this method. As a result of this deficiency the energy gap is usually underestimated in this approach. Two approximations for the exact exchange-correlation functional are the Local Density Approximation (LDA) [12] and the Generalized Gradient Approximation (GGA). The LDA approximation is most commonly used but the GGA approximations (GGA) have become of current use in recent years. Two of these approximations are those of Perdew-Wang [13] and Perdew-Burke-Ernzerhof [14]. However, it has been found that these approximations underestimate the band gap in semiconductors and describe, in particular, InN as metallic [3]. In this work two approximations for the exchange-correlation functional have been used, the GGA's of Perdew-Burke-Ernzherhof (PBE96) and Engel-Vosko (EV93) [15,16]. In the latter approximation, which is implemented in the WIEN97 code, the exchange potential V_x is accurately reproduced whereas the exchange energy E_x is less accurately reproduced [16], while the correlation potential V_c and correlation energy E_c are calculated within the LDA approximation. It is worth mentioning that quantities which depend on an accurate description of exchange-correlation potential, such as the band gap value, are well reproduced, while quantities which depend on an accurate description of exchanged-correlation energy such as equilibrium volumes are less accurately reproduced.

The results obtained in this work are compared with theoretical and experimental values. Our results show that with both approximations the band gap of the nitrides is underestimated, but the EV93 approximation gives a better description of the band gap compared to experimental values, describing correctly InN as semiconductor. This important qualitative result motivated us to use it in the ternary compounds, and to our knowledge, this is the first work where the EV93 functional is used for the study of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ band gap variation.

In Sec. 2 the structure of the binary and ternary nitrides are described; in Sec. 3, the computational approach and input parameters are provided; in Sec. 4 the results and discussion are given; and in Sec. 5 we present the conclusions.

2. Structure

The AlN, GaN and InN nitrides can grow in two different structures, wurtzite and zincblende, being wurtzite the most stable. The wurtzite structure differs from the zincblende only in the stacking sequence of the A-B atoms in the [111] direction of the AB compound.

Wurtzite structure is a hexagonal close-packed lattice, comprising vertically oriented X-N units at the lattice sites. The basal lattice parameter is a and the axial lattice parameter is c. The interatomic distance in the basic unit is described by an internal parameter u. The ideal (*i.e.*, touching hard spheres) values of the axial ratio and internal parameter are c/a = 8/3 and u = 3/8, respectively. For wurtzite, the lattice vectors are $\vec{a}$ = (1/2, - 3/2, 0)a, $\vec{b}$ = (1/2, 3/2, 0)a and $\vec{c}$ = (0, 0, c/a)a. The experimental lattice parameters of the binary nitrides are shown in Table I. There are four atoms per hexagonal unit cell. The positions, in units of a, b and c are as follows [17,18]: nitrogen atoms are in positions (0, 0, u), (1/3, 2/3, u+1/2), and {Al,Ga,In} atoms are in positions (0, 0, 0), (1/3, 2/3, 1/2).

To model $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$, an 8 atoms supercell with hexagonal geometry is used, consisting of two wurtzite unit cells piled in the [0001] direction, which correspond to 1×1×2 of the unit cell of binary nitrides. Each supercell have eight planes. Concentrations of x = 0.25,

x = 0.50 and x = 0.75 were simulated using ordered structures within this supercell (see Table II). Each one of these supercells have 8 inequivalent atoms, due to the broken symmetry of the cell. For $Al_xGa_{1-x}N$ there are four N atoms, three Ga atoms and one Al atom for x = 0.25; four N, two Ga and two Al atoms for x = 0.5, and four N, one Ga and three Al atoms for x = 0.75. For $In_xGa_{1-x}N$ there are four N atoms, three Ga atoms and one In atom for x = 0.25; four N, two Ga and two In atoms for x = 0.5, and four N, one Ga and three In atoms for x = 0.75.

To calculate lattice parameters a, c and u of the ternary nitrides (Table II), a linear interpolation from the values of the two binary semiconductors (Vegard's Law) is carried out through:

$$a_{ABN} = xa_{AN} + (1-x)a_{BN}$$
$$c_{ABN} = xc_{AN} + (1-x)c_{BN}$$
$$u_{ABN} = xu_{AN} + (1-x)u_{BN}$$

where A is Al or In, B is Ga and x is the atomic concentration. This approximation is suitable for both $Al_xGa_{1-x}N$ [19] and $In_xGa_{1-x}N$ [20] alloys. No information about u is available for the ternary alloys; therefore a linear interpolation was performed.

TABLE I. Comparison of calculated and experimental lattice parameters for AlN, GaN and InN in the wurtzite phase. The calculated values are obtained using the PBE96 approximation.

Method	Parameter	AlN	GaN	InN
FLAPW (this work)	a(Å)	3.1437	3.2301	3.5920
	c(Å)	5.0311	5.2603	5.7879
	u	0.3820	0.3769	0.3796
Experimental	a(Å)	3.111[a]	3.190[b]	3.533[a]
	c(Å)	4.978[a]	5.189[b]	5.693[a]
	u	0.385[a]	0.377[b]	0.375[a]

[a] Ref. [17]; [b] Ref. [18]

TABLE II. Stacking sequence for ternary nitrides in the [0001] direction.

Compound	Concentration x	Stacking sequence
$Al_xGa_{1-x}N$	0.0	Ga,N,Ga,N,Ga,N,Ga,N,Ga
	0.25	Ga,N,Ga,N,Al,N,Ga,N,Ga
	0.50	Ga,N,Al,N,Ga,N,Al,N,Ga
	0.75	Ga,N,Al,N,Al,N,Al,N,Ga
	1.0	Al,N,Al,N,Al,N,Al,N,Al
$In_xGa_{1-x}N$	0.0	Ga,N,Ga,N,Ga,N,Ga,N,Ga
	0.25	Ga,N,Ga,N,In,N,Ga,N,Ga
	0.50	Ga,N,In,N,Ga,N,In,N,Ga
	0.75	Ga,N,In,N,In,N,In,N,Ga
	1.0	In,N,In,N,In,N,In,N,In

3. Computational details

The study of structure and electronic band structure of wurtzite III-nitrides and wurtzite $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$, was performed using the computational code WIEN97 [11]. This computational code uses the relativistic FLAPW method [10], within the framework of the DFT [9]. In the FLAPW method, the unit cell volume is partitioned in two regions, muffin tin spheres (around each nucleus) and interstitial region. Inside each atomic sphere the wave function is approximated by a linear combination of radial functions times spherical harmonics, while in the interstitial region a plane wave expansion is used. In this work the exchange-correlation energy of the electrons is described by using two approximations, the GGA of Perdew-Burke-Ernzherhof (PBE96) [14] and the Engel-Vosko (EV93: option 25) [15,16].

For structural optimization, extended test calculations have proven to yield sufficient accuracy in total energy minimization of wurtzite nitrides AlN, GaN and InN using 250 **k** points in the First Brillouin Zone (FBZ), 24 **k** points in the irreducible Brillouin Zone. The structural optimization presented here is obtained with a convergence of the order of 1 mRy in the total energy. For calculating the electronic properties of AlN, GaN and InN, 1000 **k** points in the FBZ were used, whereas for the supercell calculations 500 **k** points were used.

For all calculations the maximum l value for the waves inside the atomic sphere was confined to l_{max} = 10. The wave function in the interstitial region was expanded in plane waves with a cut off of $K_{max} = 8/R_{mt}$, while the charge density was Fourier expanded up to G_{max} = 15. Al($1s^2$ $2s^2$), Ga($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$), In($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$) and N($1s^2$) electronic states are treated as core states, and Al($2p^6$ $3s^2$ $3p^1$), Ga($3d^{10}$ $4s^2$ $4p^1$), In($4p^6$ $4d^{10}$ $5s^2$ $5p^1$) and N($2s^2$ $2p^3$) are considered valence states.

We used R_{mt} values of 2.0 and 1.5 for Al and N, respectively, for AlN; 2.0 and 1.6 for Ga and N in GaN; and 2.2 and 1.8 for In and N in InN. For ternary compounds, two sets of R_{mt} parameter were used: one set in calculations with parameters obtained from experimental lattice parameters, and other set in calculations with parameters obtained from calculated lattice parameters. In the first case, we used 1.95, 1.95 and 1.6 for Al, Ga and N, respectively, in $Al_xGa_{1-x}N$, and 2.0, 2.0 and 1.75 for In, Ga and N, respectively, in $In_xGa_{1-x}N$. In the latter case, we used 2.0, 2.0 and 1.6 for Al, Ga and N, respectively, in $Al_xGa_{1-x}N$, and 2.05, 2.05 and 1.75 for In, Ga and N, respectively, in $In_xGa_{1-x}N$. Core and valence states are the same as those of binary nitrides.

4. Results

Structural optimization of AlN, GaN and InN nitrides is performed in their wurtzite phase. To find the equilibrium values of the structural parameters a, c and u, we proceeded as follow: First, the equilibrium value of the internal parameter u

with fixed values of $(V, c/a)$ (in our calculations we use experimental values) is determined; then a parabolic fit of total energy versus u curve was performed to calculate u_{eq} . Next, we determine $(c/a)_{eq}$ with fixed (V, u_{eq}), fitting total energy versus c/a with a parabolic function. Finally, using u_{eq} and $(c/a)_{eq}$ the optimized volume was obtained. The equilibrium lattice constants are calculated by fitting total energy versus volume according to Murnaghan's equation of state [21]. The experimental and calculated (with PBE96) lattice parameters are given in Table I. The calculated values are $\sim$1.5% above the experimental values, as usual for GGA's. With this result the computational parameters were validated. Structural optimization using EV93 gives excessively large lattice parameters values, showing a poor agreement with experimental results [16]; in particular, the lattice parameters calculated for AlN are 4.6% bigger.

Using the calculated and experimental lattice parameters, the energy bands of binary nitrides were obtained utilizing both PBE96 and EV93 approximations, finding their band gap values (Tables III and IV). Energy bands diagrams of AlN show a direct band gap over Γ point in all cases and the best approximation is obtained when experimental lattice parameters and EV93 approximation are used. For GaN, a direct band gap was observed in all cases, and the best value for the band gap is obtained with experimental lattice parameters and EV93 approximation. Nevertheless, for InN a zero band gap (conductor state) was observed with the PBE96 approximation, using both experimental and calculated lattice parameters. The calculated energy bands using the EV93 approximation revealed a direct band gap with a non-zero value (semiconductor state) for both sets of lattice parameters, obtaining the best value with experimental lattice parameters. In all nitrides band gap values are underestimated, but despite of that calculations made with the EV93 approximation give satisfactory results when compared to experimental results.

TABLE III. Energy band gap E_g of nitrides and $Al_xGa_{1-x}N$, $In_xGa_{1-x}N$ in the wurtzite phase, calculated with PBE96. The second column shows the calculated E_g when the experimental lattice parameters are used and the third column when the calculated (optimized) lattice parameters are used.

	E_g (eV)	**E_g (eV)**	**E_g (eV)**
	Experimental	**Exp. Parameters**	**Opt. Parameters**
InN	1.9^a, $0.7\text{-}0.8^b$	0.0000	0.0000
$In_{0.75}Ga_{0.25}N$		0.0496	0.0000
$In_{0.50}Ga_{0.50}N$		0.4093	0.2239
$In_{0.25}Ga_{0.75}N$		0.8799	0.6824
GaN	3.5^a	1.9188	1.6531
$Al_{0.25}Ga_{0.75}N$		2.3804	2.1196
$Al_{0.50}Ga_{0.50}N$		2.9242	2.6789
$Al_{0.75}Ga_{0.25}N$		3.4853	3.2227
AlN	6.28^a	4.1671	3.9379

[a]Ref. [3]; [b]Ref. [4,5]

TABLE IV. Energy band gap E_g of nitrides and $Al_xGa_{1-x}N$, $In_xGa_{1-x}N$ in the wurtzite phase, calculated with EV93. The second column shows the calculated E_g when the experimental lattice parameters are used and the third column when the calculated (optimized) lattice parameters are used.

	E_g (eV)	**E_g (eV)**	**E_g (eV)**
	Experimental	**Exp. Parameters**	**Opt. Parameters**
InN	1.9^a, $0.7\text{-}0.8^b$	0.3570	0.1716
$In_{0.75}Ga_{0.25}N$		0.5889	0.4004
$In_{0.50}Ga_{0.50}N$		0.9514	0.7336
$In_{0.25}Ga_{0.75}N$		1.4319	1.2207
GaN	3.5^a	2.5181	2.2211
$Al_{0.25}Ga_{0.75}N$		3.0125	2.7125
$Al_{0.50}Ga_{0.50}N$		3.6092	3.3165
$Al_{0.75}Ga_{0.25}N$		4.1841	3.9107
AlN	6.28^a	5.0021	4.7544

[a]Ref. [3]; [b]Ref. [4,5]

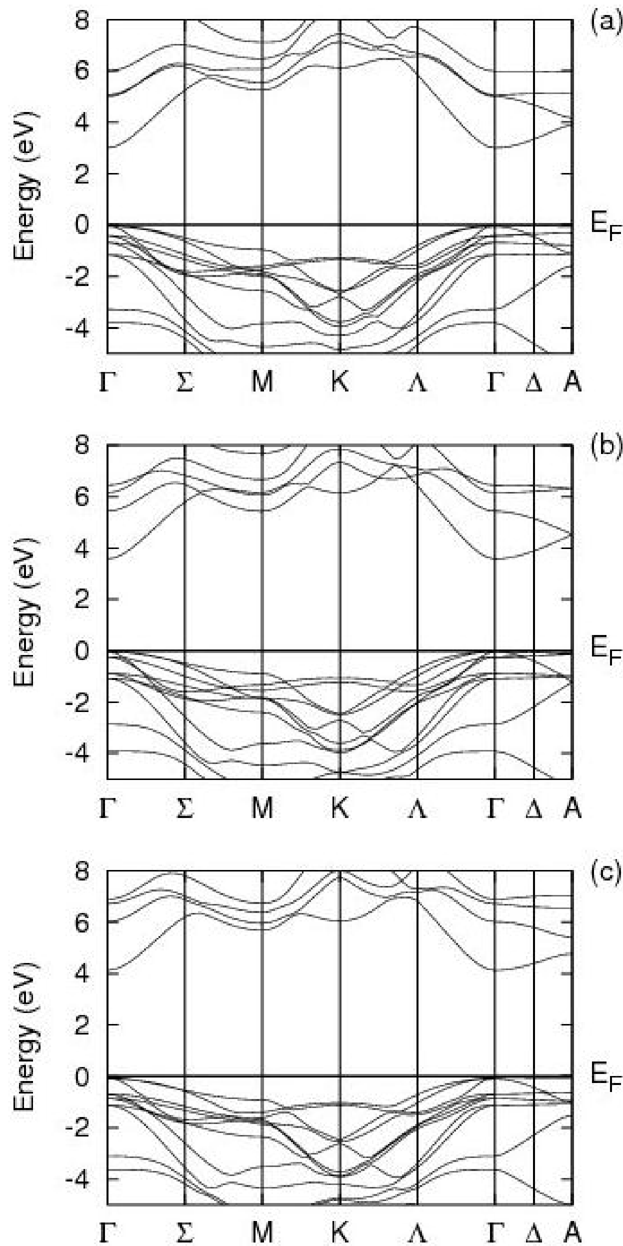

FIGURE 1. Calculated band structure of Al_x Ga_{1-x} N, using the EV93 approximation with lattice parameters obtained from experimental results. (a) x = 0.25, (b) x = 0.50 and (c) x = 0.75.

We also calculated the energy band structure of ternary nitrides. Computed band gap values are shown in Tables III and IV, and in all cases a direct band gap over the Γ point is observed (Fig. 2 and Fig. 3). Many physical properties of $A_xB_{1-x}C$ alloys can be represented as a simple analytical interpolation of the properties of its constituent compound (AC and BC). Specifically, it is found that many physical properties $P(A_xB_{1-x}C)$ of this pseudobinary alloys follow a quadratic relationship of the type:

$$P(A_xB_{1-x}C) = xP_{AC} + (1-x)P_{BC} + kx(1-x) \quad (1)$$

where k represents a general bowing parameter and is approximately composition independent. Thus, the dependence of the fundamental band gap on the mole fraction for this pseudobinary alloys is usually approximated [22] by:

$$E_g(x) = xE_{g,AN} + (1-x)E_{g,BN} - bx(1-x) \quad (2)$$

where the deviation from a linear behavior is taken into account through the bowing parameter b. In this work, A correspond to Al or In, and B to Ga. It is an experimental fact that the gap almost invariably bows below the straight-line average ($b > 0$) in pseudobinary alloys. Schilfgaarde *et al.* [19] explain this using a virtual crystal approximation. Ferhat *et al.* [23] present the physical origins of the bowing, and decompose the bowing parameter b into three physically

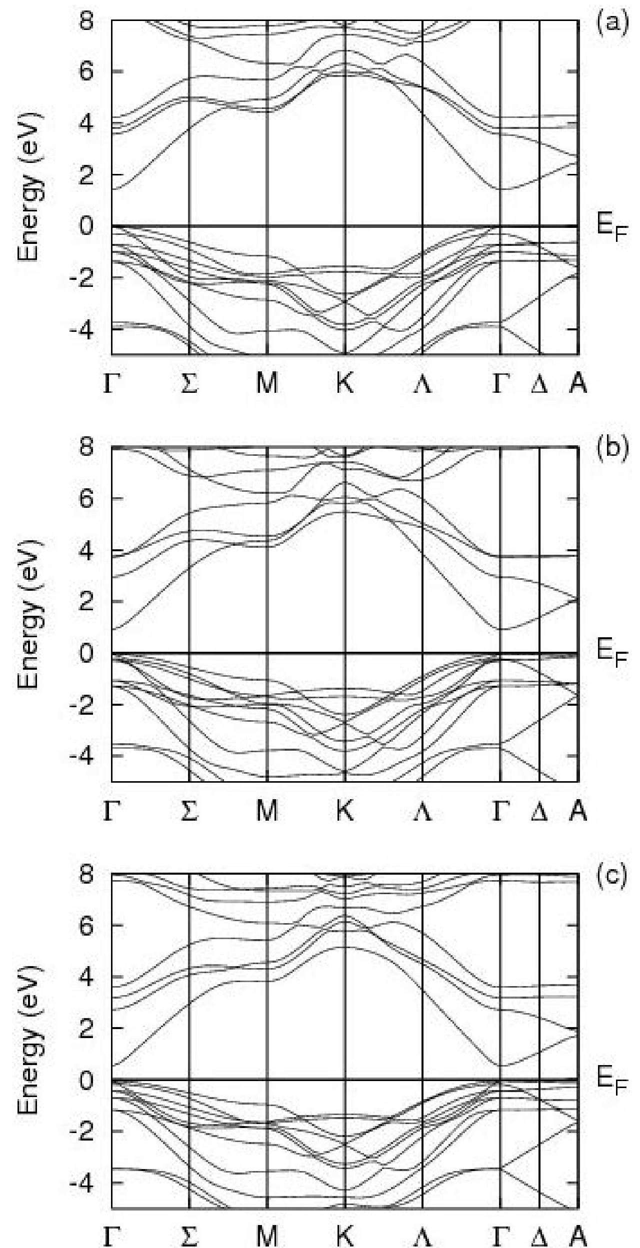

FIGURE 2. Calculated band structure of In_x Ga_{1-x} N, using the EV93 approximation with lattice parameters obtained from experimental results. (a) x = 0.25, (b) x = 0.50 and (c) x = 0.75.

TABLE V. Calculated bowing parameter **b** for $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$. The second column shows the calculated bowing parameters when the experimental lattice parameters are used and the third column when the calculated (optimized) lattice parameters are used.

		b (eV)		
		PBE96	**EV93**	**Exp. Values**
$Al_xGa_{1-x}N$	**Exp. Parameters**	0.534536	0.741106	
	Opt. Parameters	0.570546	0.819609	
				-0.8[a], 2.6[a], 0.69[a], 0.62[a]
$In_xGa_{1-x}N$	**Exp. Parameters**	2.43216	2.12132	
	Opt. Parameters	2.50501	1.96038	
				$\sim$ 1[b,c], 2.4-4.1[d]

[a]Ref. [24]; [b]Ref. [29]; [c]Ref. [30]; [d]Ref. [25]

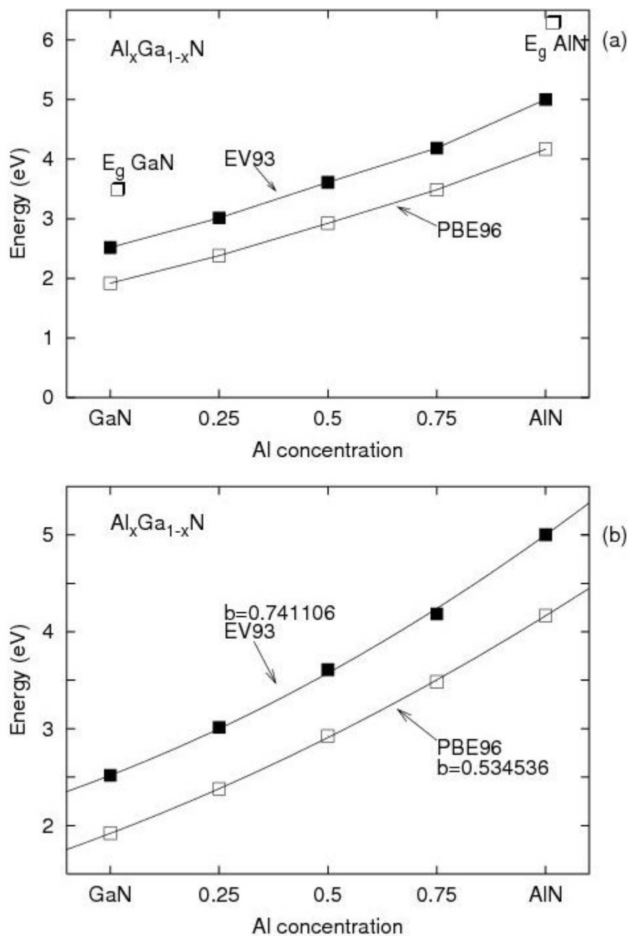

FIGURE 3. (a) Calculated band gap variation of $Al_x Ga_{1-x} N$ with Al concentration. (b) Fit of band gap variation, showing the estimated bowing parameter.

distinct contributions: volume deformation, different atomic electronegativities and structural relaxation. In this work we are interested in the value of the bowing parameter and how this value varies when different correlation-exchange approximations and different lattice parameters are used. These values were obtained fitting equation (2), through nonlinear least-squares (NLLS) Marquardt-Levenberg algorithm, to the computed band gaps (Tables III and IV). Table V shows the bowing parameter calculated for $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$.

For $Al_xGa_{1-x}N$ the experimental results for the bowing factor b range from -0.8 eV to 2.6 eV, which are summarized by Lee *et al.* [24]. In Ref. 24 it is shown that this difference can be related to the growth temperature of the AlGaN layers, reporting a value of 0.69 eV in the composition range $0 < x < 0.45$ and a value of 0.62 eV for AlGaN layers grown on sapphire by MOCVD using low temperature buffer. On the other hand, diverse theoretical studies have produced disperse results. Goano *et al.* [25] reported a value of -0.08 eV using pseudopotential method with VCA approximation; Schilfgaarde *et al.* [19] report 0.34 eV using LMTO calculations with the supercell method; Fritsch *et al.* [26] report 0.2 eV using first principles local orbital calculations with the supercell method; Dridi *et al.* [27] report 0.71 eV using FLAPW with PW91 using a 32 atom supercell. Vurgaftman *et al.* [28] proposed a value of 0.7 eV, on the basis of a compilation and analysis of band parameters for all of the nitrogen-containing III-V semiconductors. Our calculated values with PBE96 using lattice parameters interpolated from experimental and calculated parameters are 0.53 eV and 0.57 eV, respectively, and 0.74 eV and 0.81 eV using EV93 approximation. Considering the results of nitrides, our most reliable estimation is b = 0.74 eV, obtained with the EV93 approximation and using experimental lattice parameters. This value is in agreement with those reported by Lee *et al.* [24], Dridi *et al.* [27] and Vurgaftman [28].

For $In_xGa_{1-x}N$, experimental studies report a bowing parameter of $\sim$1 eV [29,30]; Goano *et al.* [25] report a bowing from 2.4 eV to 4.1 eV for low In composition. In theoretical studies, Schilfgaarde *et al.* [19] report 1.7 eV; Goano *et al.* [25] report 1.115 eV; Teles *et al.* [31] report 0.68 eV using pseudopotential plane waves with LDA and cluster expansion method; Kuo *et al.* [32] report 1.21 eV; Ferhat *et al.* [23,33] obtained a bowing parameter ranging from 1.61 eV (for x = 0.25) to 1.26 eV (for x = 0.75); Dridi *et al.* [27] report a bowing parameter of 1.7 eV; Vurgaftman *et al.* [28] proposed a value of 1.4 eV; Bo-Ting Liou *et al.* [34]

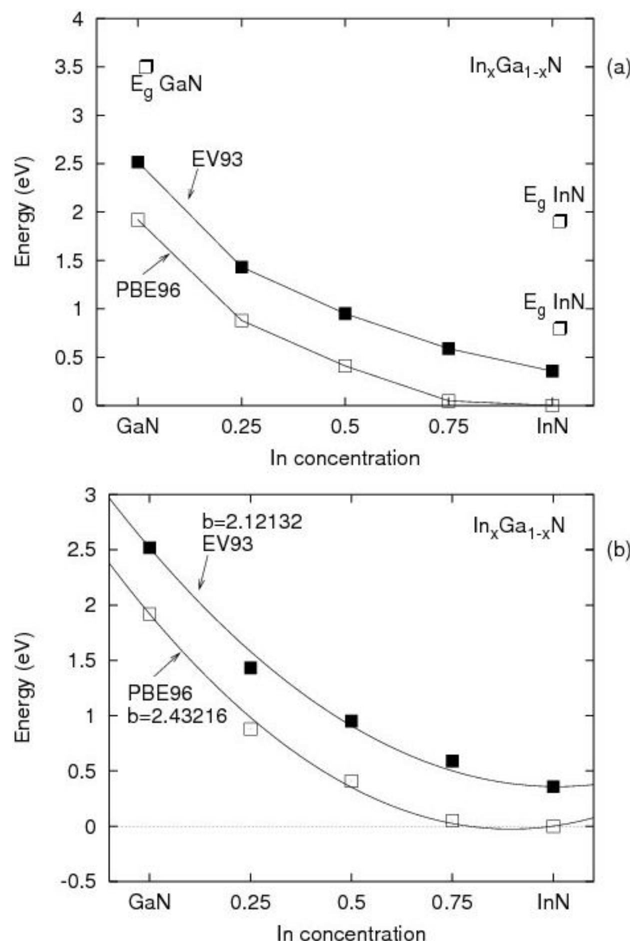

FIGURE 4. (a) Calculated band gap variation of In_x Ga_{1-x} N with In concentration. (b) Fit of band gap variation, showing the estimated bowing parameter.

calculated a value of 1.916 eV using the CASTEP program, with LDA approximation and the supercell method; Caetano *et al.* [35] calculated a value of 1.44 eV using the VASP code and the Cluster Expansion Method, using the supercell method. Our calculated values are 2.43 eV and 2.50 eV using the PBE96 approximation, and 2.12 eV and 1.96 eV using EV93. Our most reliable estimation is b = 2.12 eV, which is comparable with the calculated by Bo-Ting Liou *et al.* [34].

5. Conclusions

Band gap values of AlN, GaN and InN with FLAPW method and two approximations to exchange-correlation functional (PBE96 and EV93) have been computed. Band gap was obtained from calculated (obtained from the structural optimization) and experimental lattice parameters. The calculated band gap values for these nitrides are underestimated in all cases and the best approximation to experimental values are those obtained with the EV93 approximation using experimental lattice parameters. The results presented here show the same tendency of other studies [16,36-38], the EV93 approximation is good for calculating properties related to energy band structure, especially band gap, but it is not reliable for calculating properties related to total energy (such as structural optimization). Moreover our calculations show that the E_g of binary nitrides increases when the cell parameters decrease (see Ref. 39 for experimental work in semiconductor alloys), thus calculations with experimental parameters give us a band gap value closer to the experimental values. This might be due to the increase of both energy band width and the band gap when the interatomic distances decrease. Interacting orbitals repel each other strongly, leading to a large band gap [40,41].

For $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$, band gap values were obtained for concentrations with x = 0, x = 0.25, x = 0.50, x = 0.75 and x = 1.0. We used the PBE96 and EV93 approximations for the calculations, with lattice parameters obtained from Vegard's law using calculated and experimental lattice parameters of binary nitrides. For $Al_xGa_{1-x}N$, our calculated band gap bowing parameter, using PBE96 with lattice parameters interpolated from experimental and calculated parameters, are 0.53 eV and 0.57 eV, respectively. Using EV93 the corresponding values are 0.74 eV and 0.81 eV. Our most reliable approximation is b = 0.74, obtained with EV93 approximation with experimental lattice parameters, which is in good agreement with those reported by Lee *et al.* [24] and Dridi *et al.* [27].

For $In_xGa_{1-x}N$, our calculated band gap bowing parameters are 2.43 and 2.50 eV using PBE96, and 2.12 and 1.96 eV using EV93. Again, our most reliable estimation is b = 2.12, obtained with the EV93 approximation using experimental lattice parameters. This is a large value compared with the majority of reported band gap bowings. Figure 4 shows that for Indium low concentrations ($x < 0.25$) the variation is bigger than for high concentrations, and this behavior might in?uence the bowing parameter calculation. Therefore an improvement in the estimation of the bowing parameter can be obtained considering more points in the fitting procedure, for which it is necessary to use a bigger supercell.

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