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Structural properties of zinc-blende $Ga_xIn_{1-x}N$: ab initio calculations

S. Saib[1,a], N. Bouarissa[2,b], P. Rodríguez-Hernández[1], and A. Muñoz[1]

[1] Departamento de Fisica Fundamental II, Universidad de La Laguna, La Laguna E-38205, Tenerife, Spain
[2] Department of Physics, Faculty of Science, King Khalid University, Abha, P.O. Box 9004, Saudi Arabia

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Abstract. We present a theoretical study of the structural properties, namely lattice constant, bulk modulus and its pressure derivative of zinc-blende $Ga_xIn_{1-x}N$. The calculations are performed using first-principles calculations in the framework of the density-functional-theory within the local density approximation under the virtual crystal approximation. The computed values are in good agreement with the available experimental data. The composition dependence of the studied quantities is examined. Besides, the deviation of the alloy lattice constant from Vegard's law is evaluated.

PACS. 61.66.Dk Alloys – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 71.20.-b Electron density of states and band structure of crystalline solids

1 Introduction

Alloys of $Ga_xIn_{1-x}N$ have shown a large impact on both optoelectronic devices in the near ultra-violet, blue, and green spectral region as well as on electronic devices for high-power high-frequency operation [1–5]. Significant progress in materials physics and device development have made blue light-emitting diodes a widely available consumer product, and laser diodes emitting at about 410 nm close to flood the market as key components in next-generation optical data storage devices [5–10].

The vast majority of studies on III-V nitrides has been focused on a wurtzite crystal phase. However, cubic nitrides are also attracting much interest [11–18]. This is because of possible technological advantages with respect to wurtzite nitrides, such as easier controlled n- and p-type doping, easier cleaning (for laser facets) and easier contacting.

The structural parameters of the crystals of interest are responsible for the efficiency of optical devices. Hence, an accurate knowledge of structural properties is very important. Although a number of experimental and theoretical studies of the structural properties of zinc-blende InN and GaN pure compounds have been reported [19–23], so far to the best of our knowledge, only a few data are available for the ternary alloy $Ga_xIn_{1-x}N$ $(0 < x < 1)$ in the zinc-blende structure [24].

In the present study, first-principles calculations based on the density functional theory (DFT) within the local density approximation (LDA) under the virtual crystal approximation (VCA) are used to investigate the structural properties of zinc-blende $Ga_xIn_{1-x}N$ over the whole range of Ga concentration x. The LDA approximation has turned out to be much more successful than originally expected [25], in spite of its extreme simplicity. For weakly correlated materials, such as semiconductors and simple metals, the LDA accurately describes structural properties: the correct structure is usually found to have the lowest energy, while bond lengths, bulk moduli are accurate to within a few per cent [26]. On the other hand, the VCA assumes that the material is a nearly perfect random alloy and that the electronic structure can be generated from suitably averaged parameters of the constituent compounds. However, recent experimental and theoretical studies on several semiconductor alloys indicate that the VCA breaks down whenever the mismatch between the electronic properties of the constituent atoms exceeds a certain critical value [27–30]. In the present study, the lattice mismatch between GaN and InN appears to be large. This leaves uncertainty on the accuracy of our VCA results. Thus, one should be careful about the results of the alloy system.

2 Theoretical aspects

A first principles pseudo-potential plane-wave method based on the DFT [31] was applied using the LDA with the Ceperley-Alder form [32] of the exchange-correlation

[a] *On leave from*: Physics Department, Faculty of Science and Engineering, University of M'sila, 28000 M'sila, Algeria
[b] e-mail: n_bouarissa@yahoo.fr

Table 1. Equilibrium lattice constant a_0, bulk modulus B and pressure derivative of B (B') for zinc-blende InN, GaN and some of their ternary alloys $Ga_xIn_{1-x}N$ ($0 < x < 1$) compared with previous published data.

Material	a_0 (Å)	B(GPa)	B'
InN	4.96[a]; 4.98[b]; 4.968[c]; 4.901[c]; 5.004[d]; 5.109[d]; 4.92[e]	144[a]; 137[b]; 147[c]; 138[c]; 140[d]; 116.96[d]; 139[e]; 134.86[g]	4.69[a]; 4.4[c]; 3.8[c]; 4.38[d]; 4.4305[d]; 4.4[e]
$Ga_{0.10}In_{0.90}N$	4.93[a]	146[a]	4.66[a]
$Ga_{0.30}In_{0.70}N$	4.85[a]	152[a]	4.64[a]
$Ga_{0.50}In_{0.50}N$	4.77[a]	160[a]; 164.90[g]	4.61[a]
$Ga_{0.70}In_{0.30}N$	4.67[a]	172[a]	4.56[a]
$Ga_{0.90}In_{0.10}N$	4.56[a]	187[a]	4.46[a]
GaN	4.50[a]; 4.49–4.52[b]; 4.497[c]; 4.452[c]; 4.590[d]; 4.518[d]; 4.46[e]; 4.467[f]; 4.521[f]	196[a]; 190[b]; 196[c]; 215[c]; 191[d]; 156[d]; 201[e]; 206.90[f]; 183.69[f]; 200.21[g]	4.42[a]; 4.2[c]; 3.9[c]; 4.14[d]; 4.25[d]; 3.9[e]; 4.48[f]; 4.34[f]

[a] Present work; [b] Expt.: reference [21] and references cited therein; [c] Cal.: reference [21]; [d] Cal.: reference [20]; [e] Cal.: reference [19]; [f] Cal.: reference [22]; [g] Cal.: reference [24].

energy density of the homogeneous gas as parameterized by Perdew and Wang [33]. The pseudopotentials were generated by adopting the scheme described by Troullier-Martins [34]. Both of the $3d$ electrons of Ga and $4d$ electrons of In are treated as valence electrons. Well-converged results were obtained with the consideration of the kinetic energy cutoff of 160 Ry within an accuracy of about 1 mRy per formula unit (pfu), and a mesh of $6 \times 6 \times 6$. All the reciprocal-space integrations were performed using the Monkhorst-Pack scheme [35]. In zinc-blende GaN(InN), the Ga(In) and N-atom positions are Ga(In) (0,0,0) and N(1/4,1/4,1/4). The VCA has been used for the alloy of interest.

3 Results

The calculated equilibrium structural parameters are listed in Table 1. Also shown for comparison are the available experimental and previous theoretical data. The agreement between our results and experiment regarding the equilibrium lattice constant a_0 is very good. In terms of previous calculations, our results agree well with those reported by Serrano et al. [21] using first-principles calculation where the d electrons are included in the valence and allowed to relax. Moreover, the agreement between our result for zinc-blende GaN and that reported recently by Saib and Bouarissa [22] using the LDA approach where the exchange-correlation energy is treated with the Ceperley-Alder form [32] as parameterized by Perdew and Zunger [36] is better than 1%.

The bulk elastic properties of a material determine how much it will compress under a given amount of external pressure. The ratio of the change in pressure to the fractional volume compression is called the bulk modulus of the material. As shown in Table 1, the agreement between our results regarding the bulk modulus B and the experimental data reported in reference [21] is within 5%. Furthermore, our results agree well with the theoretical data reported in references [19–21,24]. The bulk modulus of zinc-blende GaN seems to be larger than that of zinc-blende InN. This may arise from the shorter bond length of GaN (2.08 Å [37]) when compared to that of InN (2.34 Å [37]). For lack of experimental data regarding the pressure derivative of the bulk modulus, B', our results have been compared with other published theoretical data and found to be larger than those reported in references [19–21]. In the absence of both experimental and theoretical data, our results concerning a_0, B, and B' for zinc-blende $Ga_xIn_{1-x}N$ ($0 < x < 1$) are predictions. Nevertheless, at $x = 0.50$, our result regarding B is compared with that reported by Bouarissa and Kassali [24] using the empirical pseudopotential method under the VCA combined with the Harrison bond-orbital model. The comparison shows good agreement between our result and that reported in reference [24]. The same conclusion has been drawn in our previous discussion for InN ($x = 0$) and GaN ($x = 1$). It is then more reasonable to think that it is possible to establish, in a simple manner, a relation between the first-principles electronic structure theories and the parameters entering the more empirically based models.

The variation of a_0 as a function of Ga content in $Ga_xIn_{1-x}N$ mixed crystals is shown in Figure 1. Note that as one goes from pure InN ($x = 0$) to pure GaN ($x = 1$) a_0 decreases monotonically from 4.96 Å to 4.50 Å.

Generally, in ternary alloys ($A_xB_{1-x}C$), the dependence of the energy gap (E_g) on the alloy composition is assumed to fit a simple quadratic form [38],

$$E_g(A_xB_{1-x}C) = xE_g(AC)+(1-x)E_g(BC)-bx(1-x) \quad (1)$$

where b is the so-called band-gap bowing parameter. Using the above functional form for a_0, where b was determined by making a polynomial fit of order two of the a_0 data

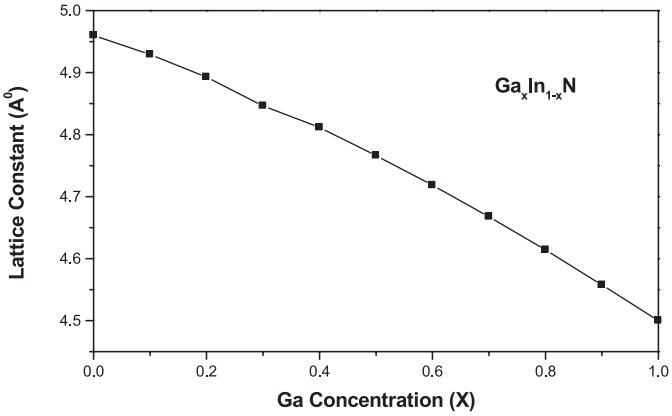

Fig. 1. Lattice constant of zinc-blende $Ga_xIn_{1-x}N$ as a function of composition x.

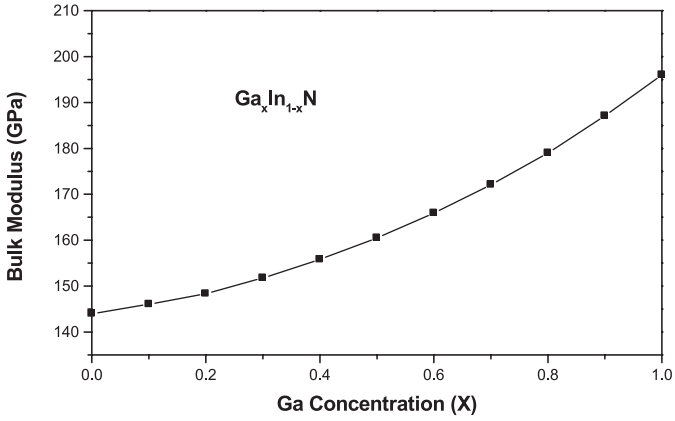

Fig. 2. Bulk modulus of zinc-blende $Ga_xIn_{1-x}N$ as a function of composition x.

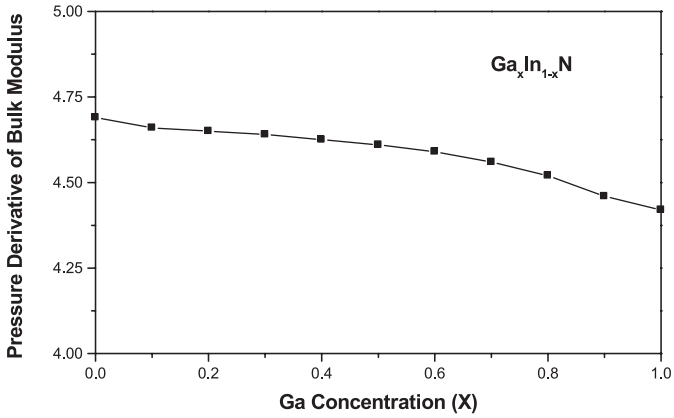

Fig. 3. Pressure derivative of bulk modulus of zinc-blende $Ga_xIn_{1-x}N$ as a function of composition x.

using a least-squares procedure, we get,

$$a_0(x) = 4.96 - 0.32x - 0.14x^2 \quad (2)$$

a_0 is expressed in Å. For calculating the lattice constant of semi conducting alloys, people often are using Vegard's law. According to Vegard's law [39], the lattice constant of alloys should vary linearly with the alloy composition x. In our case, when using Vegard's law, the lattice constant of the alloy of interest is expressed as,

$$a_0(x) = 4.96 - 0.46x. \quad (3)$$

A comparison between expressions (2) and (3) shows a clear deviation from Vegard's law. As a matter of fact, violations of Vegard's law have been already reported for other semiconductor alloys [40,41]. The quadratic deviation of the lattice constant from Vegard's law shown by expression (2) is essentially due to the lattice relaxation effect not taken into account in Vegard's rule. If we express the deviation from Vegard's law by $\Delta a_0(x)$, then

$$a_0(x) = 4.96 - 0.46x + \Delta a_0(x). \quad (4)$$

Hence, from equations (2) and (4), one can deduce,

$$\Delta a_0(x) = 0.14x(1 - x) \quad (5)$$

which shows a dependence on x.

The composition dependence of the bulk modulus B is plotted in Figure 2. Note that as the Ga concentration x increases on going from 0 (InN) to 1 (GaN), B increases monotonically and non-linearly exhibiting a large bowing parameter. This suggests that the alloy of interest becomes more compressible as far as the Ga content becomes larger. Using a similar form of equation (1) for B, one can obtain,

$$B(x) = 144 + 13.78x + 38.22x^2 \quad (6)$$

where B is expressed in GPa.

In Figure 3, we show the variation of the pressure derivative of the bulk modulus (B') as a function of Ga concentration x. In view of Figure 3, one can note that as x varies from 0 to 1, B' decreases monotonically. However, the rate of decrease is slower in the range 0.1–0.5 than that of 0.5–1. Using the functional form of equation (1), B' can be expressed as,

$$B'(x) = 4.69 - 0.03x - 0.24x^2. \quad (7)$$

4 Conclusion

In summary, using an ab initio pseudopotential plane wave method based on the DFT within the LDA under the VCA, the structural properties of $Ga_xIn_{1-x}N$ in the zinc-blende structure have been investigated. The numerically calculated results are found to be in good agreement with the available experimental data. For lack of both experimental and theoretical data in the composition range 0–1 ($0 < x < 1$), the present results in this range are predictions and may serve for a reference. The composition dependence of the studied quantities was examined and found to vary monotonically and non-linearly with x. The deviation of the alloy lattice constant from the Vegard's law showed a dependence on the composition x.

While the present calculations still leave a doubt about the validity because of the VCA, it might be worthwhile

checking with further work. Therefore, further experimental measurements and super cell calculations that simulate the effects of disorder are needed in order to obtain more accurate and reliable results for the (GaIn)N system.

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