THE STRUCTURAL AND ELECTRONIC PROPERTIES OF GAN UNDER HIGH PRESSURE

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ABSTRACT: The structural phase transformations of GaN under high-pressure are studied using the full-potential linearized augmented plane wave (FP-LAPW) approaches within the density functional formalism (DFT) in the local density approximation (LDA) and the generalized gradient approximation (GGA). We have calculated the ground-state energy, the lattice constant, the bulk modulus, its pressure derivative, and the electronic structure of the wurtzite (WZ), zinc-blende (ZB) and rocksalt (RS) phases of GaN. The GGA results of the critical pressure of the WZ→ZB and WZ→RS transitions present small but non negligible variations with respect to the LDA results. The RS-GaN is predicted to be an indirect band gap semiconductor, with a band gap of 1.68 eV.

KEYWORDS: FP-LAPW, Density functional formalism, GaN under high-pressure, Structural phase transformations.

1. Introduction

GaN has recently attracted a lot of attention due to its great potential for technological applications [1]. In the wurtzite (ground-state) structure, GaN, which has a direct energy band gap, can be used in optical devices operating at blue and ultraviolet wavelengths. In addition, GaN has a high melting point, a high thermal conductivity and a large bulk modulus [2]. These properties, as well as the wide band gap, are closely related to its strong (ionic and covalent) bonding. This material can therefore be used for short wavelength light-emitting diodes (LED's), laser diodes, and optical detectors, as well as for high-temperature, high-power, and high frequency devices.

In order to help in the understanding and control of materials and device properties, theoretical studies can be most valuable. A growing number of first-principles calculations have been performed for this material over the past few years to gain an understanding of its structural transformation under high pressure. Most of these calculations are based on density-functional theory employing the local-density approximation (LDA), either in all-electron formalism or using the pseudopotential planewave approach. A number of studies have also been carried out using *ab-initio* Hartree-Fock methods. However, these methods are much more computationally demanding than the LDA, and they significantly overestimate the band gap. It is well known that the LDA leads to an underestimate of the band gap in semiconductors [3, 4].

The use of the generalized gradient approximation (GGA) in density-functional theory calculations is currently receiving increasing attention as a possible improvement over the LDA. The GGA has generally been found to improve the description of total energies, ionization energies, electron affinities of atoms, atomization energies of molecules [5-7], and properties of solids [8-11].

GaN crystallizes in the wurtzite (WZ) structure. However, thin films of GaN can be successfully obtained by epitaxial growth in both WZ and zinc-blende (ZB) structures, depending on the

substrate [12]. WZ-GaN is known to transform under high pressure to the rocksalt (RS) structure. In spite of several experimental and theoretical investigations, the transition pressure p_t of the WZ→RS transition is still a controversial issue [13], and so is the bulk modulus B_0 of WZ-GaN. The aim of this work is to present theoretical results to further understanding of the transition pressure and bulk modulus of this material.

Using X-ray absorption spectroscopy (XAS), Perlin et al. [14, 15] report that GaN under high-pressure makes a transition to the RS phase at about 47 GPa. Using first-principles pseudopotential planewave (PP-PW) calculations, Munoz and Kunc [16] and Abu-Jafar [17] have predicted a transition of GaN under high-pressure to the RS phase. The prediction has been confirmed by the X-ray diffraction investigations of Xia et al. [18] and Ueno et al. [19], which gave values of 37 and 52.2 GPa, respectively. The discrepancies between these experimental results for p_t have been attributed to the sensitivity of the techniques used, in addition to the nature of the samples (powder [18, 19] versus single crystal [14, 15]). There were also variations in the values of bulk modulus B_0 and volume contraction $\Delta V/V_0$ associated with the WZ→RS phase transition obtained by the above experimental investigations ranging from 188 [18] to 245 GPa [14, 15] for B_0 and 14% [14, 15] to 17.9% [19] for $\Delta V/V_0$. Theoretical results concerning GaN properties (p_t, $\Delta V/V_0$ and B_0) were not any better. The linear muffin-tin orbital, using the atomic-sphere-approximation (LMTO-ASA) [20] and the full potential (FP) LMTO calculation [21] gave a value for p_t of 51.8 GPa for the WZ→RS transition and 38.2 GPa for the ZB→RS, respectively. The calculated values of B_0 and $\Delta V/V_0$ ranged between 176 and 240 GPa [13] and between 10 and 17.9% [19], respectively. Furthermore, the energy band structures of WZ-, ZB- and RS-GaN were studied and an accurate theoretical determination of p_t in addition to the structural and electronic structure properties of GaN has been calculated.

2. Calculations

In our calculation, we used the WIEN2k code [22], an all-electron full-potential linearized augmented planewave method (FP-LAPW) code, within the local-density approximation (LDA) or the generalized approximation proposed by Perdew-Brouke-Ernzerhof (GGA96). As exchange-correlation potential, we used the Ceperly-Alder [23] as parameterized by Perdew and Zunger [24] in order to see the dependence of the structural properties on the exchange-correlation potential, since it is known that the gap is highly sensitive to the form of exchange-correlation potentials. The scalar relativistic treatment was used for the valence states, whereas the core states were treated fully relativistically [25], and self-consistently updated at each iteration. The *3d* electrons of the Ga atom were treated as part of the valence band since they are relatively high in energy even though they need quite a large value for the product $R_{MT}K_{max}$ (where R_{MT} is the average radius of the muffin-tin spheres and K_{max} is the maximum value of the wave vector $\mathbf{K} = \mathbf{k}+\mathbf{G}$) in order to have a suitable number of plane waves to correctly describe these states. We used different sphere radius values for Ga and N, the use of a full-potential ensuring that the calculation is completely independent of the choice of sphere radii. Inside the muffin-tin, the sphere radii were $R_{MT} = 1.95$ *a.u.* for Ga and $R_{MT} = 1.65$ *a.u.* for N. Atomic orbital up to an angular momentum $l = 10$ were used to expand the wave functions inside the muffin-tin spheres. A satisfactory degree of convergence was achieved by considering a number of FP-LAPW basis functions up to $R_{MT}K_{max} = 9$. So, in order to keep the same degree of convergence for all the lattice constants

studied, we kept the values of the sphere radii and of K_{max} constant over all the range of lattice spacing considered. We also mentioned that the integration in reciprocal lattice space was performed using the special points method. We used a 10 × 10 × 10 mesh for the ZB and RS forms and 12 × 12 × 6 mesh for the WZ phase.

The crystal structure of the ZB phase can be fully defined by just one lattice constant a with two atoms per unit cell, one at $(0,0,0)$ and the other at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})\,a$ with unit vectors $\mathbf{a} = (0,\frac{1}{2},\frac{1}{2})\,a$, $\mathbf{b} = (\frac{1}{2},0,\frac{1}{2})\,a$, and $\mathbf{c} = (\frac{1}{2},\frac{1}{2},0)\,a$; the same holds for the RS phase, with one at $(0,0,0)$ and the other at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})\,a$ with unit vectors $\mathbf{a} = (\frac{1}{2},0,0)\,a$, $\mathbf{b} = (0,\frac{1}{2},0)\,a$, and $\mathbf{c} = (0,0,\frac{1}{2})\,a$. For the wurtzite phase, there are four atoms per hexagonal unit cell. Using unit vectors $\mathbf{a} = (\frac{1}{2},\frac{\sqrt{3}}{2},0)\,a$, $\mathbf{b} = (\frac{1}{2},-\frac{\sqrt{3}}{2},\frac{1}{2})\,a$, and $\mathbf{c} = (0,0,c/a)\,a$, the position of the atoms are $(0,0,0)$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$ for atoms of the first type, and $(0,0,u)$ and $(\frac{2}{3},\frac{1}{3},u+\frac{1}{2})$ for atoms of the second type, where u is the dimensionless internal parameter. For the ideal wurtzite structure, $c/a=\sqrt{\frac{8}{3}}$ and $u=\frac{3}{8}$.

To determine the equilibrium geometry of the wurtzite phase, we optimize the independent parameters, V (volume of the unit cell), *c/a*, and *u* as follows: In the first step, we assume the ideal wurtzite structure and determine the equilibrium volume by varying the lattice constant *a*; then, keeping the equilibrium volume fixed and $u=\frac{3}{8}$, the *c/a* ratio is varied (generally in the range from 1.593 to 1.663 in steps of 0.01) to find the optimum value. At the new *c/a* ratio we vary the lattice constant *a* once again, to determine the new equilibrium volume V' ; then, having *c/a* and V', we vary the internal parameter *u* (generally from 0.365 to 0.390 in steps of 0.005) to minimize the total energy. It has been found that the equilibrium *c/a* is V-independent. This finding is consistent with the experimental result of Ueno et al. [19], which shows that basically the *c/a* ratio does not change for GaN under hydrostatic compression. The GGA values of *c/a* and *u* are 1.628 and 0.379 whereas, according to the LDA calculations, they are 1.633 and 0.377, respectively. These values are in excellent agreement with the experimental and theoretical values [19, 26, 27].

3. Results and discussion

We have calculated the total energy curves for the three considered structures of GaN, with the GGA and LDA approximations. The ground-state structural parameters have been obtained by minimizing the total energy with respect to the volume by fitting this total energy versus volume data on the nonlinear Murnaghan equation of state [33] as shown in Figs.1.(a, b). We have obtained values for the lattice parameters, the bulk modulus and its pressure derivative, the details of which are shown with other values in Table.1. The important feature to note from these figures is that the WZ phase is the ground state structure, the difference between the WZ and ZB phases ground state energies being very small (0.0078 eV from LDA and 0.0087 eV from GGA) due to the fact that both phases have local tetrahedral bonding but differ only in their second-nearest neighbors. The difference between WZ and RS phases is 0.4221 eV/atom from LDA, and 0.4708 eV/atom from GGA. Comparison between LDA and GGA calculations of the relative stability of all these structures show small but non negligible differences.

Table.1: Structural parameters for the three phases of GaN.

Method	a_0(Å)	c_0(Å)	B(Mbar)	B'
Wurtzite				
FP-LAPW: LDA*	3.1555	5.1529	2.05	4.37
FP-LAPW GGA*	3.2241	5.2488	1.72	5.23
FP-LAPW: LDA[17]	3.163	5.140	2.08	5.79
FP-LAPW: GGA[17]	3.226	5.243	1.72	4.86
PPPW(3d): LDA[28]	3.162	5.142	2.02	
AE :LDA[29]	3.17	5.13	2.07	4.5
PPPW(3d): GGA[27]	3.245	5.296	1.72	5.11
Expt[27, 29, 30]	3.180,3.192	5.166	1.88-2.45	3.41-3.65
Zinc-Blende				
FP-LAPW: LDA*	4.4638		2.05	4.29
FP-LAPW: GGA*	4.5564		1.74	3.75
FP-LAPW: LDA[17]	4.466		2.08	4.64
FP-LAPW: GGA[17]	4.554		1.75	5.30
FPLMTO: LDA[21, 31]	4.462,4.47		199,198	3.8
PPPW(3d): LDA[28]	4.460		1.87	
PPPW(3d): LDA[32]	4.524		2.06	3.7
AE: LDA [31]	4.466		1.98	
PPPW(3d): GGA[27]	4.590		1.56	4.25
Expt [2, 29, 30]	4.50,4.531		1.90	3.45,3.21
Rocksalt				
FP-LAPW: LDA*	4.1847		2.51	4.44
FP-LAPW: GGA*	4.2694		2.22	4.24
FP-LAPW: LDA[17]	4.185		2.52	4.49
FP-LAPW: GGA[17]	4.271		2.12	4.50
PPPW: LDA[17]	4.240		2.35	4.71
FPLMTO: LDA[21]	4.221		2.48	3.00

*Present work.

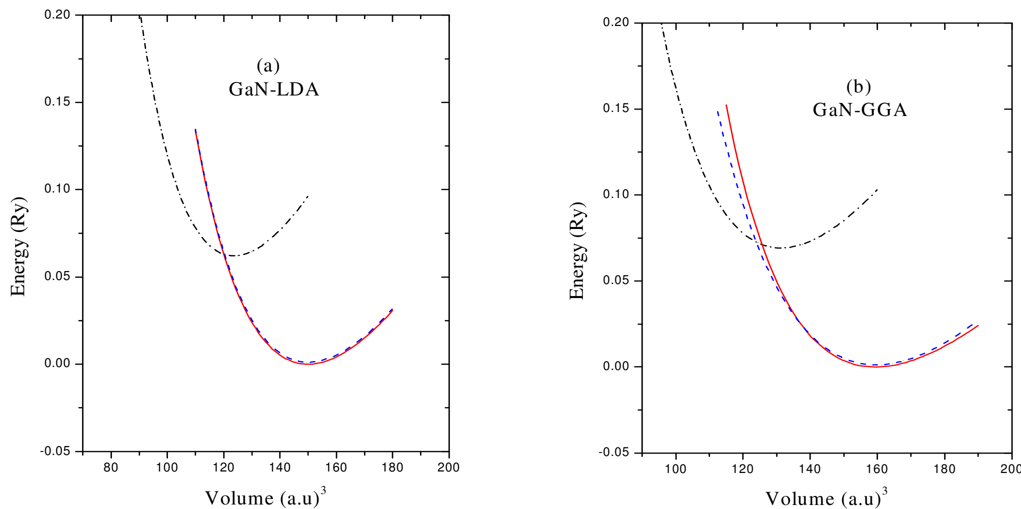

Figure 1: Energy versus volume curves of the WZ (Solid line), ZB (Dash line) and RS (Dash-Dot line) phases for GaN, (a) of LDA and (b) of GGA.

The ground state structural parameters are calculated by treating the Ga *3d* electrons as valence. The important features to note are as follows. Firstly, our results for WZ and ZB phases are almost identical to those of [17, 28 and 27], except for the bulk modulus and its pressure derivative. Secondly, the experimental values of the lattice parameters and bulk moduli of WZ and ZB phases lay between our LDA and GGA results.

The transition pressures p_t of the WZ→RS and ZB→RS transitions of GaN were determined by construction as minus the slope of the common tangent to the respective E(V) curves. Results obtained for p_t are listed in Table.2 with a few theoretical results and experimental data.

Our results for the transition pressure p_t of WZ→RS and ZB→RS of the LDA and GGA approximation differ slightly by 4.52 GPa. This is expected from the use of well truthful approach and the close similarity between the WZ and ZB phases. These values can be favorably compared with the theoretical results from Abu-Jafar and Qteish [17]. In contrast, this also shows that the GGA approximation has very small effects compared to the LDA one on the critical pressure of GaN even though this is not the case with the result of Christensen [20]. This discrepancy can be understood in the latter case by their use of the Atomic Sphere Approximation (ASA) whereas, in the result of Munoz [21], this is caused by their treatment of the Ga *3d* electrons as part of a frozen core.

The present results agree very well with XAS results [14, 15], compared to the results obtained by Abu-Jafar and Qteish [17], for both p_t and $\Delta V/V_0$. The difference on the GGA value of p_t is equal to 2.41 GPa for the WZ→RS transition. The difference between XAS results and those of other X-ray diffraction measurements may be due to the nature of the samples used (powder [18] versus single crystal [14, 15]). The exceptional agreement between our results for $\Delta V/V_0$ and those of Perlin et al. [14, 15] supports further the consistency of our results.

Table.2: Transition pressure (p_t) and volume contraction ($\Delta V/V_0$)

Method	p_t (Gpa)	$\Delta V/V_0$ (%)
WZ→RS transition		
FP-LAPW: LDA*	40.07	13.18
FP-LAPW: GGA*	44.59	15.11
FP-LAPW: LDA[17]	38.10	14.96
FP-LAPW: GGA[17]	42.30	13.62
ASALMTO:LDA[20]	51.8	12
PPPW: LDA[21]	56	18.4
XAS [14, 15]	47	14
X-ray diffraction[18]	37	17
X-ray diffraction[19]	52	17.9
ZB→RS transition		
FP-LAPW: LDA*	40.15	13.25
FP-LAPW: GGA*	41.85	15.75
FP-LAPW: LDA[17]	38.15	14.32
FP-LAPW: GGA[17]	40.80	14.10
PPPW: LDA[17]	42.60	12.80
PPPW: LDA[21]	53.80	18
FPLMTO: LDA[21]	38.21	13.4

*Present work.

The calculated band structures in both LDA and GGA approximations of the three phases of GaN are shown in Figs.2.(a, b and c). These figures show that both the WZ and ZB phases are direct band gap semiconductors at the Γ point, whereas the RS one is an indirect band gap semiconductor, with the valence band maximum at the L point and the conduction band minimum very close to the X point along the XW direction. The LDA band gap of WZ-GaN is 2.09 eV, underestimated by 1.21 eV with respect to the experimental value of 3.3 eV. As shown the use of GGA does not solve the underestimating of the band gap by the LDA. In the opposite, GGA band gaps are smaller than those of LDA by 0.41 eV for both WZ and ZB phases and 0.17 eV for the RS phase. The same tendency has been observed for the *3d* Ga band, which was underestimated by 2.32 eV (13.38 eV compared to the experimental result of 15.7 eV [34]), and for the upper valence band value of 7.52 eV and 7.41 eV from LDA and GGA, respectively, compared to the experimental result of 6.5 eV [34], contrary to the result of Abu-Jafar and Qteish [17] were observed divergence between the LDA and GGA result, and this due to the difference in the calculation parameters like the mesh and the $R_{MT}K_{max}$ in their calculations.

As shown in Figures 2, the electronic structures of WZ and ZB phases are very similar and this is due to the similarity of these phases. Previously, we had seen that the LDA and GGA approximations underestimate the band gap; we expect the same trend for the band gap of RS-GaN, our calculated indirect band gap equaling 1.68.

In summary, results of the present work for p_t and $\Delta V/V_0$ at the WZ$\rightarrow$RS phase transition agree well with experimental data of Refs.[14, 15] and theoretical results of Ref.[17]. Structural parameters are in excellent agreement with experimental data and theoretical results. The use of GGA is found to have a slight advantage on LDA in the calculation of structural properties and p_t; however, this is not the case for the electronic structural properties where LDA gave improved results. RS-GaN is predicted to be an indirect band gap semiconductor with a band gap of 1.68 eV.

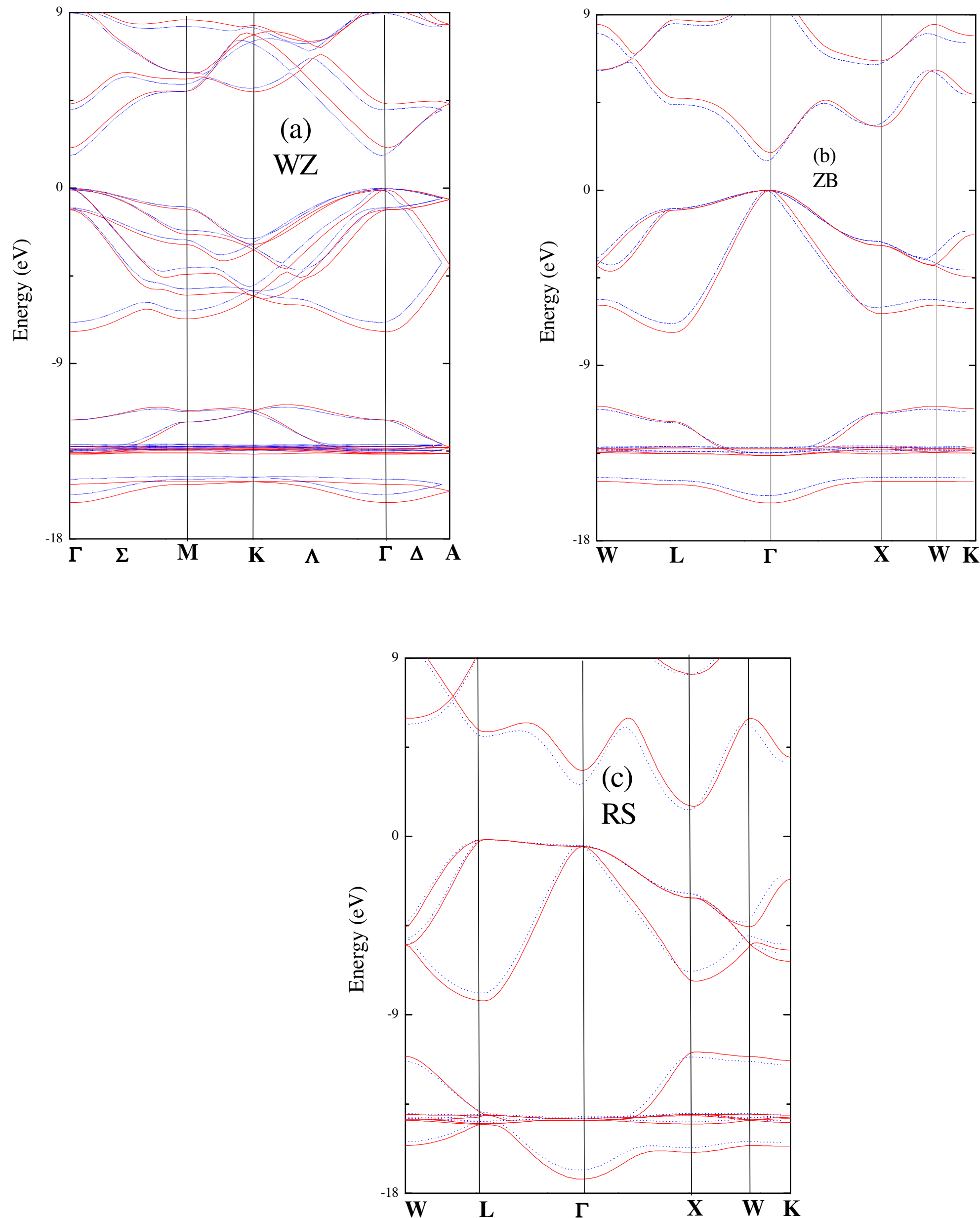

Figure 2: Calculated Band structure of GaN (a) WZ, (b) ZB and (c) RS structure, using LDA (Solid lines) and GGA (Dot lines).

Références

[1] *Wide-band gap semiconductor*; proceeding of the seventh Trieste semiconductor symposium; 1992, edit by C. G. Van de Walle (North-Holland, Amsterdam, 1993).

[2] *Properties of Group-III Nitrides*; edited by J. H. Edgard, EMIS Data Reviews Series (IEE, London, 1994).

[3] J. P. Perdew and M. Levy; Phys. Rev. Lett. **51**, 1884 (1983).

[4] L. J. Sham and M. Schlüter; Phys. Rev. Lett. **51**, 1888 (1983).

[5] J. P. Perdew, J. A. Chevay, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhis; Phys. Rev. B **46**, 6671 (1992).

[6] B. G. Johnsen, P. M. W. Gill and J. A. Pople; J. Chem. Phys. **98**, 5612 (1993).
[7] A. D. Becke; in The Challenge of d and f Electron; ACS Symposium Series No. 394; edited by D. R. Salahub and M. C. Zerne (American Chemical Society, Washington, DC, 1989), p. 165.
[8] A. Garcia, C. Elsaesser, J. Zhu, S. Louie and M. L. Cohen; Phys. Rev. B **46**, 9829 (1992).
[9] Y. M. Juan, E. Kaxiras and R. G. Gordon; Phys. Rev. B **51**, 9521 (1995).
[10] A. Dal Corso, A. Pasquarello, A. Baldereschi and R. Car; Phys. Rev. B **53**, 1180 (1996).
[11] M. Körling and J. Häglund;Phys. Rev. B **45**, 13 293 (1992).
[12] M. J. Paisley, Z. Sitar, J. B. Posthill and R. F. Davis; J. Vac. Sci. Technol. A **7**, 701 (1989).
[13] N. E. Christensen; in: T. Suski, W. Paul (Eds.); High Pressure in Semiconductor Physics, Academic Press, New York, 1997, p. 49.
[14] P. Perlen, C. Jauberthie-Carillon, Lti, A. S. Miguel, I. Grzegory and A. Polian; High Press. Res. **7**, 96 (1991).
[15] P. Perlen, C. Jauberthie-Carillon, Lti, A. S. Miguel, I. Grzegory and A. Polian; Phys. Rev. B **45**, 83 (1992).
[16] A. Muñoz and K. Kunc; Phys. Rev. B **44**, 10 372 (1991).
[17] M. Abu-Jafar, A. I. Al-Sharif and A. Qteish; Solid. State. Commun. 116. 389 (2000).
[18] H. Xia, Q. Xia and A. L. Ruoff; Phys. Rev. B **47**, 12 925 (1993).
[19] M. Ueno, M. Yoshida, A. Onodera, O. shimomura and Takemura; Phys. Rev. B **49**, 49 (1994).
[20] N. E. Christensen and I. Gorezyca; Phys. Rev. B **50**, 4397 (1994).
[21] A. Muñoz and K. Kunc; Comput. Mater. Sci. 2. 400 (1994).
[22] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz; WIEN2k, An Augmented Plane Wave + Local Orbital Program for Calculating Crystal Properties (Karlheinz Schwartz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2.
[23] D. M. Ceperley and G. L. Alder; Phys. Rev. Lett. **45**, 566 (1980).
[24] J. P. Perdew and A. Zunger; Phys. Rev. B **23**, 5048 (1981).
[25] D. D. Koelling and B. N. Harmon; J. Phys. C. Sol. St. Phys. **10**, 3107 (1977).
[26] H. Shultz and K. H. Thiemann; Solid State Commun. **23**, 851 (1977).
[27] C. Stampfl and C. G. Van de Walle; Phys. Rev. B **59**, 5521 (1999).
[28] A. F. Wright and J. S. Nelson; Phys. Rev. B **51**, 7866 (1995).
[29] K. Kim, W. R. Lambrecht and B. Segall; Phys. Rev. B **53**, 16 310 (1996).
[30] R. C. Powell, N. E. Lee, Y. M. Kim and J. E. Greene; J. Appl. Phys. **73**, 189 (1993); R. C. Powell, G. A. Tomasch, Y. M. Kim, J. A. Thornton and J. E. Greene, in *Diamond, Silicon Carbide and Related Wide Band Gap Semiconductor*; edited by J. T. Glass, R. Messier, N. E. Fujimori, MRS Symposia Proceedings No. 162 (Materials Research Society, Pittsburgh, 1990) p. 525.
[31] V. Fiorentini, M. Methfessel and M. Scheffler ; Phys. Rev. B **47**, 13 353 (1993).
[32] V. Fiorentini, A. Satta, D. Vanderbilt, S. Massidda and F. Meloni; in *the physics of Semiconductors*; edited by D. J. Lock-Wood (Word scientific, Singapore, 1995), p. 137.
[33] F. D. Murnaghan; Proc. Natl. Acad. Sci. USA, **30,** 244 (1944).
[34] T. Maruyama, Y. Miyajima, K. Hata, S. H. Cho, K. Akimoto, H. Okumura, S. Yoshida, and H. Kato, J. Electron. Mater. **27**, 200 (1998).