PERGAMON

Solid State Communications 116 (2000) 389–393

solid state communications

www.elsevier.com/locate/ssc

FP-LAPW and pseudopotential calculations of the structural phase transformations of GaN under high-pressure

M. Abu-Jafar[a], A.I. Al-Sharif[b], A. Qteish[b,*]

[a]*Department of Physics, An-Najah National University, Nablus, Palestine*
[b]*Department of Physics, Faculty of Science, Yarmouk University, Irbid, Jordan*

Received 12 June 2000; accepted 4 August 2000 by E. Molinari

Abstract

FP-LAPW and pseudopotential approaches have been used to investigate the structural phase transformations of GaN under high-pressure. In these calculations the local density and generalized gradient approximations (LDA and GGA) for the exchange-correlation potential have been used. Moreover, the electronic structure of the wurtzite (WZ), rocksalt (RS) and zinc-blende (ZB) phases of GaN have been calculated. The GGA result for the transition pressure of the WZ → RS transition is of 42.3 GPa, which is in very good agreement with the X-ray absorption spectroscopy value of 47 GPa. The gradient corrections to the LDA, included via GGA, have small, but not negligible, effects on the properties studied. RS-GaN is predicted to be an indirect-band-gap semiconductor, with a band-gap of 1.7 eV.

Keywords: A. Semiconductors; D. Equation of state; D. Phase transitions; D. Electronic band structure

PACS: 64.20.+t; 64.70.Kb; 71.20.Nr

GaN has recently attracted a lot of attention because of its use in optical devices operating in blue and ultraviolet wavelengths, and in high-temperature electronic devices [1]. At ambient pressure, 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 [2]. The 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 (for a review see Ref. [3]), and so does the compressibility (or bulk modulus (B_{eq})) of WZ-GaN. The main goal of this work is to contribute toward an accurate theoretical determination of p_t and B_{eq} of this system.

The first evidence of a transition of GaN under high-pressure to an unknown crystal structure was provided by the X-ray absorption spectroscopy (XAS) measurements of Perlin et al. [4,5], at about 47 GPa. Muñoz and Kunc [6] have predicted the unknown high-pressure structure to be the RS phase, using first-principles pseudopotential plane-wave (PP-PW) calculations. This prediction has been confirmed by the X-ray diffraction investigations of Xia et al. [7] and Ueno et al. [8], which gave values for p_t of 37 and 52.2 GPa, respectively. One should note that the above values for p_t were obtained upon pressure increase. The discrepancies between the above experimental results for p_t have been attributed to the sensitivity of the techniques used, as well as to the nature of the samples (powder [7,8] versus single crystal [4,5]). Moreover, there are also discrepancies in the obtained values for B_{eq} and the volume contraction, $\Delta V/V_0$, associated with the WZ → RS phase transition, obtained by the above experimental investigations: ranging from 188 [7] to 245 GPa [4,5] for B_{eq}; 14 [4,5] to 17.9% [8] for $\Delta V/V_0$. The situation of the theoretical results for the above properties of GaN is not any better. The pseudopotential [6] (with the Ga 3d electrons treated as part of the frozen core) and LMTO-ASA (linear mufin-tin orbital, using the atomic-sphere-approximation) [9] results for p_t lie above the range of the experimental values. This is not consistent with the rational that the theoretical results must lie below the experimental values obtained upon pressure increase. On the other hand, full-potential (FP)-LMTO calculations [10] gave a value of 38.2 GPa, for the ZB → RS transition, in accord with the experimental result

* Corresponding author.
E-mail address: aqteish@yu.edu.jo (A. Qteish).

0038-1098/00/$ - see front matter
PII: S0038-1098(00)00336-7

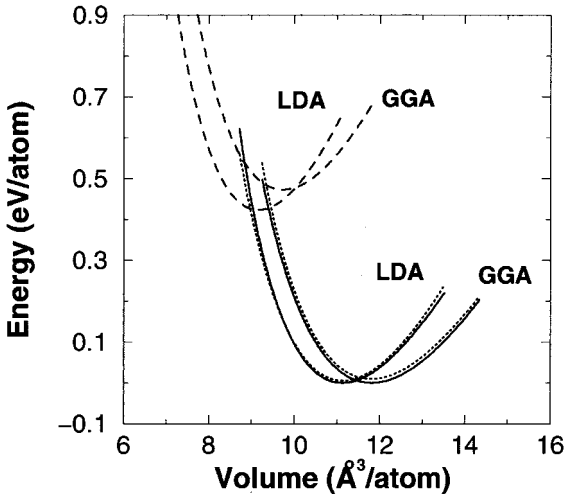

Fig. 1. Energy versus volume curves of the WZ (solid lines), ZB (dashed–dotted lines) and RS (dashed lines) phases of GaN.

of Refs. [4,5]. However, it has been found [10,11] that the FP-LMTO results for p_t are sensitive to the computational ingredients used. The calculated values for B_{eq} and $\Delta V/V_0$ range between 176 and 240 GPa [3] and between 10 and 17.9% [8], respectively. Moreover, to the best of our knowledge, the electronic band structure of RS-GaN has not been studied before. Therefore, an accurate theoretical determination of p_t, as well as the structural and electronic structure properties of GaN is in order.

In this work, a full-potential linearized augmented plane-wave (FP-LAPW) method is used to investigate the structural and electronic structure properties of the WZ, ZB and RS phases of GaN. The so-obtained equations of state are used to investigate its WZ → RS and ZB → RS phase transitions under high-pressure. In these calculations both the local density and generalized gradient approximations (LDA and GGA) have been used. Moreover, as a further check we also performed PP-PW calculations in which the Ga 3d electrons are treated as valence. Both methods have been successfully applied to study structural phase transitions of semiconductors under high-pressure.

The computational details of the FP-LAPW calculations are as follows. The calculations were performed by using the WIEN97 computer code [12]. The Ga 3d electrons were treated as valence. For the LDA and GGA exchange-correlation (XC) potentials, we have used the Perdew and Wang [13], and the Perdew, Burke, and Ernzerhof [14] interpolation formulae, respectively. Atomic orbitals up to an angular momentum equal to ten were used to expand the wavefunctions inside the muffin-tin spheres. Whereas, in the interstitial regions they are expanded in terms of PWs. The wavefunctions and their derivatives are made continuous at the boundary of the spheres, and there are no shape approximations imposed on either the crystalline charge density or potential. The PWs cut-off was chosen from the highly recommended condition [12] $R_{MT}K_{max} = 8.0$ for LDA and $R_{MT}K_{max} = 9.0$ for GGA calculations, where K_{max} is the PW cut-off and R_{MT} is the muffin-tin radius. In order to use the same K_{max} for all the lattice constants studied, we kept constants the values for R_{MT}. The values used were $R_{MT}(Ga) = 1.95\ a_0$ and $R_{MT}(N) = 1.65\ a_0$, for the three structures considered. Full relativistic effects were included for the core states, while scalar relativistic treatment was used for the valence ones. A sufficiently dense k-point grid was used to achieve a convergence of the total energy, E_{tot}, to better than 0.1 mRy, namely a regular $8 \times 8 \times 8$ Monkhorst–Pack (MP) [15] mesh for the ZB and RS forms, and a $8 \times 8 \times 4$ mesh for the WZ phase.

The computational details of the PP-PW calculations are as follows. This approach has been used to study only the structural properties of the ZB and RS phases, and the ZB → RS phase transition. The Ga and N pseudopotentials were generated by using the Kerker scheme [16]. The valence atomic configuration used for Ga is $3d^{10}4s^24p^1$, whereas for N we used $2s^22p^3$ for the extraction of the s and p components and the ionic $2s^22p^{1.752}3d^{0.25}$ for the d one. The core radii used for the s, p and d components are 1.675, 1.946 and 1.370 a_0 for Ga; 0.864, 1.289 and 2.022 a_0 for N, respectively. Then, the Ga d- and N p-components were optimized according to the Lin et al. [17] scheme. This is done by expanding the pseudo-wavefunctions, inside the core region, in terms of four Bessel's functions. The expansion coefficients are then adjusted to minimize the kinetic energy beyond a chosen wave-vector cut-off, q_c, which is assumed to be equal to q_4 (q for the fourth order Bessel's function). With the above values of core radii, the obtained values for q_c^2 are 104.8 and 94.3 Ry, respectively. Thus, the PW energy cut-off used was 120 Ry, which is found to give an excellent E_{tot} convergence. For the XC potential we have used the LDA data of Ceperley–Alder, as parametrized by Perdew and Zunger [18]. The integration over the first Brillouin zone was done by using a regular $4 \times 4 \times 4$ MP mesh, which, in the PP-PW calculations, was found to give an excellent convergence [19].

The crystal structure of the ZB and RS phases can be fully defined by just the lattice parameter, a. The WZ form is a hexagonal structure (with two formula units per unit cell), which can be described by three structure parameters: a, c and an internal parameter, u. The optimal values of c/a ratio and u, at a specific volume (V), were determined as follows. First, the E_{tot} is calculated at several values for the c/a ratio, at fixed V and a guessed value for u. The obtained results are then fitted to a parabola to find $(c/a)_{eq}$. Second, the optimal value of u is similarly determined, using the obtained $(c/a)_{eq}$. Third, the first step is repeated to ensure that the $(c/a)_{eq}$ determination was properly done. It has been found that the $(c/a)_{eq}$ is V-independent. This finding is consistent with the experimental results of Ref. [8], which show that basically the c/a ratio does not change for GaN under hydrostatic compression. The LDA and GGA values are identical

Table 1
Structural parameters

Approach	a_{eq} (Å)	c_{eq} (Å)	B_{eq} (GPa)	B_{eq}
WZ-GaN				
FP-LAPW: LDA[a]	3.163	5.140	208.3	5.79
FP-LAPW:GGA[a]	3.226	5.243	172.4	4.86
PP-PW:LDA [22]	3.162	5.142	202.0	–
PP-PW:LDA [21]	3.193	5.218	–	–
PP-PW:GGA [21]	3.245	5.296	172	5.11
Experiment [3,20]	3.190	5.189	188–245	–
ZB-GaN				
FP-LAPW:LDA[a]	4.466	–	208.1	4.64
FP-LAPW:GGA[a]	4.554	–	175.4	5.30
PP-PW:LDA[a]	4.512	–	193.7	4.29
PP-PW:LDA [22]	4.460	–	187	–
PP-PW:LDA [21]	4.518	–	191	4.14
PP-PW:GGA [21]	4.590	–	156	4.25
FP-LMTO:LDA [10,23]	4.462,4.47	–	199, 198	3.8
Experiment [24,25]	4.50	–	190	–
RS-GaN				
FP-LAPW:LDA[a]	4.185	–	251.8	4.49
FP-LAPW:GGA[a]	4.271	–	211.6	4.50
PP-PW:LDA[a]	4.240	–	235.4	4.71
FP-LMTO:LDA [10]	4.221	–	248	3.00

[a] Present work.

and equal to 1.625. This value is in an excellent agreement with the experimental values of 1.626 [8] and 1.627 [20]. The optimal value for u, u_{eq}, is of 0.377, which is identical to the experimental results of Ref. [20], and it is also V-independent.

The E_{tot} versus V curves of the three structures considered for GaN are determined by calculating E_{tot} at seven or eight different volumes, and fitting the results obtained to the Murnaghan equation of state. For WZ-GaN, the values for $(c/a)_{eq}$ and u_{eq} have been determined for each of the values of V considered, as described above. Fig. 1 shows the fitted E_{tot} versus V curves of the three phases of GaN considered, calculated by using the FP-LAPW approach and both LDA and GGA. The important features to note from this figure are as follows. (i) The WZ phase is the ground state structure, in agreement with nature. (ii) The difference between the equilibrium E_{tot} of the WZ and ZB phases is very small (the LDA and GGA results are of 0.0056 and 0.0098 eV, respectively). This is expected, since the ZB and WZ phases have local tetrahedral bonding and they only differ in the second-nearest neighbors. This also explains the epitaxial growth of GaN in the WZ or ZB forms, depending on the substrate [2]. (iii) The changes in the relative stability of the considered structures by going from LDA to GGA are quite small, but not negligible: the GGA results for the ground state E_{tot} of the ZB and RS phases, relative to that of WZ, are 0.0098 and 0.4728 eV/atom, respectively. Whereas, according to the LDA calculations they are of 0.0056 and 0.4232 eV/atom, respectively. (iv) The GGA curves are shifted to the right with respect to those of the LDA.

Our calculated structural parameters of the phases of GaN considered are listed in Table 1, together with some theoretical results (because of space limitations, for an extensive review see Ref. [21]) and the available experimental data. All of the theoretical results reported in Table 1 were

Table 2
Transition pressures (p_t) and volume contractions ($\Delta V/V_0$)

Approach	p_t (GPa)	$\Delta V/V_0$ (%)
ZB → RS transition		
FP-LAPW:LDA[a]	38.15	14.32
FP-LAPW:GGA[a]	40.80	14.10
PP-PW:LDA[a]	42.60	12.80
PP-PW:LDA [10]	53.80	18
FP-LMTO:LDA [10]	38.21	13.4
WZ → RS transition		
FP-LAPW:LDA[a]	38.10	14.96
FP-LAPW:GGA[a]	42.30	13.62
ASA-LMTO:LDA[9]	51.8	12
PP-PW:LDA [10]	56	18.4
XAS [4,5]	47	14
X-ray diffraction[7]	37	17
X-ray diffraction[8]	52	17.9

[a] Present work.

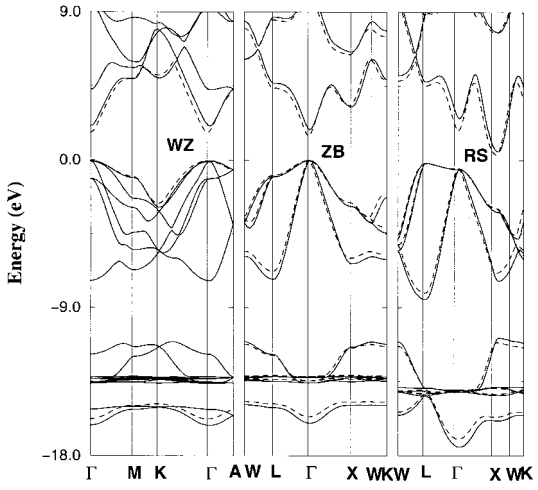

Fig. 2. Band structure of the WZ, ZB and RS phases of GaN, calculated by using LDA (solid lines) and GGA (dashed lines). For the WZ phase, only the GGA results for the lowest conduction band, and the lowest and upper valence bands are shown.

obtained by treating the Ga 3d electrons as valence. The remarkable features to note are as follows. (i) Our FP-LAPW:LDA results for the WZ and ZB phases are almost identical with the PP-PW:LDA results of Ref. [22], obtained by using non-optimized pseudopotentials, except for the B_{eq} of the ZB phase. Whereas, our PP-PW:LDA results (obtained by using optimized pseudopotentials) are almost identical to the similarly obtained results by Stampfl and Van de Walle [21]. (ii) The pseudopotential optimization leads to softer materials. (iii) The same effect is observed when our GGA results and those of Ref. [21] are compared with the corresponding LDA ones, which is already a well-established trend. (iv) The experimental values of the lattice parameters of the WZ and ZB phases lie between our LDA and GGA results obtained using the FP-LAPW approach. Thus, one expects that the true value of B_{eq} also does so. This is the case of the most accurate experimental value for the WZ phase of 207 ± 3 GPa, obtained by high-resolution X-ray diffraction measurements [26].

The p_t of the WZ → RS and ZB → RS transitions of GaN were determined from the constraint of equal static lattice enthalpy. The results for p_t obtained from both the FP-LAPW and PP-PW calculations are listed in Table 2, compared with other available theoretical results and experimental data. The important features to note here are as follows.

First, our results for p_t of the ZB → RS and WZ → RS transitions calculated by using both the FP-LAPW and PP-PW methods, and the LDA and GGA, lie within a narrow pressure range, of 4.5 GPa. This is expected from the use of highly accurate approaches, and the close similarity between the WZ and ZB phases. On the other hand, this also shows that the gradient corrections to the LDA (included via GGA) have very small effects on p_t of GaN.

Second, our results agree very well with those of FP-LMTO [10], for both p_t and $\Delta V/V_0$. Whereas, this is not the case with the results of the LMTO-ASA [9] and previous PP-PW [6] calculations. These discrepancies can be understood in the former case as due to the use of ASA, while in the latter case as due to the inaccuracy of the calculations of Ref. [6] and their treatment of the Ga 3d electrons as part of the frozen core.

Third, the present results agree very well with the XAS results [4,5], for both p_t and $\Delta V/V_0$. The difference between the XAS result and our GGA value for p_t of the WZ → RS transition is of 4.7 GPa. Whereas, it has been found [7] that this transition is not reversible, with a difference in the obtained value for p_t upon pressure increase and decrease of 7 GPa. As noted by Ueno et al. [8], the 5 GPa difference between their X-ray diffraction result and that of XAS is reasonable, in spite of the enhanced sensitivity of the latter approach. The difference between XAS result and that of the other X-ray diffraction measurements can be understood as due to the samples used (powder [7] versus single crystal [4,5]), since grains with very small radii may cause surface related effects which reduces the measured value of p_t. These arguments and the excellent agreement between our results for $\Delta V/V_0$ and that of Ref. [4,5], enhances further the reliability of our results and the experimental results obtained by using XAS.

The band structures of the WZ, ZB and RS phases of GaN, calculated by using the FP-LAPW approach and both LDA and GGA, are shown in Fig. 2. This figure shows that both the WZ and ZB phases are direct-band-gap semiconductors, at the Γ-point, while the RS form is an indirect-band-gap semiconductor (with the valence band maximum at the L-point and the conduction band minimum along the X-W direction). There are two main deficiencies in the LDA band structures of such compounds. (1) The band-gaps are underestimated. The LDA band-gap of WZ-GaN is of 2.08 eV (1.22 eV smaller than the experimental value, of 3.3 eV). (2) The position of the Ga 3d bands are overestimated, by about 2.3 eV (13.4 compared to the experimental result [27] of 15.7). As expected, the use of GGA does not solve these problems. In the contrary, the GGA band-gaps are smaller than those of the LDA by 0.4, 0.4 and 0.2 eV for the WZ, ZB and RS phases, respectively. Moreover, the use of GGA has negligible effects on the position of the Ga 3d bands. However, the upper-valence band width is improved by the use of GGA (the LDA and GGA values for WZ-GaN are 7.35 and 6.89 eV, respectively, compared to the experimental result of 6.5 eV [27]).

The other features to note from Fig. 2 are as follows. (1) The very close similarity between the electronic structures of the ZB and WZ phases. This is expected, because of the similarity of these two phases. (2) By assuming that the underestimation of the band-gap of RS-GaN is similar to

that of the WZ phase, the indirect band-gap of RS-GaN is expected to be about 1.7 eV.

In a summary, the results of the present FP-LAPW and PP-PW investigations (in which the Ga 3d electrons were treated as valence) for the p_t of the WZ → RS phase transition of GaN under high-pressure and the associated volume contraction agree very well with the XAS results, and the FP-LMTO calculations. The *c/a* ratio and the internal parameter *u* are found to be volume-independent, and their values are in excellent agreement with the experimental data. The use of GGA is found to have small, but not negligible, effects on the calculated structural and electronic structure properties, and on p_t of the above phase transition. The RS-GaN is predicted to be an indirect-band-gap semiconductor with a band-gap of about 1.7 eV.

Acknowledgements

One of us (M.A.) would like to thank the Abdul-Salam International Center for Theoretical Physics (Trieste-Italy) for financial support and kind hospitality, where part of this work has been done. We are indebted to P. Balha, S. Cottainer, J. Luitz, K. Kunc and A. Muñoz for interesting discussions.

References

[1] S. Nakamura, M. Seno, T. Mukai, Appl. Phys. Lett. 62 (1993) 2390 (see for example).
[2] M.J. Paisley, Z. Sitar, J.B. Posthill, R.F. Davis, J. Vac. Sci. Technol. A 7 (1989) 701.
[3] N.E. Christensen, in: T. Suski, W. Paul (Eds.), High Pressure in Semiconductor Physics, Academic Press, New York, 1997, p. 49.
[4] P. Perlin, C. Jauberthie-Carillon, Lti, A.S. Miguel, I. Grzegory, A. Polian, High Press. Res. 7 (1991) 96.
[5] P. Perlin, C. Jauberthie-Carillon, Lti, A.S. Miguel, I. Grzegory, A. Polian, Phys. Rev. B 45 (1992) 83.
[6] A. Muñoz, K. Kunc, Phys. Rev. B 44 (1991) 10 372.
[7] H. Xia, Q. Xia, A.L. Ruoff, Phys. Rev. B 47 (1993) 12 925.
[8] M. Ueno, M. Yoshida, A. Onodera, O. Shimomura, Takemura, Phys. Rev. B 49 (1994) 49.
[9] N.E. Christensen, I. Gorczyca, Phys. Rev. B 50 (1994) 4397.
[10] A. Muñoz, K. Kunc, Comput. Mater. Sci. 2 (1994) 400.
[11] A. Qteish, M. Abu-Jafar, A. Nazzal, J. Phys.: Condens. Matter 10 (1998) 5069.
[12] P. Blaha, K. Schwarz, J. Luitz, WIEN97 (Vienna University of Technology, Vienna, 1997): an improved and unpated UNIX version of the original copyright WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, Comput. Phys. Commun. 59 (1990) 399.
[13] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[14] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Let. 77 (1996) 3865.
[15] H.J. Monkhorst, L.D. Pack, Phys. Rev. B 13 (1976) 5188.
[16] G.P. Kerker, J. Phys. C 13 (1980) L189.
[17] J.S. Lin, A. Qteish, M.C. Payne, V. Heine, Phys. Rev. B 47 (1993) 4174.
[18] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
[19] A. Qteish, M. Parrinello, Phys. Rev. B 61 (2000) 6521.
[20] H. Shultz, Thiemann, Solid State Commun. 23 (1977) 851.
[21] C. Stampfl, C.G. Van de Walle, Phys. Rev. B 59 (1999) 5521.
[22] A.F. Wright, J.S. Nelson, Phys. Rev. B 50 (1994) 2159.
[23] V. Fiorentini, M. Methfessel, M. Scheffler, Phys. Rev. B 47 (1993) 13 353.
[24] I. Petrov, E. Mojab, R.C. Powell, J.E. Greene, Appl. Phys. Lett. 60 (1992) 2491.
[25] M.E. Sherwin, T.J. Drummond, J. Appl. Phys. 69 (1991) 8423.
[26] M. Leszczynski, et al., J. Phys. D: Appl. Phys. 28 (1995) 1.
[27] T. Maruyama, et al., J. Electron. Mater. 27 (1998) 200.