Structural properties of AlN from first principles calculations

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Abstract. We present first-principles calculations of structural properties of AlN in wurtzite, zinc-blende and rocksalt structures. The calculations are performed within the framework of the density-functional theory with both the local-density approximation and the generalized gradient approximation. The results are roughly in good agreement with the available experimental data and found to yield improved structural properties for AlN compared to the previous theoretical calculations. This may give a consistent theoretical description of the structural properties of AlN.

PACS. 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 – 71.20.Nr Semiconductor compounds

1 Introduction

In recent years, the group-III nitrides have emerged as having important technological applications. They are basic materials in optoelectronic devices operating in visible and near ultraviolet ranges [1–5]. They are also attractive for use in field effect transistors intended to operate at high power and/or temperature [6].

Aluminum nitride (AlN) is one of the III–V nitride semiconductors. It is characterized by having very short strong bonds, the bond lengths in group-III nitrides are approximately 20% shorter than those of other III-V semiconductors, and high ionicity which is roughly two times higher than those of other III-V materials [7,8]. Such properties make it a good candidate for optoelectronic devices operating under extreme condictions. Pressure is a thermodynamic variable that is as fundamental as temperature. It can have a very large effect on the chemical and physical properties of matter. Recently, there have been revolutionary advances in high-pressure technology that open new opportunities.

Under very high pressure, AlN experiences a phase transition to the rocksalt lattice structure [9]. Large theoretical efforts to properly describe structural and electronic properties of this material have been made and considerable progress has been achieved in recent years [4,5,10]. Yet, a fully consistent picture is still lacking.

In this paper, we report the results of an ab initio pseudopotential study within both the local density ap-

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proximation (LDA) and the generalized gradient approximation (GGA) of the high-pressure phase transformation undergoes by AlN. The results include the structural parameters of wurtzite, zincblende and rocksalt structures as well as the transition pressure and relative volume changes from both the wurtzite and zincblende to the rocksalt phases.

2 Method of calculation

A first principles pseudopotential method based on the density functional formalism [11] is applied using the local-density approximation (LDA) with the Ceperley-Alder [12] form of the exchange-correlation energy as parameterized by Perdew and Zunger [13], and the generalized gradient approximation (GGA) with the Perdew et al. [14] form of the exchange-correlation potential. The interaction of the valence electrons with the ionic cores was represented with a separable, norm-conserving non-local Troullier-Martins [15] pseudopotentials. An energy cutoff of 160 Ry was used. Reciprocal space integration was performed by k-point sampling with sets of special points obtained by using the standard special k points technique of the Monkhorst and Pack (MP) [16]. In present study, a $4 \times 4 \times 4$, $8 \times 8 \times 4$, and $6 \times 6 \times 6$ MP meshes were used for the semi-conducting zincblende, wurtzite and rocksalt AlN, respectively. In zincblende AlN the Al and N atoms are at the positions : Al(0, 0, 0) and N(1/4, 1/4, 1/4). For wurtzite AlN, there are four atoms per hexagonal unit cell where the positions of the atoms Al and N

are: Al(0, 0, 0), (1/3, 2/3, 1/2) and N(0, 0, u), (1/3, 2/3, $u+1/2$), where u is the dimensionless internal parameter that represents the distance between Al plane and its nearest neighbor N plane, in the unit of c. For rocksalt AlN the Al and N atom positions are Al(0, 0, 0) and N(1/2, 1/2, 1/2).

In contrast to the zincblende and rocksalt structures which can be described only by their lattice constants a, the wurtzite form that is hexagonal structure requires three parameters a, c and u. To determine the equilibrium geometry of the wurtzite phase, we optimize the parameters V (volume of the unit cell), c/a , and u as follows: in the first step, we calculate the total energy for several values of c/a (the c/a ratio is varied), keeping the volume V fixed and taking a guessed value for u. The obtained results are then fitted to a polynomial form in order to find the equilibrium c/a ratio. At the obtained optimum value of c/a ratio and a fixed value of V, the optimum value of u is determined similarly. These steps are repeated by varying the internal parameter u to ensure that the equilibrium c/a ratio is consistent. This procedure is repeated for various volumes we considered in our study.

3 Results

The total energy per atom as a function of volume for AlN obtained from LDA and GGA calculations, respectively are shown in Figures 1 and 2. Note that the lowest energy state is that of the wurtzite structure for both LDA and GGA calculations. The wurtzite structure is slightly favored over the zincblende, as is typical for constituents with large electro negativity differences [17]. The ground-state structure of AlN is wurtzite. However, one may note that the energy difference between the zincblende and wurtzite structures is very small. This is consistent with the fact that AlN has also been reported to stabilize in the zincblende (cubic) structure [18]. The zincblende structure is of technological interest as it can be doped more easily than the wurtzite structure [19]. A similar trend has been reported for GaN [20]. According to the authors of reference [20], this trend is expected, since the zincblende and wurtzite phases have local tetrahedral bonding and they only differ in the second-nearest neighbors.

The curves of Figures 1 and 2 are fit to the Murnaghan's equation of state so as to determine the equilibrium structural parameters. Table 1 gives the LDA and GGA calculated equilibrium lattice constants a, structural parameters c/a, internal parameter u, volume by atom V, bulk modulus B, and pressure derivative B' of the bulk modulus for the AlN wurtzite, zinc blende and rocksalt structures. For comparison this table contains also the available experimental values and other theoretical data. Note that the experimental values of the lattice parameters of the all phases being studied here are in perfect agreement with our obtained ones from the GGA calculation. Our LDA calculation is slightly lower than the experimental values. Furthermore, our GGA results regarding the lattice constants are improved with respect to experiment as compared to previous calculations. In the wurtzite
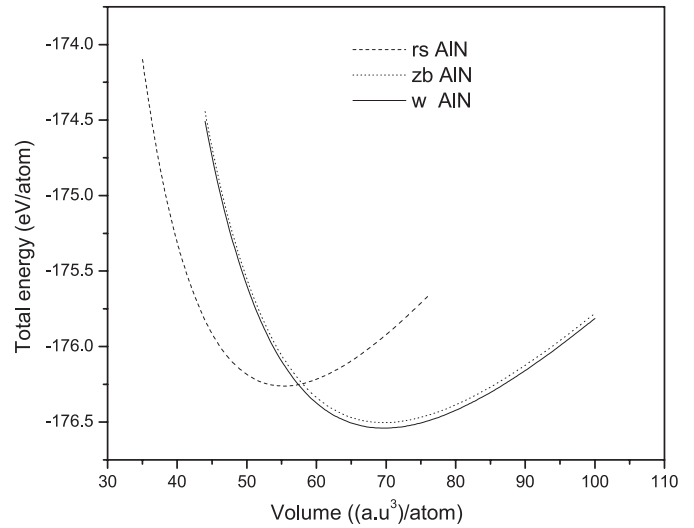

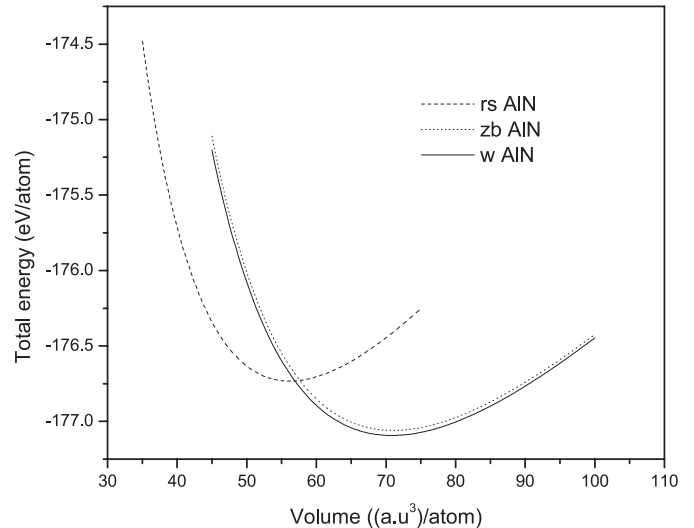**Fig. 1.** Total energy per atom as a function of volume for AlN using LDA calculation.

Fig. 2. Total energy per atom as a function of volume for AlN using GGA calculation.

configuration, that is not fixed by any symmetry consideration [19], at the ideal values $u_0 = \frac{3}{8}$ and $(c/a)_0 = \sqrt{\frac{8}{3}}$, all four nearest-neighbor distances are equal and all bond angles ideal tetrahedral angles. The numerically calculated values of u and c/a obtained in the present work for the relaxed structures are close to their ideal values and are in excellent agreement with the experimental values, as shown in Table 1.

Hence, the local environment of each atom is very much the same as in the case of the zinc-blende phase and thus the resulting semi-conducting structure is very close in energy to the zinc-blende one as shown in Figures 1 and 2. This is consistent with the results of Serrano et al. [19]. Both approximations, namely LDA and GGA give almost the same values for u and c/a. The bulk modulus for AlN in the wurtzite structure as illustrated by our

Table 1. Equilibrium lattice constant a, structural parameters c/a, internal parameter u, volume V by atom, bulk modulus B, and pressure derivative of $B(B')$ for the different phases analyzed for AlN.

Structure phase	$a(\text{Å})$	c/a	u	$V((\text{a.u})^3)$	$B(\text{Gpa})$	B'	Reference
Wurtzite	3.100	1.6	0.3823	69.70	207.84	3.87	This work[a]
	3.114	1.603	0.3816	70.84	197.83	3.84	This work[b]
	3.11	1.601	0.382	_	_	_	[21][c]
	_	_	_	_	207.9(6.3)	_	[19][c]
					201.7		
					205.7		
	3.057	1.617	0.3802	_	209	5.58	[22][d]
	3.113	1.6193	0.3798	_	192	3.96	[22][e]
	3.061	1.600	0.382	_	209	3.7	[19][f]
	3.05	1.603	0.382	_	_	_	[10][g]
	3.10	1.603	0.381	_	_	_	[10][h]
	3.091	1.602	0.381	_	_	_	[17][i]
	3.135	1.602	0.381	_	_	_	[17][j]
Zincblende	4.36	_	_	_	208.27	3.95	This work[a]
	4.38	_	_	_	197.92	3.91	This work[b]
	4.29	_	_	_	_	_	[10][g]
	4.36	_	_	_	_	_	[10][h]
	4.37	_	_	_	_	_	[18][c]
	4.38	_	_	_	_	_	[23][c]
	4.34	_	_	_	214	3.3	[24][d]
	4.32	_	_	_	203	3.2	[25][k]
	4.3742	_	_	_	218	_	[26][l]
	4.302	_	_	_	210	3.7	[19][f]
	4.37	_	_	_	215	4.0	[27][m]
Rocksalt	4.031	_	_	55.29	274.87	4.02	This work[a]
	4.052	_	_	56.37	260.60	3.99	This work[b]
	4.045	_	_	_	221 ± 5.0	4.8 ± 1.0	[28][c]
	_	_	_	_	295 ± 17	3.5 ± 0.4	[29][c]
	3.978	_	_	_	272	3.8	[19][f]
	4.06(3.99)	_	_	_	281(348)	4.0	[27][m]

[a] LDA calculation; [b] GGA calculation; [c] Experiment; [d] Theory: using pseudopotential plane-wave LDA calculation; [e] Theory: using pseudopotential plane-wave GGA calculation; [f] Theory: using DFT + LDA calculations; [g] Theory: pseudopotential; [h] Theory: Self-interaction corrections pseudopotential; [i] LDA-LMTO; [j] GGA-LMTO; [k] Theory: All-electron method (LDA calculation); [l] Theory: Hartree-Fock LDA calculation; [m] Theory: Self-consistent LMTO band-structure calculations.

LDA calculation agrees very well with the experimental value reported in reference [19] within the experimental uncertainties, while our GGA obtained value is somewhat lower. So far, to the best of our knowledge, no experimental data have been reported for B for AlN in the zincblende structure. However, as compared with other published theoretical values, our results agree reasonably well with those reported in references [19,25]. For the rocksalt structure, our LDA result is in good agreement with the experimental value reported in reference [29] within the experimental uncertainties, whereas the GGA value lies between the experimental values reported in references [28,29]. Moreover, our LDA value is consistent with the LDA results of previous calculations. The numerically calculated results for B obtained from LDA seem to be better than those obtained from GGA for both wurtzite and rocksalt structures. The B' for the wurtzite and zinc-

blende phases has almost the same value as illustrated by either LDA or GGA. These values compare well with the theoretical results reported in references [19,22,27]. For the rocksalt structure our both LDA and GGA results are in good agreement with the X-ray diffraction data reported in reference [29] within the experimental uncertainties. It is worth noting that the lattice constants obtained from LDA are smaller than those calculated from GGA, however the reverse is seen for the bulk moduli. This is a well-known trend. As a matter of fact, on the basis of Figures 1 and 2 where the LDA and GGA curves are almost similar (the difference in energy is too small) and are fit to the Murnaghan's equation of state, and giving the fact that the lattice constant is overestimated by the GGA and underestimated by the LDA, one may expect an underestimation of the bulk moduli by the GGA and an overestimation by the LDA.

Table 2. Transition pressures and relative volume changes for the wurtzite to rocksalt and zincblende to rocksalt structures.

Phase transition	P_t(Gpa)	$\Delta V_t/V_0$(%)	Reference
Wurtzite to rocksalt	20.91	20.67	This work[a]
	26.91	20.43	This work[b]
	22.9	17.9	[30][c]
	14-20	18.6	[28][c]
	20.0	–	[29][c]
	16.6	–	[27][d]
	9.2	20.1	[19][e]
Zincblende to rocksalt	19.69	20.99	This work[a]
	25.75	20.56	This work[b]
	7.1	20.4	[19][e]

[a] LDA calculation; [b] GGA calculation; [c] Experiment; [d] Theory: Self-consistent LMTO band-structure calculations; [e] Theory: DFT + LDA calculation.

The transition pressure (P_t) between wurtzite to rocksalt and zinc-blende to rocksalt of AlN were determined directly from the information contained in Figures 1 and 2. We have determined the common tangent between the stable structures as pressure is increased (or volume is decreased). The slope of the common tangent, corresponds to minus the coexistence pressure for the low-and high pressure phases, and the volume of each phase at the transition (the transition volume V_t) corresponds to that at the tangent point. In Table 2, our calculated P_t and relative volume changes ($\Delta V_t/V_0$) are presented and compared with experiment where possible as well as with other available theoretical results. According to our LDA calculation, a structural phase transformation from the wurtzite phase to a six fold coordinated rocksalt phase occurs at 20.91 Gpa with a relative volume change of 20.67%. However, our GGA value is somewhat larger as regards P_t. Experimentally, the wurtzite to rocksalt transition in AlN has been reported to start at 22.9 Gpa by Ueno et al. [30], at 14 Gpa by Xia et al. [28], and more recently at 20.0 Gpa by Uehara et al. [29]. Our LDA value is in good agreement with the experimental one reported more recently by Uehara et al. [29], whereas the GGA value is larger than those reported in references [28–30]. In contrast, our $\Delta V_t/V_0$ obtained from both LDA and GGA calculations are close to each other and are somewhat larger than the experimentally reported ones in references [28,30]. Comparing to theoretical data published previously, our results regarding P_t are larger than those reported by Christensen and Gorczyca [27] using the self-consistent linear-muffin-tin orbitals (LMTO) band-structure calculations, and significantly different from those reported recently by Serrano et al. [19] performed within the framework of the density-functional theory (DFT) with the local-density approximation (LDA). We are more confident to our results since they are closer to the experiment than those of references [19,27]. The transition pressure for AlN from the zinc-blende phase to the rocksalt phase is found to occur at $P_t = 19.69$ and 25.75 Gpa with $\Delta V_t/V_0$ of 20.99 and 20.56% within the LDA and GGA, respectively. Our re-

sults in both approaches are once again very different from that reported in reference [19] as regards P_t. However, our $\Delta V_t/V_0$ obtained from both LDA and GGA are close to each other and agree very well with that of reference [19]. In the absence of the experimental data regarding the P_t from zinc-blende to rocksalt, to the best of our knowledge, no comments could be ascribed to the accuracy of our results. In addition, one can note that the use of a GGA in dealing with the exchange-correlation energy functional, instead of the LDA adopted in the present work, enlarges the value of P_t in both transition cases: Wurtzite → Rocksalt and zinc-blende →Rocksalt. However, this does not result in any clear difference as regards $\Delta V_t/V_0$. According to Uehara et al. [29] the maximum pressure achieved in high-pressure experiments on AlN was 132 Gpa and up to this pressure the rocksalt structure does not undergo any further transitions. The local dynamical stability of the high-pressure rocksalt phase in the group-III nitrides has been explained by Serrano et al. [19] to be due particularly to the large ionicity in group-III nitrides as compared to the rest of the III–V compounds.

4 Conclusion

In conclusion, we have presented structural parameters of wurtzite, zinc-blende and rocksalt AlN as calculated using the DFT with both the LDA and GGA. The transition pressures and their corresponding relative volume changes for both transformations from the wurtzite to rocksalt and from the zinc-blende to rocksalt structures have also been determined. The results are in good agreement with available experimental data and showed significant improvement as compared to the previous published theoretical calculations yielding thus a consistent theoretical description of the material of interest that belongs to a class of technologically important semiconductor compounds.

References

1. H. Morkoc, S.N. Mohammad, Science **267**, 51 (1995)
2. J.W. Orton, C.T. Foxon, Rep. Prog. Phys. **61**, 1 (1998) and references cited therein
3. S.C. Jain, M. Willander, J. Narayan, R. Van Overstraeten, J. Appl. Phys. **87**, 965 (2000) and references cited therein
4. I. Vurgaftman, J.R. Meyer, L.-R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001) and references cited therein
5. I. Vurgaftman, J.R. Meyer, J. Appl. Phys. **94**, 3675 (2003) and references cited therein
6. Y.F. Wu, B.P. Keller, S. Keller, D. Kapolnek, P. Kozodoy, S.P. Denbaars, U.K. Mishra, Appl. Phys. Lett. **69**, 1438 (1996)
7. A. Rubio, J.L. Corkill, M.L. Cohen, E.L. Shirley, S.G. Louie, Phys. Rev. B **48**, 11810 (1993)

8. K. Lawniczak-Jablonska, T. Suski, I. Gorczyca, N.E. Christensen, K.E. Attenkofer, R.C.C. Perera, E.M. Gullikson, J.H. Underwood, D.L. Ederer, Z.L. Weber, Phys. Rev. B **61**, 16623 (2000)

9. G.J. Ackland, Rep. Prog. Phys. **64**, 483 (2001) and references cited therein

10. D. Vogel, P. Kruger, J. Pollmann, Phys. Rev. B **55**, 12836 (1997)

11. X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty, D.C. Allan, Comput. Mater. Sci. **25**, 478 (2002)

12. D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980)

13. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981)

14. J. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B **46**, 6671 (1992)

15. J.L. Martins, N. Troullier, S.H. Wei, Phys. Rev. B **43**, 2213 (1991)

16. H.J. Monkhorst, J.D. Pack, Phys. Rev. B **13**, 5188 (1976)

17. M. van Schilfgaarde, A. Sher, A.-B. Chen, J. Cryst. Growth **178**, 8 (1997)

18. Properties of Group-III Nitrides, edited by J.H. Edgar, *EMIS Data-reviews Series* (IEE, London, 1994)

19. J. Serrano, A. Rubio, E. Hernandez, A. Munoz, A. Mujica, Phys. Rev. B **62**, 16612 (2000) and references cited therein

20. M. Abu-Jafar, A.I. Al-Sharif, A. Qteish, Solid State Commun. **116**, 389 (2000)

21. H. Schulz, K.H. Thiemann, Solid State Commun. **23**, 815 (1977)

22. C. Stampfl, C.G. Van de Walle, Phys. Rev. B **59**, 5521 (1999)

23. P. Petrov, E. Mojab, R.C. Powell, J.E. Greene, Appl. Phys. Lett. **60**, 2491 (1992)

24. K. Karch, F. Bechstedt, P. Pavone, D. Strauch, Physica B **220**, 445 (1996)

25. K. Kim, W.R.L. Lambrecht, B. Segall, Phys. Rev. B **53**, 16310 (1996)

26. B. Paulus, E.J. Shi, H. Stoll, J. Phys.: Condens. Matter **9**, 2745 (1997)

27. N.E. Christensen, I. Gorczyca, Phys. Rev. B **50**, 4397 (1994)

28. Q. Xia, H. Xia, A.L. Ruoff, J. Appl. Phys. **73**, 8198 (1993)

29. S. Uehara, T. Masamoto, A. Onodera, M. Ueno, O. Shimomura, K. Takemura, J. Phys. Chem. Solids **58**, 2093 (1997)

30. M. Ueno, A. Onodera, O. Shimomura, K. Takemura, Phys. Rev. B **45**, 10123 (1992)