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Structural and thermodynamic properties of wurtzite-type aluminium nitride from first-principles calculations*

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The lattice parameter, bulk modulus and its pressure derivative of the wurtzite-type aluminium nitride (w-AlN) are investigated by using the Cambridge Serial Total Energy Package (CASTEP) program in the framework of Density Functional Theory (DFT). The calculated results are in good agreement with the available experimental data and other theoretical results. Through the quasi-harmonic Debye model, the dependences of the normalized lattice parameters a/a_0 and c/c_0, axial ratio c/a, normalized primitive-cell volume V/V_0, Debye temperature $\Theta_{\rm D}$ and heat capacity $C_{\rm V}$ on pressure P and temperature T are obtained. It is found that the interlayer covalent interactions (Al-N bonds) are more (even a little) sensitive to temperature and pressure than intralayer ones (N–N bonds), which gives rise to a little lattice anisotropy in the w-AlN.

Keywords: thermodynamic property, generalized gradient approximation (GGA), w-AlN
PACC: 6740K, 7115M, 7360P

1. Introduction

The ionic III–V nitride compound aluminium nitride (AlN) has presently around much interest because of its vast applications in opto-electronics areas such as short-wavelength light-emitting diodes (LEDs), semiconductor lasers, and optical detectors, in high-temperature, high-power, and high-frequency devices[1,2], and in the constructing of devices in the violet region.[3] AlN is generally reported to be a non-polymorphous material having the wurtzite structure.[4–8] Thus, the wurtzite structure AlN (w-AlN) has been a subject of extensive theoretical[9–17] and experimental[18,19] studies.

In 1991, Van Camp *et al*[9] theoretically evaluated the ground-state properties for both the wurtzite structure AlN and the rocksalt structure AlN in the local-density-functional formalism by using nonlocal norm-conserving pseudopotentials. They obtained $a = 3.129$ Å, $c = 4.988$ Å, and $u = 0.3825$ (u is the cell-internal dimensionless parameter) for the wurtzite structure and $a = 4.032$ Å for the rocksalt structure as well as $P = 12.9$ GPa (P is the transition pressure from the hexagonal structure to the cubic structure). Since then, a lot of investigations on the w-AlN have been made.[10–17] In 2005, Ahmed Rashid *et al*[16] applied the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory to the band structures of the zinc-blende and the wurtzite structure aluminium nitride, indium nitride and gallium nitride. They have found that the w-AlN presents a direct band gap, and the calculated band gap from the generalized gradient approximation (GGA) method is 4.21 eV and from the GGA-EV (an alternative form of GGA proposed by Engel and Vosk) it is 5.034 eV.

In experiments, Schulz and Thiemann[18] refined the structure parameters for AlN and GaN by using x-ray intensities from single crystals, collected with an automatic single crystal diffractometer. They obtained $a = 3.110$ Å, $c = 4.980$ Å, and $u = 0.3821$. The

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final R-value for anisotropic temperature factors is equal to 0.015 for the w-AlN. Xia *et al* [19] carried out the energy-dispersive x-ray diffraction studies on the aluminium nitride under 65 GPa using a synchrotron x-ray source. They found that the transformation pressure from the wurtzite structure to the rocksalt structure of AlN lies in a range of 0–14 GPa. Liu *et al* [2] observed the visible photoluminescence (PL) from rare earth (Tm, Sm and Dy)-doped AlN films grown by radio-frequency magnetron reactive sputtering on Si (001) substrate. They have found that the films are the *c*-axis-oriented hexagonal wurtzite-type structure with an average crystal size of about 80–110 nm from x-ray diffraction.

In this work, we focus on investigating the structural and thermodynamic properties of the w-AlN by using the Cambridge Serial Total Energy Package (CASTEP) program[20,21] and the quasi-harmonic Debye model.[22] The results obtained are in agreement with the available experimental data and other theoretical results. In Section 2, we give a brief review of the theoretical method. The results and discussion are presented in Section 3. And some conclusions drawn from the present study are given in Section 4 finally.

2. Theoretical method

2.1. Total-energy electronic-structure calculations

In our electronic-structure calculations, we adopt the non-local ultrasoft pseudopotential generated from the Perdew–Burke–Ernzerhof (PBE)[23] generalized gradient approximation for the interactions of the electrons with the ion cores, in the GGA for exchange-correlation functional in the PBE scheme.[23] The electronic wave functions are expanded in a plane wave basis set with an energy cut-off of 300 eV. Pseudo-atom calculations are performed for N $2s^2 2p^3$ and Al $3s^2 3p^2$. For the Brillouin-zone sampling, we use the $12\times12\times9$ Monkhorst-Pack meshes, where the self-consistent convergence of the total energy is 10^{-8} eV/Atom. All the electronic-structure calculations are implemented through the CASTEP code.[20,21]

2.2. Thermodynamic properties

The quasi-harmonic Debye model,[22] in which the phononic effect is considered, is applied to investigating the thermodynamic properties of AlN. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ can be written in the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm Vib}(\Theta(V);T), \quad (1)$$

where $E(V)$ is the total energy per primitive cell for AlN, PV corresponds to the constant hydrostatic pressure condition, and $\Theta(V)$ is the Debye temperature. The vibrational Helmholtz free energy $A_{\rm Vib}$ can be written as[24,25]

$$A_{\rm Vib}(\Theta;T) = nkT\Big[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-{\rm e}^{-\Theta/T}) - D(\Theta/T)\Big], \quad (2)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed as

$$\Theta = \frac{\hbar}{k}[6\pi^2 V^{1/2} n]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{M}}\,, \quad (3)$$

where M is the molecular mass, $B_{\rm S}$ is the adiabatic bulk modulus, which is approximated by the static compressibility[10,26]

$$B_{\rm S} \cong B(V) = V\Big\{\frac{{\rm d}^2 E(V)}{{\rm d}V^2}\Big\}, \quad (4)$$

$f(\sigma)$ can be obtained from Refs.[27,28], the Poisson σ is taken as 0.24. For the w-AlN, $n = 2$, $M = 40.9882$ a.u., and $f(\delta) = 0.8795$. Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V

$$\Big(\frac{\partial G^*(V;P,T)}{\partial V}\Big)_{P,T} = 0. \quad (5)$$

By solving Eq.(5), one can obtain the thermal equation of state (EOS). The heat capacity $C_{\rm v}$ and the thermal expansion coefficient α are given by[28]

$$B_{\rm T}(P,T) = V\Big(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\Big)_{P,T}, \quad (6)$$

$$C_{\rm V} = 3nk\Big[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T}-1}\Big], \quad (7)$$

$$\alpha = \frac{\gamma C_{\rm V}}{B_{\rm T} V}, \quad (8)$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma = -\frac{{\rm d}\ln\Theta(V)}{{\rm d}\ln V}\,. \quad (9)$$

Through the quasi-harmonic Debye model, one can calculate the thermodynamic quantities of the w-AlN

at 0–16 GPa (The transition pressure in reality is close to 17 GPa[29]) and 0–2700 K (The melting temperature of the w-AlN is 2800 K.[30]) By using this method, we can obtain the thermodynamic properties of some materials.[31−34].

3. Results and discussion

There are three independent structural parameters in the w-AlN, i.e. the primitive cell volume V_0, the axial ratio c/a, and the cell-internal dimensionless parameter u, which denotes the position of the second atom along the c-axis. For the ideal w-AlN, the axial ratio $c/a = \sqrt{8/3} \approx 1.633$, and the internal parameter $u = 3/8$. The initial structural model is built according to a typical wurtzite structure, with the N atom arbitrarily set at (1/3, 2/3, 0) and the Al atom at (1/2, 2/3, u).

In order to determine the equilibrium geometry of the w-AlN, we take the following procedures: In the first step, for a given u, we fix the primitive cell volume V, and take a series of different values of a and c to calculate total energy E. No constraints are imposed on the c/a ratio, that is, lattice parameters a and c both are optimized simultaneously. In the second step, this procedure is repeated over a wide range of the volume V. By obtaining a minimum total energy for each fixed value of V, a minimum total energy is also obtained for the given u. In the third step, we repeat the above procedures for several values of u (u is varied generally in a range from 0.3807 to 0.3827 in steps of 0.0002), and then find a minimum total energy for each value of u. By fitting the $E-u$ data to a third-order polynomial, we find the optimized internal parameter $u = 0.3817$.

For the obtained internal parameter u, we can find that the most stable structure of the w-AlN corresponds to the equilibrium lattice parameters a = 3.125 Å and c = 5.009 Å (the axial ratio c/a = 1.6028). Our results are well consistent with other theoretical results[9−17] and the experimental data,[18,19] as shown in Table 1.

Table 1. The calculated structure parameters, bulk moduli (B_0) and their pressure derivatives B_0' compared with the experimental and other theoretical results.

	c/Å	a/Å	c/a	u	B_0/GPa	B_0'
GGA (present)	5.009	3.125	1.603	0.3817	187.99	3.83
Ref.[9]	4.988	3.129	1.594	0.3825	195.0	3.74
Ref.[10]	4.89	3.05		0.382		
	4.97	3.10		0.381		
Ref.[11]	4.91	3.06	1.60	0.383		
Ref.[12]	4.948	3.084	1.604	0.3814		
Ref.[13]	4.997	3.099	1.612	0.381		
Ref.[14]		3.144	1.605	0.381	194	
Ref.[15]		3.061	1.600	0.382	209	3.7
Ref.[16]				0.383		
Ref.[17]	4.948	3.084	1.604	0.3814		
Exp.[18]	4.980	3.110	1.601	0.3821		
Exp.[19]a					185.0± 5.0	5.7±1.0

[a]Derived from the x-ray diffraction data at room temperature.

By fitting the corresponding $E-V$ data to the spinodal EOS proposed by Baonza *et al* [35] we have

$$V = V_{\rm sp}\exp\Big\{-\Big[\frac{K^*}{1-\beta}\Big](p-p_{\rm sp})^{1-\beta}\Big\}, \tag{10}$$

$$V_{\rm sp} = V_0\exp\Big\{\frac{\beta}{(1-\beta)B_0'}\Big\}, \tag{11}$$

where $P_{\rm sp}$ and $V_{\rm sp}$ are the spinodal pressure and volume, respectively, the fitting parameters are $P_{\rm sp}$, K^*, and β (it is customary to use $\beta = 0.85$). In terms of them, we have $B_0 = [K^*]^{-1}(-P_{\rm sp})^{\beta}$ and $B_0' = (-P_{\rm sp})^{-1}\beta B_0$. At any temperature and pressure, B_T, $B_{\rm T}'$ and $B_{\rm T}''$ are straightforwardly given by

$$B_{\rm T} = [K^*]^{-1}(P-P_{\rm sp})^{\beta}, \tag{12}$$

$$B_{\rm T}' = \beta[K^*]^{-1}(P-P_{\rm sp})^{\beta-1}, \tag{13}$$

$$B''_{\rm T} = \beta(\beta-1)[K^*]^{-1}(P-P_{\rm sp})^{\beta-2}. \quad (14)$$

Expression (12) is used to optimize $(-P_{\rm sp})$, K^*, and β from the $B_{\rm T}$ value obtained from

$$B_{\rm T}(p,T) = \Big[V\Big(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\Big)_{P,T}\Big]_{{\rm Vopt}(P,T)}. \quad (15)$$

Putting it in the following equation

$$\ln B_{\rm T} = \beta \ln(P-P_{\rm sp}) - \ln K^* \quad (16)$$

and giving a trial value of $(-P_{\rm sp})$ and a set of data $(P, B_{\rm T})$, K^* and β are obtained by solving the corresponding linear least squares problem. The optimum $(-P_{\rm sp})$ is trivially found by using monodimensional minimization algorithms. The obtained isothermal bulk modulus B_0 and its pressure derivative B'_0 for the w-AlN at $P=0$ and $T=0$ are also listed in Table 1, together with other theoretical results[9,14,15] and the experimental data derived from the x-ray diffraction data at room temperature.[19] Our results are in good agreement with other theoretical results. The bulk modulus B_0 is slightly larger and its pressure derivative B'_0 is slightly lower than those in Ref.[19], which are derived from the x-ray diffraction data at room temperature. The result is just consistent with the relations between the bulk modulus B and temperature T, which will be described below.

We now employ the calculated $E-V$ data to investigate the dependence of bulk modulus B on temperature T and pressure P through the quasi-harmonic Debye model. The isothermal bulk modulus is defined by

$$B_{\rm T}(P,T) = -V\Big(\frac{\partial P}{\partial V}\Big)_{\rm T}. \quad (17)$$

From Eq.(17), we have B_0= 187.99 GPa. By fitting the $B-T$ data to a third-order polynomial, we have the following relationship:

$$B_0 = 187.963 + 0.002047T - 2.41083\times10^{-5}T^2 + 8.789\times10^{-10}T^3 \quad (P=0\ {\rm GPa}). \quad (18)$$

In Fig.1(a), we illustrate the relationship between bulk modulus B_0 and temperature T at $P=0$. From expression (18), we obtain the slope of $B-T$ curve in Fig.1(a)

$$K = ({\rm d}B/{\rm d}T)_{P=0} = 0.002047 - 4.82166\times10^{-5}T + 2.637\times10^{-9}T^2. \quad (19)$$

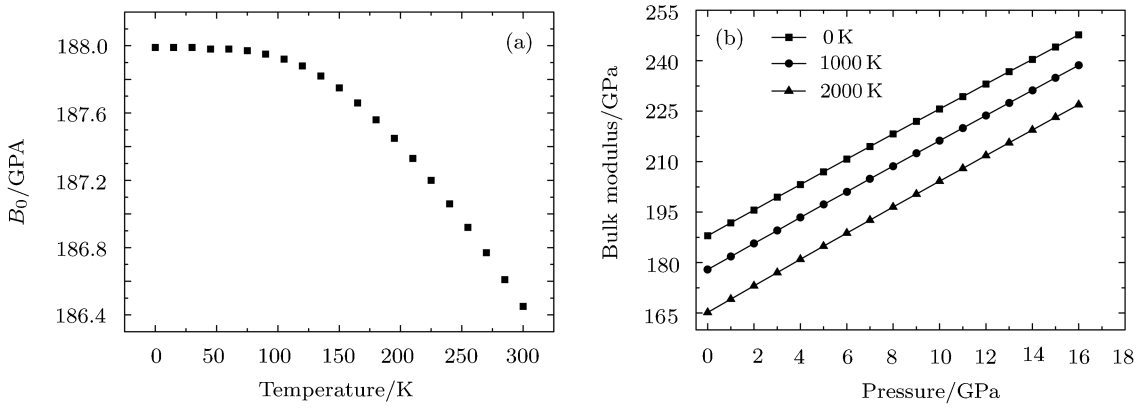


Fig.1. The bulk modulus B_0 of the w-AlN versus temperature T from 0 K up to 300 K at $P=0$ GPa (a) and the bulk modulus B of the w-AlN versus pressure P at 0, 1000 and 2000 K, respectively (b).

It is obvious that when $T<100$ K, B nearly keeps constant; when $T>100$ K, B decreases dramatically as T increases. Correspondingly, when $T<100$ K, the primitive cell volume for the w-AlN has little change, however when $T>100$ K, the primitive cell volume increases as T increases. It is the rapid variation in volume that makes the bulk modulus B rapidly decrease. The relationships between bulk modulus B and pressure P at different temperatures $T=0$, 1000 and 2000 K are shown in Fig.1(b). These results indicate that B increases with P increasing at a given temperature and decreases with T increasing at a given pressure. This result shows that the effect of increasing pressure on the w-AlN is the same as the influence of decreasing temperature on the w-AlN.

The pressure dependences of the normalized lattice parameters a/a_0 and c/c_0, axial ratio c/a, and normalized volume V/V_0 of the w-AlN are presented

in Fig.2(a). It is found that as pressure increases from 0 to 16 GPa, the c/a ratio decreases by 0.232%. The interlayer linear compressibility, $\mathrm{d}\ln c/\mathrm{d}P = 0.0016367503\ \mathrm{GPa}^{-1}$ is about 1.103 times the basal plane value, $\mathrm{d}\ln a/\mathrm{d}P = 0.0014843953\ \mathrm{GPa}^{-1}$. The compression along the c-axis is a little larger than along the a-axis in the basal plane, which implies that the intralayer N-N bonds are a little stronger than the interlayer Al-N bonds. Moreover, the equilibrium lattice parameters a/a_0 and c/c_0, the axial ratio c/a, and the normalized volume V/V_0 as functions of temperature are plotted in Fig.2(b).

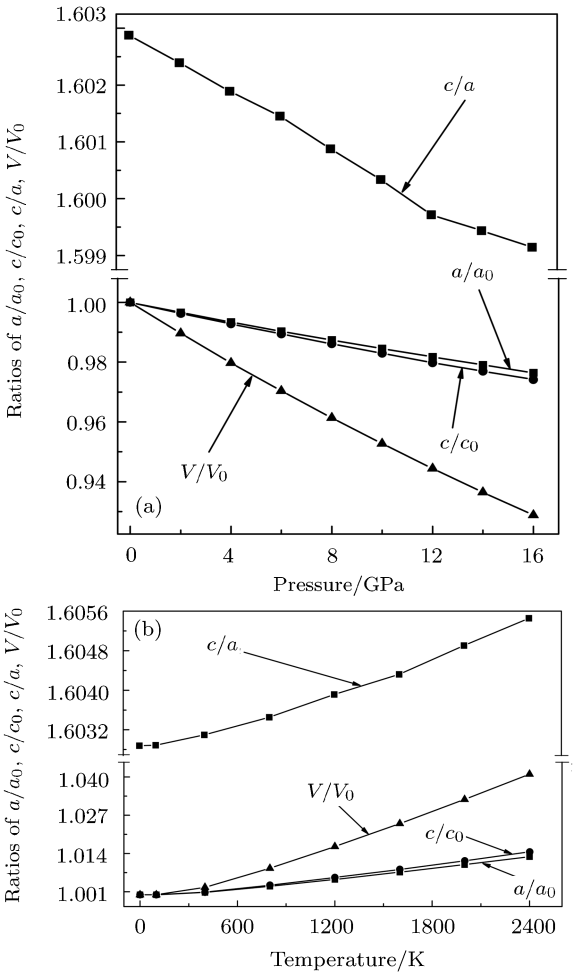


Fig.2. The equilibrium ratio c/a, corresponding normalized parameters a/a_0 and c/c_0, and normalized volume V/V_0 of the w-AlN versus pressure at 0 K (a) and temperature at 0 GPa (b).

It is obvious from Fig.2 that lattice constant c is more sensitive to temperature and pressure than lattice constant a. To further investigate the thermal anisotropy, we calculate the linear thermal expansion parameters α_a and α_c in the intralayer and interlayer directions, respectively. From the following equation at zero pressure:

$$\alpha = \frac{(\Delta l/\Delta T)}{l_0} = \frac{1}{l_0}\frac{\partial l}{\partial T}\Big|_P, \tag{20}$$

where l represents lattice constants a and c, we obtain $\alpha_a = 3.24087\times10^{-6}\ \mathrm{K}^{-1}$ and $\alpha_c = 3.67428\times10^{-6}\ \mathrm{K}^{-1}$ at room temperature. It is shown that the thermal expansion along the c-axis is about 1.134 times that along the a-axis, and the interlayer bonding is especially weaker in the w-AlN.

The obtained Debye temperatures at various temperatures (300, 800, 1300, 1500 and 1800 K) and pressures (0, 3, 6, 9, 12 and 15 GPa) are listed in Table 2. It is found that when temperature is constant, the heat capacity C_V decreases as pressure increases, while the Debye temperature Θ_D increases as pressure increases. When the applied pressure increases from 0 GPa to 15 GPa, the heat capacities decrease by 11.5%, 2.1%, 0.83%, 0.63%, 0.44%, and the Debye temperatures increase by 13.56%, 13.24%, 13.76%, 13.97%, 14.32% at T = 300, 800, 1300, 1500 and 1800 K, respectively. The heat capacity C_V in the present study is 29.89 $\mathrm{Jmol}^{-1}\ \mathrm{K}^{-1}$ at zero pressure and an ambient temperature. In Fig.3, we plot the heat capacity C_V of the w-AlN at a constant volume. It is shown that when $T < 2000$ K, the heat capacity C_V is dependent on temperature, which is due to the anharmonic approximation of the Debye model used here. However, at higher temperatures, the anharmonic effect on C_V is suppressed, and the heat capacity C_V increases with temperature increasing, and then approaches the Dulong–Pettit limit $6Nk$ ($\approx 49.90\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$), as is followed for all solids at high temperatures, where N represents Avogadro's constant.

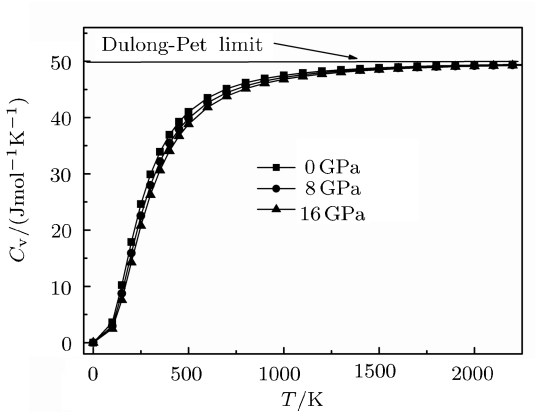


Fig.3. The heat capacity of the w-AlN versus temperature at different pressures.

Table 2. The heat capacities (C_V (Jmol^{-1} K^{-1})) and the Debye temperatures (Θ_D(K)) of the w-AlN over a wide range of temperatures (T (K)) and pressures (P (GPa)).

T		P					
		0	3	6	9	12	15
300	Cv	29.89	29.14	28.42	27.74	27.09	26.47
	Θ_D	1015.58	1043.70	1070.62	1104.96	1121.44	1153.32
800	Cv	46.18	45.98	45.78	45.59	45.40	45.21
	Θ_D	1001.97	1030.82	1058.31	1084.76	1110.13	1134.64
1300	C_v	48.48	48.40	48.32	48.24	48.16	48.08
	Θ_D	985.81	1015.35	1043.54	1070.52	1096.44	1121.44
1500	C_v	48.84	48.78	48.71	48.65	48.59	48.53
	Θ_D	979.14	1008.94	1037.38	1064.64	1090.75	1115.91
1800	C_v	49.17	49.13	49.08	49.04	49.00	48.96
	Θ_D	968.81	999.13	1028.02	1055.59	1082.07	1107.51

4. Conclusions

We apply the CASTEP program and the quasi-harmonic Debye model to determining the equilibrium structural parameters and the thermodynamic properties of the w-AlN under high pressures. The calculated lattice constants are in good agreement with the experimental data and other theoretical results. The dependences of the normalized lattice parameters a/a_0 and c/c_0, axial ratio c/a, and normalized primitive volume V/V_0 on pressure and temperature are obtained. The interlayer linear compressibility is about 1.103 times the basal plane value under high pressures and the thermal expansion coefficient along the c-axis is about 1.134 times that along the a-axis. These results show that the interlayer covalent interactions (Al–N bonds) are more sensitive to temperature and pressure than intralayer ones (N–N bonds), resulting in a little lattice anisotropy in the w-AlN.

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