First-principle studies of phonons and thermal properties of AlN in wurtzite structure

J Q Fu, T L Song[1], X X Liang and G J Zhao

Department of Physics, School of Physical Science and Technology, Inner Mongolia University, Hohhot, 010021, P. R. China

E-mail: songtl@126.com

Abstract. We calculate the band structure, density of states, phonon dispersions and thermodynamic properties of wurtzite Aluminum nitride (AlN) using the local density approximation (LDA) and the generalized gradient approximation (GGA). The results show that wurtzite AlN is a direct gap semiconductor. The phonon, dielectric, and thermodynamic properties are discussed in detail. The calculated values are in agreement with available experimental data.

1. Introduction

Group-III nitrides have attracted considerable attention during the past decade due to technological applications in optoelectronic and electronic devices. Aluminum nitride (AlN) is one of the important materials among them. It has high thermal conductivity, high melting point, large bulk modulus, and large band gap. Attention has also been paid to the lattice vibrations (phonons), which related closely to their electric, optical as well as thermal properties. Some investigations have given the phonon dispersions and phonon frequencies at the Γ point of hexagonal AlN by the first-principles [1, 2, 3].

In this work, we have performed the first-principle calculations for the band structure, density of states, phonon dispersion, dielectric and thermodynamic properties of hexagonal AlN based on two different exchange-correlation potentials (GGA and LDA).

2. Calculation method

Wurtzite AlN belongs to the space group P63mc and its unit cell contains four atoms (see figure 1). In our calculation, the software Quantum-Espresso [4] is used, which is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale based on density functional theory. Two different exchange-correlation potentials (GGA and LDA) have been adopted and the energy cut-off is chosen as 105Ry for GGA and 75Ry for LDA, respectively, in the band structure calculation. A 10×10×10 Monkhorst-Pack mesh have been used to perform the Brillouin zone (BZ) integration. Phonon calculation is presently a two-step process. First, find the ground-state atomic and electronic configuration; Second, calculate phonons using Density Functional Perturbation Theory. In order to obtain the phonon dispersion curves, we have selected a 4×4×4 q mesh for the force constant calculation.

[1] Corresponding author E-mail address: songtl@126.com

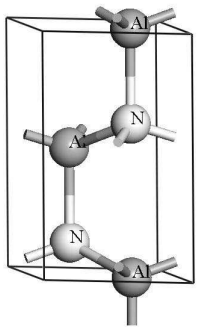

Figure 1. Schematic of the primitive cell of wurtzite AlN after the optimization

3. Result and discussion

3.1. Lattice parameters

It is read from table 1 that our results for the optimized lattice parameters very closer to the previous theoretical [5, 6] and experimental data [7]. However, the corresponding values by LDA is slightly smaller than the experimental values but those by GGA larger.

Table 1. The lattice parameters of wurtzite AlN compare with other theories and the experimental data.

		a(Å)	c(Å)	a/c
AlN	This work$^{\mathrm{GGA}}$	3.120	5.000	1.606
	This work$^{\mathrm{LDA}}$	3.090	4.910	1.589
	Theory[5]	3.100	5.100	1.615
	Theory[6]	3.096	4.959	1.602
	Experiment[7]	3.110	4.980	1.601

3.2. Band structures and density of states

Figures 2 and 3 show wurtzite AlN band structures and density of states (DOS) obtained by GGA and LDA, respectively. The results indicate that the AlN is the direct band gap semiconductor. The band gap for GGA is 4.2eV and for LDA is 4.5eV. Compared with the experimental value 6.2eV, the LDA results are better than the GGA, but they are all lower than experimental value. The band splits up into 3 sub-bands. We can also see that the valence band are mostly dominated by N-2s,2p and A1-3s electronic states, but the conduction band comes from Al-3s, 3p and a little N-2s,2p electron.

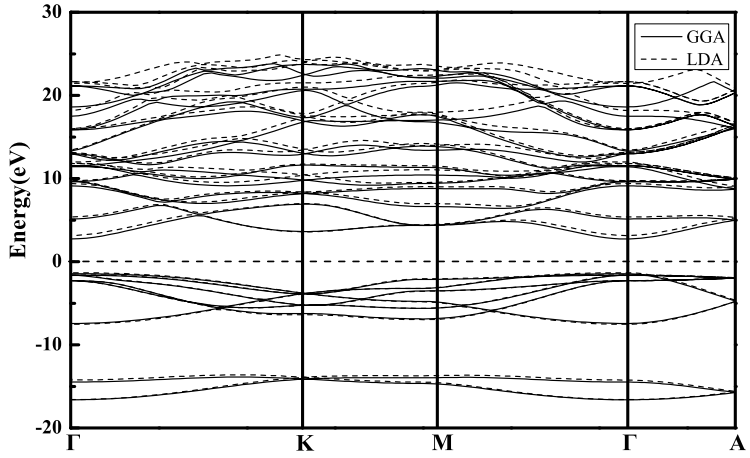

Figure 2. Band structure of wurtzite AlN obtained by GGA (solid line) and LDA (dash line).

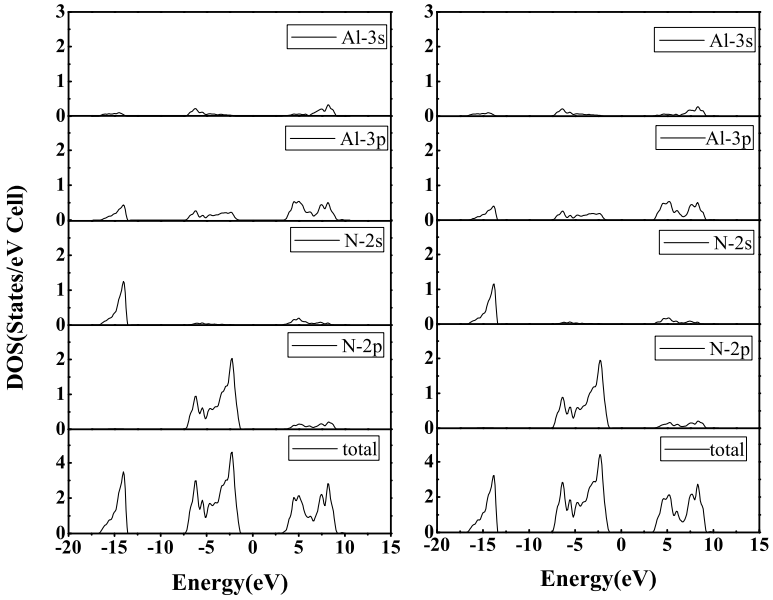

Figure 3. Total and projected DOSs of wurtzite AlN by (a) GGA and (b) LDA

3.3. Phonon dispersion curves

The unit cell of wurtzite AlN contains 4 atoms. We can see from figure 4 that there are totally 12 phonon branches containing 3 acoustic phonon branches and 9 optical phonon branches. The phonon modes degenerate at some high symmetry points of BZ. For example, at A point, only 4 phonon modes can be observed, but 8 modes appear at the Γ point. The calculated phonon frequencies at the Γ point in this work are listed in table 2. The corresponding results given by previous theories are also listed partly for comparison. The calculated results are closer to the available experimental values.

$\{\omega[E_1(\mathrm{TO})] - \omega[A_1(\mathrm{TO})]\}/\omega[E_1(\mathrm{TO})]$ could be used to measure the anisotropy of materials of wurtzite structure. The calculated value is 0.09 for GGA and 0.06 for LDA, respectively. It is seen that the wurtzite AlN displays obviously the anisotropy.

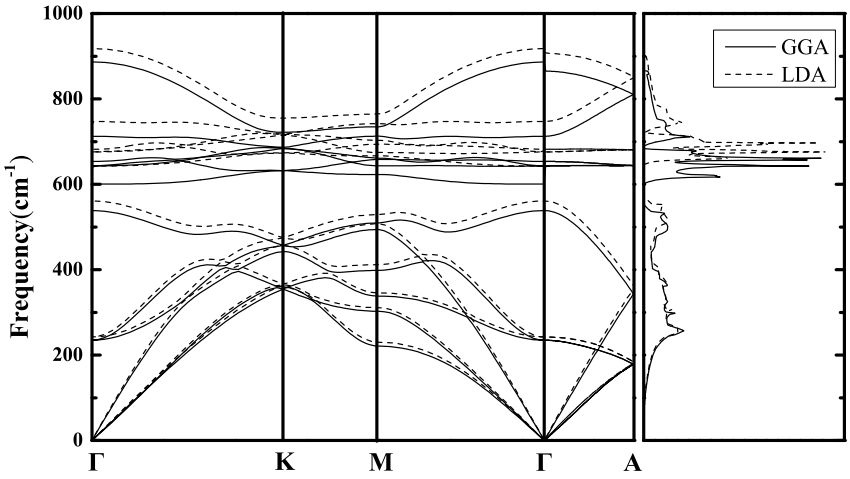

Figure 4. Phonon dispersion curves (left) and DOS (right) of wurtzite AlN by GGA (solid line) and LDA (dash line).

Table 2. The phonon frequencies at the Γ point for wurtzite AlN by GGA and LDA as well as some other theoretical and experimental data.

	E_2^l	B_1^l	A_1(TO)	E_1(TO)	E_2^h	B_1^h	A_1(LO)	E_1(LO)
This work$^{\mathrm{GGA}}$	238	538	599	655	645	711	866	887
This work$^{\mathrm{LDA}}$	241	560	643	681	675	749	905	918
Theory[1]	215	557	640	668	652	764	883	922
Theory[5]	–	–	619	677	–	–	893	918
Experiment[2]	248	–	614	673	–	–	894	917
Experiment[3]	241	–	607	–	660	–	–	924

3.4. Dielectric properties

We have calculated the high-frequency dielectric tensor and the Born effective charge tensors. The calculated results are listed in table 3. For wurtzite AlN, $\varepsilon(\infty)$ is composed of two independent components, corresponding respectively to the directions parallel to the c axis, $\varepsilon_{\parallel}(\infty) = \varepsilon_{zz}(\infty)$, and perpendicular to the c axis, $\varepsilon_{\perp}(\infty) = \varepsilon_{xx}(\infty) = \varepsilon_{yy}(\infty)$. The average dielectric constants $\varepsilon(\infty) = 1/3\mathrm{Tr}\varepsilon(\infty)$ is also given. We also consider Born effective charge tensors with two independent components $Z_{\perp}^* = Z_{xx}^* = Z_{yy}^*$ and $Z_{\parallel}^* = Z_{zz}^*$. It is seen that the wurtzite AlN displays obviously the anisotropy in the dielectric constant and the Born effective charge. The our results for the high-frequency dielectric tensors are in agreement with the experimental data.

Table 3. The born effective charge and high-frequency dielectric tensors

	$Z^*_\perp$	$Z^*_\parallel$	Z^*	$\varepsilon_\perp(\infty)$	$\varepsilon_\parallel(\infty)$	$\varepsilon(\infty)$
This work$^{\mathrm{GGA}}$	2.50	2.66	2.56	4.40	4.64	4.47
This work$^{\mathrm{LDA}}$	2.53	2.67	2.57	4.30	4.58	4.45
Theory[8]	2.53	2.69	2.58	4.38	4.61	4.46
Theory[9]	–	2.70	–	4.42	4.70	4.51
Theory[10]	–	–	–	4.4	4.8	–
Experiment[11]	–	–	–	–	–	4.68

3.5. Thermodynamic properties

To understand thermodynamic properties we have performed the computations for some main thermodynamic functions, such as the inner energy, free energy, specific heat and entropy for the wurtzite AlN lattice system. The auxiliary code of Quantum-Espresso called quasi harmonic approximation (QHA) is used in the calculation. The calculated results for the thermodynamic function are illustrated in figure 5.

The values of ΔE and F_v by GGA are slightly lower than those by LDA, but the values of C_v and S by LDA are slightly lower than those by GGA. From curve of Internal energy, the change of ΔE is more slowly when T below 200K. It is seen that the specific heat presents T^3 at low temperature and tend to a certain value when the temperature is high.

The Debye temperature (Θ_D) is also calculated by QHA at 0 K and room temperature

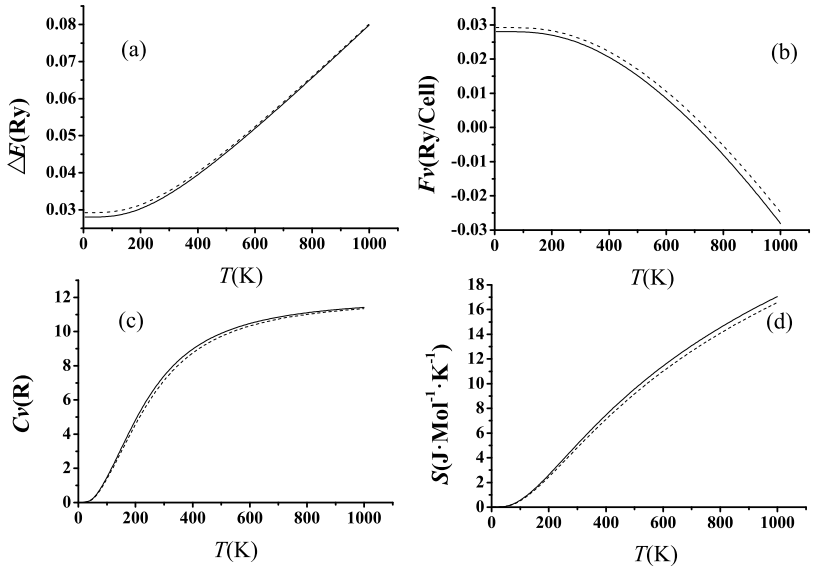

Figure 5. The phonon internal energy ΔE (a), vibrational free energy F_v (b), specific heat C_v (c) and entropy S (d) of AlN as functions of temperature. The specific heat is measured in $R = 8.31\mathrm{JMol}^{-1}\mathrm{K}^{-1}$.

Table 4. Debye temperature (Θ_D) for wurtzite AlN by GGA and LDA

		Θ_D,K	
		$T = 0$K	$T = 298$K
AlN	This work$^{\mathrm{GGA}}$	984	1017
	This work$^{\mathrm{LDA}}$	1026	1063
	Theory[13]	991	1057
	Theory[14]	1028	–
	Experiment[12]	950	1010

(298K). The calculated results of the Debye temperature for wurtzite AlN by GGA and LDA are listed in table 4. Our calculated values by GGA are very close to the experiment data [12] obtained from specific heat measurements, and better than the other theoretical values [13, 14].

4. Conclusion

In this work, we calculate the electronic states and the lattice dynamics of wurtzite AlN with two different pseudo potentials, LDA and GGA. The band structure of electrons and the phonon dispersion characteristics as well as the dielectric and thermal properties are showed. The calculated values are in agreement with available experimental data.

Acknowledgments

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References

[1] Tütüncü H M and Srivastava G P 2000 *Phys. Rev. B* **62** 5028–5035
[2] Davydov V Y, Kitaev Y E, Goncharuk I N, Smirnov A N, Graul J, Semchinova O, Uffmann D, Smirnov M B, Mirgorodsky A P and Evarestov R A 1998 *Phys. Rev. B* **58** 12899–12907
[3] Perlin P, Polian A and Suski T 1993 *Phys. Rev. B* **47** 2874–2877
[4] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G L, Cococcioni M, Dabo I, Corso A D, Gironcoli S d, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen A P, Smogunov A, Umari P and Wentzcovitch R M 2009 *J. Phys.: Condens. Matter* **21** 395502
[5] Bungaro C, Rapcewicz K and Bernholc J 2000 *Phys. Rev. B* **61** 6720–6725
[6] Ferreira da Silva A, Souza Dantas N, de Almeida J S, Ahuja R and Persson C 2005 *Journal of Crystal Growth* **281** 151–160
[7] Wright A F and Nelson J S 1995 *Phys. Rev. B* **51** 7866–7869
[8] Karch K 1997 *Phys. Rev. B* **56** 7404–7415
[9] Christensen N 1994 *Phys. Rev. B* **50** 4397–4415
[10] Adachi S 2005 *Properties of Group-IV, III-V and II-VI Semiconductors* 1st ed (Chichester, England: Wiley)
[11] Akasaki I and Hashimoto M 1967 *Solid State Communications* **5** 851–853
[12] Bruls R J, Hintzen H T, de With G and Metselaar R 2001 *Journal of the European Ceramic Society* **21** 263–268
[13] Marmalyuk A A, Akchurin R K and Gorbylev V A 1998 *High Temperature* **36** 817–819
[14] Peng F, Chen D, Fu H and Cheng X 2008 *Physica B: Condensed Matter* **403** 4259–4263