First-Principle Studies of Phonons III-N Compound Semiconductors in Wurtzite Structure

J. J. Zhang, G. J. Zhao, and X. X. Liang

***Abstract*—The phonon dispersion relations and density of states of the nitrides BN, AlN, GaN and InN in the wurtzite structure are investigated by using separately the local density approximation (LDA) and the generalized gradient approximation (GGA) within the framework of density functional theory. The results show that the highest optical phonon frequency at the Brillouin zone center decreases, but the phonon band gap increases, with increasing the cation/anion mass ratio. The frequencies calculated with GGA are lower than those with LDA. The GGA is more suitable for AlN and GaN, but the LDA for BN and InN.**

***Index Terms*—Phonon dispersion, phonon density of states, III-N compound semiconductor, wurtzite structure.**

I. Introduction

In recent years, the group III-nitride compound semiconductors have been attracting considerable attention, for their distinguished features. It is known that the nitrogen in III-N compounds forms rather short bonds with the trivalent metallic elements [1], and then the corresponding materials have a considerable hardness, high thermal conductivity and direct energy gap related to a substantial range from the visible to ultraviolet region of spectra. Consequently, nitride materials have shown a large impact on the optoelectronic devices in the deep ultraviolet [2] as well as on the electronic devices for high power, high-frequency operation. The nitride-based visible light emitting diodes are recently given more priority due to their application in solid state lightings [3], [4]. Current activities in optoelectronic devices have led to significant interest in studies of the structural and electronic properties in both wurtzite and zinc-blende phases of III-N semiconductors [5], [6]. The lattice dynamics of these materials have also been studied theoretically [7]-[11].

In present paper, the first-principle calculations for the lattice dynamics properties of AlN, GaN, BN and InN in wurtzite structure are performed with two different exchange- correlation functionals. The computed results by two different approaches are compared with each other as well as with the existing theories and experiments.

II. Theoretical Methods

We have considered the III-N compound semiconductors in wurtzite structure and obtained the structural and dynamical properties of the GaN, AlN, BN and InN by the first-principle calculation based on the density functional theory. The exchange-correlation potentials in the local density approximation (LDA) [12] and the generalized gradient approximation (GGA) [13] are separately used in the calculations. The optimum plane-wave energy cut-off has been tested carefully by keeping the total energy error less than 0.001 Hartree, and is determined as 45 Ryd for all these compounds. A $3 \times 3 \times 3$ Monkhorst-Pack mesh and ten special k point have been used to perform the Brillouin zone (BZ) integration. The self-consistent convergence of the total energy is taken to be 10^{-6}eV/atom, in order to obtain accurately the phonon dispersion curves. Moreover, a 4×4×4 q mesh is employed for the force constant calculation in the first BZ by interpolation. The whole calculation is carried out by using the Quantum ESPRESSO code [14], and the calculated results of the phonon frequencies and densities of states (DOS) are shown in Fig. 1 to Fig. 4.

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III. Results and Discussion

To obtain the equilibrium lattice constant a, c and the internal geometrical constant u, we fit the energy versus volume curves to the Murnaghan equation of state. Table I lists the calculated values of the structural parameters in this work. It is seen that our results are in good agreement with the previous theoretical and experimental values.

TABLE I: Lattice Constants a, c and Internal Parameters u for BN, ALN, GaN and InN in Wurtzite

		a(Å)	*c*(Å)	*c/a*	*u*
BN	This work^{LDA}	2.52	4.19	1.660	0.374
	This work^{GGA}	2.55	4.24	1.664	0.375
	Theroy [9]	2.53	4.19	1.654	0.374
	Experiment[15]	2.56	4.23	1.656	
AlN	This work^{LDA}	3.07	4.92	1.603	0.380
	This work^{GGA}	3.11	5.01	1.604	0.380
	Theroy[10]	3.10	5.01	1.615	0.380
	Experiment[16]	3.11	4.98	1.601	0.382
GaN	This work^{LDA}	3.19	5.12	1.606	0.374
	This work^{GGA}	3.22	5.21		0.375
	Theroy [17]	3.15	5.13		0.372
	Experiment [16]	3.19	5.20	1.630	0.377
InN	This work^{LDA}	3.55	5.66	1.596	0.378
	This work^{GGA}	3.60	5.80	1.611	0.377
	Theroy [17]	3.53	5.72		0.378
	Experiment [16]	3.54	5.71	1.613	

We have calculated the phonon dispersion curves and DOS of AlN, BN, GaN, InN of wurtzite structure by using

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the exchange-correlation potentials GGA and LDA, respectively, and the results are plotted in Figs. 1-4. Similar qualitatively dispersive curves and DOS of phonons for 4 different nitride semiconductors are obtained. It is expected that there are 12 branches of phonon frequency curves for every material, because a unit cell contains 4 atoms and then 12 degrees of freedom for wurtzite III-N compounds. The phonon modes degenerate at some high symmetry points of BZ. At *A* point, only 4 phonon modes can be observed, but 8 modes called $2A_1$, $2B_1$, $2E_1$ and $2E_2$ respectively appear at the Γ point. However, the quantitative characteristics of phonon frequency branches for the calculated materials are different from each other's upon the different cations.

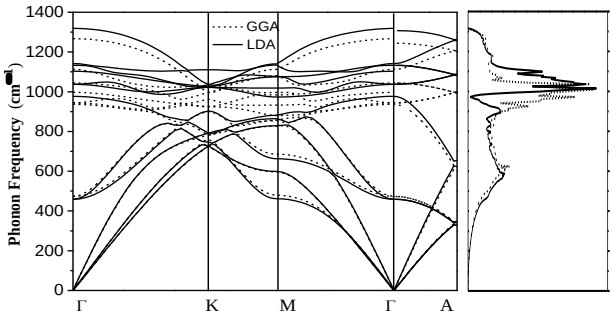

Fig. 1. Phonon dispersion curves (left) and DOS (right) of wurtzite BN.

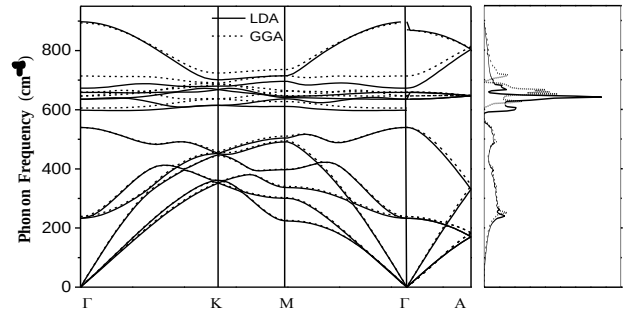

Fig. 2. Phonon dispersion curves (left) and DOS (right) of wurtzite AlN.

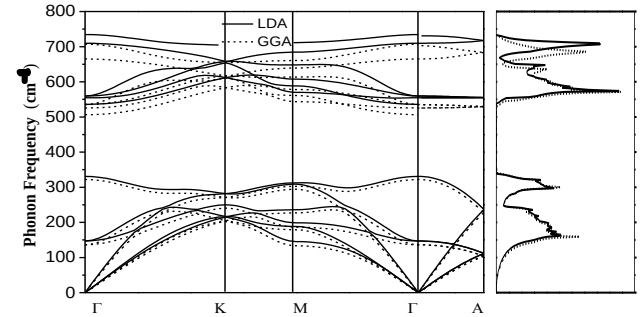

Fig. 3. Phonon dispersion curves (left) and DOS (right) of wurtzite GaN.

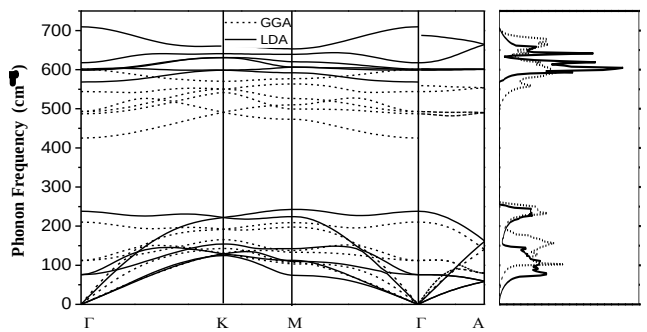

Fig. 4. Phonon dispersion curves (left) and DOS (right) of wurtzite InN.

For ease of understanding the mass influence to the frequency characteristic, we list the relative masses m_A of the cations, mass ratios m_A/m_C, and reduced masses $m_Am_C/(m_A+m_C)$ in Table II. The anion mass m_C is same as 14.01 for the 4 calculated materials.

TABLE II: RELATIVE MASSES OF CATION AND ANION, MASS RATIOS AND REDUCED MASSES $M_AM_C/(M_A+M_C)$

Material	BN	AlN	GaN	InN
Cation mass m_A	10.81	26.98	69.72	114.8
m_A/m_C	0.77	1.93	4.98	8.19
$m_Am_C/(m_A+m_C)$	6.10	9.24	11.67	12.49

It can be read from the figures that the characteristics of phonon frequencies are sensitive to the cation/anion mass ratios. Firstly, the highest frequency of optical phonons at the BZ center (Γ point) increases obviously with decreasing the cation mass and then the reduced mass in InN, GaN, AlN, BN order. Meanwhile, it is also seen in the DOS curves that there are the phonon band gaps between the acoustic and optical phonon branches in InN, GaN and AlN because of the cation-anion mass mismatches, and the gap width increases with increasing the cation mass, consistent with the previous work [10]. However, the band gap can not be observed in BN whose cation-mass is closes to the anion-mass. Fig. 5 shows the widths of the phonon band gaps for the BN, AlN, GaN and InN. One can clearly see that the band gap expend non-linearly with enhancing cation/anion mass ratio. The ratio of the cation to anion mass in BN is slight lower than 1, and then the gap can not be observed.

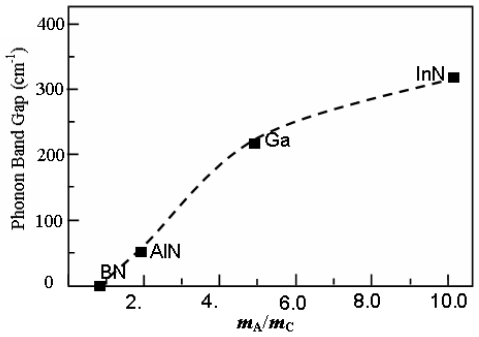

Fig. 5. Phonon ban gaps as functions of cation/anion mass ratio for BN, AlN, GaN and InN.

Now we turn to analyze the scale of the LO-TO splitting in the phonon spectrums. The calculated relative splitting $(\omega_{LO}-\omega_{TO})/\omega_{TO}$ for E_1 (A_1) mode are 0.21(0.25) in BN, 0.37 (0.46) in AlN, 0.33(0.36) in GaN and 0.26(0.29) in InN, respectively. It may be seen that the greater the relative value of splitting, the more LO mode dispersion is evident. It is also seen that there exist a deviation of the frequency value around Γ along the direction of *M*-Γ and *A*-Γ due to the anisotropy of the wurtzite structure. The ratio $[\omega_{TO}(E_1)-\omega_{TO}(A_1)]/\omega_{TO}(E_1)$ is usually used to measure the anisotropy of materials, for which our calculated values are 0.05, 0.09, 0.03 and 0.05 for BN, AlN, GaN and InN, respectively. Therefore, the anisotropy of wurtzite AlN crystal is strongest in the calculated materials, but that of GaN weakest. The conclusion is in agreement qualitatively with Ref. [10] except for BN.

TABLE III: PHONON FREQUENCIES AT BZ CENTER FOR WURTZITE NITRIDES IN UNITS OF CM^{-1}

		E_2^l	B_1^l	$A_1(\mathrm{TO})$	$E_1(\mathrm{TO})$	E_2^h	B_1^h	$A_1(\mathrm{LO})$	$E_1(\mathrm{LO})$
BN	This work^{LDA}	459	977	1106	1137	1041	1142	1305	1318
	This work^{GGA}	473	936	997	1104	945	1113	1244	1267
	Theory[7]	447	918	988	1024	948	1179	1258	1286
	Theory [18]			1006	1053			1258	1285
AlN	This work^{LDA}	233	540	597	659	638	679	871	899
	This work^{GGA}	236	541	604	661	647	716	866	892
	Theory [10]	233	547	614	666	655	719	875	898
	Experiment [19]	252		614	673	660		893	916
	Experiment[20]	241		607		660			924
GaN	This work^{LDA}	147	331	536	554	559	710	731	735
	This work^{GGA}	137	322	506	524	536	665	703	708
	Theory[1]	137	337	545	563	572	702	736	732
	Experiment[21]	145		533	561	570		735	742
InN	This work^{LDA}	79	239	570	598	603	618	687	709
	This work^{GGA}	85	226	459	481	496	582	596	605
	Theory[10]	83	225	443	467	483	576	586	595
	Theory [22]	87	200	480	476	488	540	580	570
	Experiment[23]					495		596	

For the sake of comparison, we list the calculated frequencies at Γ point in wurtzite BN, AlN, GaN and InN by using the LDA and GGA, as well as other theoretical and experimental values in Table II. It is found that there are some differences between the calculated results by two different exchange-correlation potentials to some extent, even the differences sometimes are very small such as for AlN. The better or worse of the calculated results by two exchange- correlation potentials depends on the specific materials. For example, the results of LDA are more consistent with experimental data and other theoretical results for AlN, GaN. As for BN and InN, the GGA potential may be befitting in the calculations. Generally, the frequencies obtained by the GGA are lower than those by LDA especially for InN. In general our calculated results are agreement with existing experi- mental and theoretical data.

IV. CONCLUSION

We have calculated the phonon dispersion relations for BN, AlN, GaN and InN in the wurtzite structure, by employing both the LDA and the GGA to treat the exchange correlation energy. The results show that the characteristics of phonon frequencies are sensitive to the cation and anion masses. The highest optical phonon frequency at the BZ center decreases, but the phonon band gap increases obviously, with increasing the cation/anion mass ratio. The frequencies calculated with GGA are lower than those with LDA, especially for InN. The GGA is more suitable for AlN and GaN, but the LDA for BN and InN. The anisotropy of wurtzite AlN crystal is stronger than BN, GaN and InN. The results are agreement with existing experimental and theoretical data.

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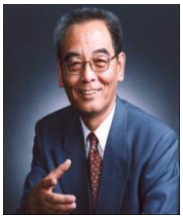

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