Optical phonon modes in GaN and AlN

I. Gorczyca,* N.E. Christensen, E.L. Peltzer y Blancá,† and C.O. Rodriguez†

Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

Self-consistent full-potential linear muffin tin orbital calculations of the electronic structures are used to investigate the optical phonon modes and their behavior under hydrostatic pressure. The calculations are performed for AlN and GaN in the wurtzite and zinc-blende structures. The calculated phonon frequencies and their pressure coefficients agree well with experimental results, best in the case of GaN.

I. INTRODUCTION

In this work we present a theoretical study of optical phonons in GaN and AlN. These materials are of great interest due to their properties important to both applications in optoelectronics and to fundamental materials science.[1,2] First-principles total-energy calculations are used to derive the frequencies of zone-center optical phonons in the wurtzite as well as the zinc-blende structures. Also the effects of applying hydrostatic pressures are examined.

The "frozen-phonon" approximation has been used to obtain optical phonon frequencies at the center of the Brillouin zone (BZ), and the total-energy calculations are performed using the local-density approximation (LDA) to the density-functional theory in conjunction with the linear muffin tin orbital (LMTO) method.[3] The frozen-phonon calculation where the atoms are being moved away from the high-symmetry positions requires that the total energies are calculated by means of a method that does not make shape approximations to the charge densities and potentials. We use the full-potential LMTO method (FP-LMTO) as implemented by Methfessel.[4] The basis set used in the present work includes 52 LMTO's per formula unit (two real atoms and two so-called "empty spheres"[5]). The wurtzite structure contains two formula units in the primitive cell. Brillouin-zone integrations are performed using ≈ 150 k points in the irreducible zone.

The phonon frequencies are derived from the evaluation of the total energy as a function of the atomic displacements, where all the other parameters related with the calculations are kept fixed. The radii of the muffin-tin spheres are chosen so that they stay fixed and nonoverlapping under the distortions. Moving the atoms we keep the empty spheres in fixed positions. It was found by Weyrich et al.[6] that the calculated frequency values are insensitive to whether the empty spheres were moved along with the atoms or not.

II. AMBIENT PRESSURE

First we examine the optical zone-center phonons in the zinc-blende structure. The frequency of the transverse-optical (TO) mode is obtained from the total energy calculated as a function of the displacement in the (111) direction of the anion with respect to the cation. The vibration frequency is then evaluated from the sec-

TABLE I. Optical Γ-phonon frequencies (in cm^{-1}) for AlN in wurtzite and zinc-blende structures.

Mode	Present work	Other calc.		Experiment						
		Miwa[a]	Ruiz[b]	Carlone[c]	Sanjuro[d]	Brafman[e]	Hayashi[f]	Perlin[g]	McNeil[h]
Wurtzite									
E_1	649	650	734	614	671	667	672	–	673
E_2^1	236	228	301	303	–	–	–	241	252
E_2^2	631	638	704	426	–	665	–	660	660
A_1	629	601	668	–	659	667	660	607	614
B_1^1	553	534	723	–	–	–	–	–	–
B_1^2	717	703	772	–	–	–	–	–	–
Zinc blende									
TO	652	648	–	–	–	–	–	–	–

[a]Reference 7.
[b]Reference 16.
[c]Reference 11.
[d]Reference 13.
[e]Reference 10.
[f]Reference 19.
[g]Reference 12.
[h]Reference 14.

TABLE II. Optical Γ-phonon frequencies (in cm^{-1}) for GaN in wurtzite and zinc-blende structure.

Mode	Present work	Other calculations		Experiment	
		Miwa[a]	–	Nakahara[b]	Perlin[c]
Wurtzite					
E_1	555	556	–	558	560
E_2^1	150	146	–	144	144
E_2^2	558	560	–	568	568
A_1	537	534	–	533	531
B_1^1	330	335	–	–	–
B_1^2	677	697	–	–	–
Zinc blende					
TO	551	558	603[d] 600[e]	–	–

[a]Reference 7.
[b]Reference 15.
[c]Reference 9.
[d]Reference 17.
[e]Reference 18.

ond derivative as obtained from a least-squares polynomial fit of the energy shifts.[6] The calculated (angular) frequencies of the zone-center TO phonons are 652 cm^{-1} for AlN and 551 cm^{-1} for GaN, in very good agreement with pseudopotential calculations[7] (see Tables I and II).

The analysis of the phonon modes in the wurtzite structure is slightly more complex due to the larger number of atoms in the basis. However, also here we consider only zone-center modes, and the small group at the Γ point is the C_{6v} point group. The full, reducible representation may be decomposed into irreducible representations according to $\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2$ (labeled as in Ref. 8). The various modes are illustrated in Fig. 1. Only optical modes are considered. The acoustic modes are, since the wave vector is zero, just translations.
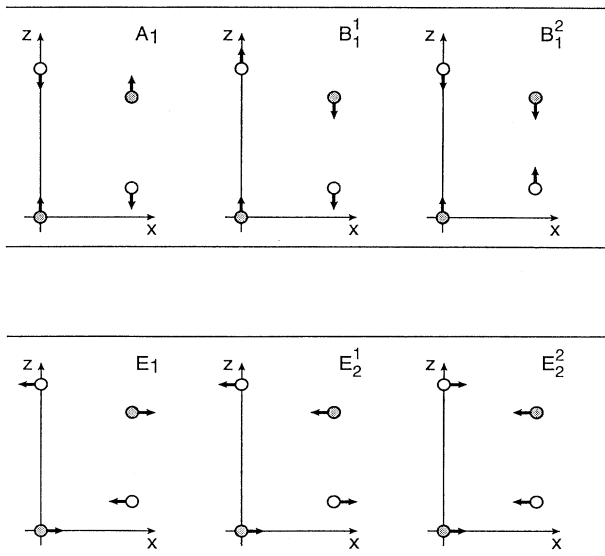

FIG. 1.   Optical phonon modes in the wurtzite structure.

The E_2 modes are Raman active, and A_1 and E_1 modes are both Raman and infrared active, and B_1 modes are silent, i.e., forbidden in Raman as well as infrared excitation modes. There is a close relation between the cubic zinc-blende and the hexagonal wurtzite structure—the difference in the neighboring atoms begins only in the third shell. However, the primitive cell in the wurtzite structure contains twice as many atoms as that of zinc-blende. This results in a folding of the Brillouin zone of the zinc-blende in the $\Gamma \to L$ direction, and then in a doubling of the number of modes. Thus instead of the TO mode in the zinc-blende structure we have in the wurtzite structure two modes: E_2^1 and TO modes. At the Γ point of the BZ the latter is split into A_1 and E_1 modes (see Fig. 6 of Ref. 9).

The calculated phonon frequencies for the wurtzite and zinc-blende structures are given in comparison with experiments[10–15,9] and other calculations[7,16–19] in Table I for AlN and in Table II for GaN. Our results are in excellent agreement with the recent pseudopotential calculations.[7] A small discrepancy ($\approx 5\%$) exists only for the A_1 (AlN) mode. More serious differences are found when we compare with the Hartree-Fock calculations[16] for AlN. The GaN results agree very well with Raman data.[15,9] For AlN some experiments are not consistent with each other (see Table I). They are performed on epitaxial layers (strained), on whiskers,[10] or on layers grown by epitaxy on sapphire[13] or silicon[11] substrates. Only recent experiments use large single crystals grown by sublimation recondensation[14] or by high-pressure, high-temperature synthesis.[20,12] If we consider these as being most reliable we see that the differences between experiment and our values are below 5%.

III. PRESSURE DEPENDENCE

The pressure and volume dependences of the phonon frequencies were derived from phonon calculations carried out for five different volumes, and the correspond-
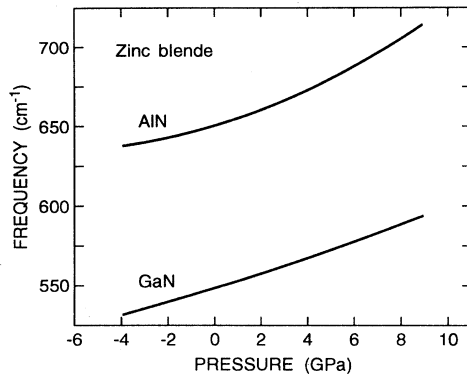
FIG. 2. TO-phonon frequencies for the zinc-blende structure as functions of hydrostatic pressure.
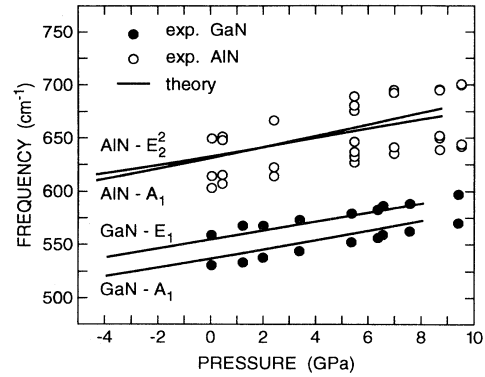

FIG. 3. Optical zone-center phonon frequencies for the wurtzite structure (high-frequency modes) as functions of hydrostatic pressure. Calculated values (solid lines) are compared with experimental data (open and filled circles) obtained by Perlin et al. [GaN (Ref. 9), AlN (Ref. 12)].

TABLE III. First- and second-order pressure coefficients, ω' and ω'' in units of $cm^{-1}GPa^{-1}$ and $cm^{-1}GPa^{-2}$, repectively, and mode Grüneisen parameter, γ, for the optical zone-center phonons in AlN. Experimental results are from Ref. 12.

Mode	Present work			Experiment		
	ω'	ω''	γ	ω'	ω''	γ
Wurtzite						
E_1	4.36	0.059	1.48	–	–	–
E_2^1	-0.29	-0.022	-0.28	–	–	–
E_2^2	4.79	0.063	1.66	3.99	0.035	1.34
A_1	4.29	0.019	1.50	4.63	-0.01	1.68
B_1^1	2.72	-0.013	1.08	–	–	–
B_1^2	3.76	0.021	1.15	–	–	–
Zinc blende						
TO	4.32	0.082	1.42	–	–	–

TABLE IV. First- and second-order pressure coefficients, ω' and ω'' in units of $cm^{-1}GPa^{-1}$ and $cm^{-1}GPa^{-2}$, repectively, and mode Grüneisen parameter, γ, for the optical zone-centre phonons in GaN. Experimental data are from Ref. 9.

mode	Present work			Experiment		
	ω'	ω''	γ	ω'	ω''	γ
Wurtzite						
E_1	4.10	0.013	1.48	3.68	-0.0078	1.32
E_2^1	-0.15	0.006	-0.20	-0.25	-0.0017	-0.34
E_2^2	4.46	0.018	1.60	4.17	-0.0136	1.47
A_1	4.08	0.024	1.52	4.06	-0.0127	1.53
B_1^1	1.72	-0.007	1.04	–	–	–
B_1^2	4.36	0.033	1.29	–	–	–
Zinc blende						
TO	4.54	0.033	1.52	–	–	–

ing values of the pressure were determined from the theoretical[21] equations of state.[21] The calculated pressure dependence of the TO modes in the zinc-blende structure is illustrated in Fig. 2. The behavior is more linear for GaN than AlN, and this also follows from the second-order pressure coefficients given in Tables III and IV (bottom). Some of the phonon frequencies in wurtzite GaN and AlN as functions of an applied hydrostatic pressure are shown in Figs. 3 and 4. Our calculated results (full curves) are compared with experimental data.[9,12] Mode Grüneisen parameters, γ, as well as first- and second-order pressure coefficients are listed in Tables III and IV and compared with experiments.[9,12] The Grüneisen parameter of the E_2^1 mode is small and negative for both AlN and GaN. This reflects the relation between this mode and the zone-edge TA(X) mode in the zinc-blende structure.[22,23] It was suggested[22,9] that the "softness" of the E_2^1 mode is related to the phase transition pressure (see also Refs. 24–26). Actually, comparing results for GaN and AlN, the E_2^1 mode is softer (γ is negative and larger in magnitude) for AlN, where the phase transition to the rocksalt structure occurs at much lower pressure.[21] The Grüneisen parameters of the E_1, E_2^2, and
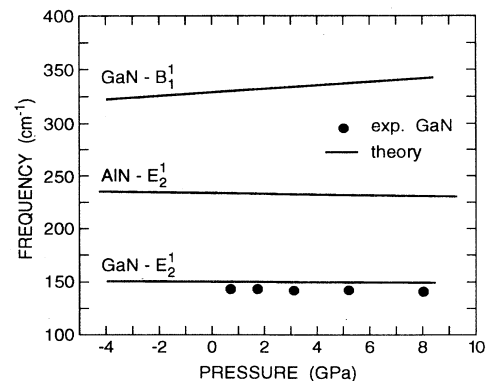

FIG. 4. Same as Fig. 3, but for low-frequency modes.

A_1 modes are close to 1.5, which is the value obtained for the TO mode in the zinc-blende structure (almost the same for AlN and GaN). The experimental values of γ for these modes scatter somewhat more, 1.32 to 1.68.

IV. CONCLUSION

The frequencies of the zone-center phonons as well as their pressure coefficients, as derived from first-principles density-functional calculations agree well with experiments. This agreement is particularly good for GaN. At first this may seem surprising since the calculations are simpler for AlN where there are no complications due to cation $3d$ semicore states (like Ga $3d$) that need to be treated as band states.[21] An explanation might be that the experimental data for AlN are less reliable than those of GaN due to poorer defined sample specifications.

It was mentioned that the fact that the E_2^1 mode has a lower Grüneisen parameter (negative in both compounds) in AlN than GaN is consistent with the pressure of the wurtzite→rocksalt transition being lower in AlN. As in the case of the transition pressure[21] we also suggest that the presence of the Ga $3d$ semicore states causes the difference in softness of the E_2^1 mode.

*Permanent address: High Pressure Research Centre, Polish Academy of Sciences, Sokolowska 29, 01-142 Warsaw, Poland.

†Permanent address: Instituto de Física de Liquidos y Sistemas Biológicos, University of La Plata, 1900 La Plata, Argentina.

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