Ab initio study of phonons in hexagonal GaN

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Phonon dispersion relations for the hexagonal wurtzite phase of 2H-GaN are estimated using the local-density approximation with ultrasoft pseudopotentials and plane-wave basis, calculating the Hellmann-Feynman forces and applying the direct method. *Ab initio* calculations are performed on the rhombohedral supercell, which lowers the crystal space group. We propose a method to restore the proper symmetry. The calculated phonon frequencies at the Γ point are compared with Raman and infrared measurements, phenomenological models and other *ab initio* calculations, and a very good agreement is obtained. Phonon frequencies at high-symmetry zone-boundary points and phonon density of states are deduced as well.
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The GaN crystal is currently being actively investigated in view of its potential application for short-wavelength electroluminescence devices and high-temperature, high-power, and high-frequency electronics. The GaN is a basic material for realization of light-emitting diodes and lasers in blue and UV region. The knowledge of lattice dynamics and phonon characteristics helps to understand the mechanism of the photon emission process used in design of an efficient photonic material. The 2H-GaN crystallizes in the hexagonal wurtzite structure with the space group $P6_3mc(C_{6v}^4)$. Several attempts have been made to calculate the phonon dispersion curves for 2H-GaN. Phenomenological models[1–4] report results determined by fitting model parameters to experimental data. Up to now the *ab initio* phonon calculations are available only for zone-center Γ wave vector. These calculations have used either a mixed basis method,[5] a linear muffin-tin orbital method[6,7], or a density-functional theory with a linear-response approach.[8] To our best knowledge *ab initio* calculations of the phonon dispersion relations for 2H-GaN have not yet been performed. Moreover, this information is also not provided by inelastic neutron scattering measurements because of the absence of sufficiently large GaN single crystals. For completness, however, we add that epitaxy of thin GaN film has demonstrated existence of the cubic zinc-blende $F43m$ structure, for which *ab initio* phonon dispersion relations are available from the linear response method.[8]

The goal of this *ab initio* study is to obtain the phonon dispersion relations and phonon density of states for 2H-GaN, using the direct method approach. The *ab initio* calculations of 2H-GaN are performed using the pseudopotential method within the local-density approximation, as implemented in the Vienna *Ab initio* Simulation Package (VASP),[9,10] and with ultrasoft pseudopotentials provided with VASP. The pseudopotentials for Ga and N atoms are representing $d^{10}s^2p^1f^0$ and $s^2p^3d^0$ electron configurations, respectively. A plane-wave basis set with 348-eV cutoff is used to expand the electronic wave functions at special k points generated by a $2\times2\times2$ Monkhurst-Pack scheme. We have used a rhombohedral supercell with 48 atoms, and with basis vectors defined as $\mathbf{a}_s=2\mathbf{a}+\mathbf{c}$, $\mathbf{b}_s=2\mathbf{b}+\mathbf{c}$, and $\mathbf{c}_s=-2\mathbf{a}-2\mathbf{b}+\mathbf{c}$, where $\mathbf{a},\mathbf{b},\mathbf{c}$ are the primitive translation vectors of the hexagonal unit cell.

The optimized supercell of 2H-GaN provides the following lattice constants expressed in Cartesian coordinate system: $\mathbf{a}=(a_0,0,0)$, $\mathbf{b}=(-a_0/2,\sqrt{3}/2a_0,0)$, $\mathbf{c}=(0,0,c_0)$, where $a_0=3.1328$ Å and $c_0=5.1078$ Å. The fractional positions of atoms are: Ga: (1/3, 2/3, 0) and N: (1/3, 2/3, u), where $u=0.3770$. As seen from Table I these structural data are in good agreement with other calculations[5,7,8] and with crystallographic measurements.[11,12]

Within the direct method[13] the phonons are found from the Hellmann-Feynman forces computed using optimized supercell with displaced atoms one at the time. The phonon frequency is computed correctly either when the potential interaction ceases out within the supercell size, or, independent of the potential range, when the phonon wave vector is commensurate with the supercell size, and the supercell shape guaranties complete list of neighbors of each coordination shell, such that the dynamical matrix conserves its symmetry. Unfortunately, for 2H-GaN one cannot find a supercell shape, which fulfils both requirements. The symmetry of the selected rhombohedral supercell breaks the twofold symmetry axis 2_z, and lowers the 2H-GaN space group $P6_3mc$ to $P31c(C_{3v}^4)$. Thus, the present *ab initio* calculations are carried on within the $P31c$ symmetry.

The phonon dispersion relations are determined using the direct method[14] and PHONON program.[15] For that the Hellmann-Feynman forces are computed for six independent displacements, along x and y and z for Ga and N atoms, as required by the rhombohedral supercell. The displacement amplitude is 0.03 Å. Each displacement generates $3\times48=144$ components, hence six displacements give 864 data of Hellmann-Feynman forces. Next, the symmetry of so-called

TABLE I. Structural parameters of hexagonal 2H-GaN.

	a [Å]	c [Å]	u
Present calc.	3.133	5.108	0.377
Calc.[8]	3.143	5.111	0.377
Calc.[5]	3.146	5.125	0.377
Calc.[7]	3.170	5.135	0.379
Exp.[11]	3.189	5.185	
Exp.[12]	3.160	5.122	

TABLE II. Comparison of the phonon frequencies [in THz] at the Γ point of optical modes of hexagonal 2H-GaN.

Reference	E_2	B_1	A_1(TO)	E_1(TO)	E_2	B_1	A_1(LO)	E_1(LO)
Present calc.	4.26	10.14	16.04	16.70	16.91	20.69	22.00	22.31
Calc.[5]	4.38	10.00	16.01	16.67	17.03	20.90		
Calc.[6]	4.50	9.89	16.10	16.64	16.73	20.30		
Calc.[8]	4.29	10.10	16.22	17.03	17.35	21.58	22.48	22.69
Calc.[4]	4.59	9.56	16.37	16.61	16.94	21.82	22.00	22.15
Calc.[19]	5.70	9.86	16.13	16.88	16.97	21.43		
Exp.[20]	4.38		15.98	16.76	17.03		21.29	22.21
Exp.[21]				16.61	17.06		22.18	
Exp.[22]			16.10	16.67	17.12		22.09	
Exp.[23]	4.35		15.92	16.82	17.09		22.03	22.24
Exp.[24]			15.92	16.82	17.03		22.03	22.18

cummulant force constants,[14] following the $P31c$ space group, is established. These force constants depend on 190 independent parameters spread over 25 coordination shells, and are found from fitting them to the calculated Hellmann-Feynman forces.

The values of the cummulant force constants diminish with distance between involved atoms. The largest ones are the on-site force constants (zero distance). The longest distance from the center of the supercell to an atom in latteral direction is 5.4262 Å and along the threefold symmetry axis 7.0334 Å . A check of the value of the force constants shows that their largest elements at the surfaces of the supercell are at least two order of magnitude smaller than the on-site force constants. Such a distance decrease of force constans is quite sufficient to get phonon frequencies at all wave vectors with an appreciate accuracy. Moreover, the present rhombohedral supercell provides correct phonon frequencies at commensurate wave vectors Γ: (0,0,0), M: (0,1/2,0), (1/6,1/6,1/3), and (1/3,1/3,1/3) and symmetry equivalent points, even, if the force constants would not vanish within the range of the supercell.

For the C_{6v} point group the group theory predicts at Γ the following optic modes: $A_1(R,I)+2B_1+E_1(R,I)+2E_2(R)$. The E modes are twofold degenerate, and R and I denote Raman and infrared activity, respectively. Since GaN has a mixed ionic-covalent nature of chemical binding, the macroscopic electric field splits the infrared active modes A_1 and E_1 to transverse A_1(TO), E_1(TO) and longitudinal A_1(LO), E_1(LO) components. The TO phonon frequencies are calculated within the direct method. The LO modes depend on the nonanalytical term,[16,17] which in turn depends on the effective charge tensors $\mathbf{Z}^*$. We find the values of the effective charges in a semiempirical way by adjusting the A_1(LO), E_1(LO) phonon frequencies to the experimental ones (see Table II), and hence $Z_{xx}(\mathrm{Ga})=Z_{yy}(\mathrm{Ga})=-Z_{xx}(\mathrm{N})=-Z_{yy}(\mathrm{N})=1.12$ and $Z_{zz}(\mathrm{Ga})=-Z_{zz}(\mathrm{N})=1.14$. The values calculated in Ref. 8 with density functional theory are similar $Z_{xx}(\mathrm{Ga})=1.12$ and $Z_{zz}(\mathrm{Ga})=1.18$. These effective charges are used to compute the LO phonon dispersion curves by extrapolating them from the Γ point to the Brillouin zone boundary.[18,15] Technically it is done by adding to the analytical dynamical matrix $\mathcal{D}^{(o)}_{\alpha,\beta}(\mathbf{k};\mu\nu)$, derived from Hellmann-Feynman forces, the following nonanalytical contribution:

$$4\pi e^2/V\sqrt{M_\mu M_\nu}\{[\mathbf{k}\cdot\mathbf{Z}^*(\mu)]_\alpha[\mathbf{k}\cdot\mathbf{Z}^*(\nu)]_\beta/|\mathbf{k}|^2\}\times\exp\{-2\pi i\mathbf{g}\cdot[\mathbf{r}(\mu)-\mathbf{r}(\nu)]\}\times(1/2)(1+\cos\pi|\mathbf{k}|/|\mathbf{k}_{BZ}|).$$

Here, $\mathbf{k}$ is the wave vector within a Brillouin zone with center at reciprocal lattice vector $\mathbf{g}$, V stays for the volume of the primitive unit cell, M_μ, $\mathbf{r}_\mu$ are atomic masses and positions. The $\mathbf{k}_{BZ}$ is a wave vector parallel to $\mathbf{k}$, and of the length from Γ to the Brillouin zone surface. Strictly speeking the nonanalytical term appears only at $\mathbf{k}=0$. However, many experimental results suggest that an extrapolation between zone center LO mode and Brillouin zone boundary, where the contribution from the macroscopic electric field disappears, can be accepted. This behavior is guarantied by the last factor which is equal to 1 and 0 at the zone center and zone boundary, respectively. This extrapolation can be performed more properly if one could calculate phonon frequencies at commensurate wave vector with n times elongated supercell, and then extrapolate the LO branch to $\mathbf{k}=0$. Such procedure was used succesfully for MgO crystal.[16] However, in the case of GaN the elongated rhombohedral supercell becomes too large for such treatment. Finally, we would like to underline that the nonanalytical term contributes only to A_1(LO) and E_1(LO) modes, whereas the remaining zone-center and zone-boundary modes are not altered by the effective charges.

First, the phonon dispersion relations were calculated directly from the rhombohedral supercell and they obeyed the $P31c$ symmetry. Therefore, majority of modes along $A-H-L-A$ directions are split, in disagreement with the mode's degeneracy required by the $P6_3mc$ space group. The observed splittings are not large and do not exceed 0.7 THz. The splittings occur since the calculated force constants do not obey the local symmetry of $P6_3mc$ structure. To rebuild the correct phonon degeneracy the force constant symmetry is restored in the following way. Denote by $\mathbf{\Phi}^{(H)}$ and $\mathbf{\Phi}^{(L)}$ the force constant matrices between the same pair of atoms in $P6_3mc$ and $P31c$ structures, respectively. Each (3×3) force constant matrix can be written as (9×1) column matrix, and then decoupled to $(9\times p)$ symmetry dependent matrix $\mathcal{A}$, and $(p\times1)$ column matrix $\mathcal{P}$ of p parameters:[14]

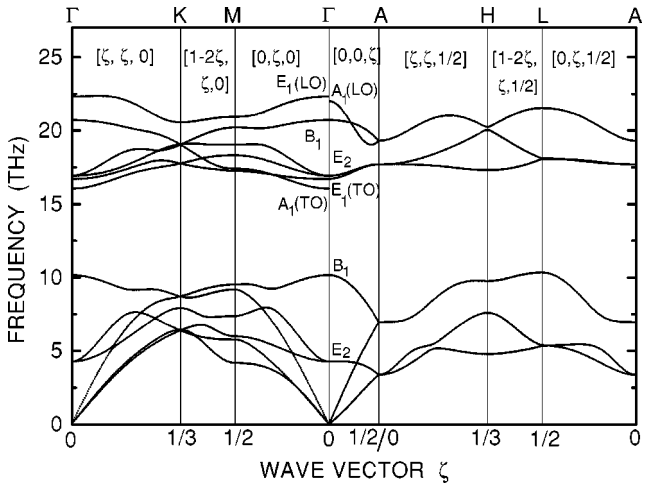

FIG. 1. Phonon dispersion relations of 2H-GaN crystal calculated from rhombohedral supercell with force constants adapted to the $P6_3mc$ space group symmetry.

$\mathbf{\Phi}^{(i)}_{(9\times1)}=\mathcal{A}^{(i)}_{(9\times p)}\cdot\mathcal{P}^{(i)}_{(p\times1)}$, where $i=H$ or L, and usually the number of parameters $p_L\geqslant p_H$. From the crystal structures and space groups one finds $\mathcal{A}^{(H)}$ and $\mathcal{A}^{(L)}$ matrices uniquely. The direct method with rhombohedral supercell provides the force constants $\mathbf{\Phi}^{(L)}$. Thus, we increase the symmetry of $\mathbf{\Phi}^{(L)}$ to symmetry of $\mathbf{\Phi}^{(H)}$, firstly by solving with respect to $\mathcal{P}^{(H)}$ the overdetermined linear system of equations $\mathbf{\Phi}^{(L)}=\mathcal{A}^{(H)}\cdot\mathcal{P}^{(H)}$, and secondly by generating symmetry adapted force constants from equation $\mathbf{\Phi}^{(H)}=\mathcal{A}^{(H)}\cdot\mathcal{P}^{(H)}$. The solution of the overdetermined system of equations is done by a singular value decomposition method, which provides simultaneously the best least-square fit. We have determined all force constants $\mathbf{\Phi}^{(H)}$ of 2H-GaN crystal from the rhombohedral supercell data $\mathbf{\Phi}^{(L)}$ using the above described procedure, and the modifications are found to be not large.

The rhombohedral supercell generates another problem. Namely, some coordination shells, which touch the supercell surfaces contain smaller number of atoms than really present in the crystal. For example, Ga atoms at the distance 5.4243 Å from the supercell center form a coordination shell with 6 atoms, instead of 12 like in the bulk crystal. In such a case we regenerate the lost force constants by equation $\mathbf{\Phi}^{(H)}=\mathcal{A}^{(H)}\cdot\mathcal{P}^{(H)}$, and renormalize all elements of these force constants to the new total number of neighbors in a given coordination shell. In the above example, 6 missing force constants were added to the neighbor list, and the values of elements of all 12 force constants were devided by two. This procedure preserves the translational-rotational invariance conditions, and restores the $P6_3mc$ symmetry of 2H-GaN dynamical matrix.

In Fig. 1, we show the phonon dispersion relations calculated with the force constants adapted to $P6_3mc$ symmetry, and with effective charges $Z_{xx}(\mathrm{Ga})=1.12$ and $Z_{zz}(\mathrm{Ga})=1.14$. The coordinates of high-symmetry points $\mathbf{Q}=(q_1,q_2,q_3)$ are given in terms of reciprocal lattice constants $\mathbf{Q}=q_1\mathbf{g}_1+q_2\mathbf{g}_2+q_3\mathbf{g}_3$. The $(\mathbf{g}_1,\mathbf{g}_2,\mathbf{g}_3)$ can be expressed in Cartesian coordinates as $\mathbf{g}_1=(0.3192,0.1843,0.0)$ Å^{-1}, $\mathbf{g}_2=(0.0,0.3686,0.0)$ Å^{-1}, $\mathbf{g}_3=(0.0,0.0,0.1958)$ Å^{-1}. These phonon dispersion curves do not differ much from those calculated directly from the rhombohedral supercell. One has the impression that the phonon dispersion curves of 2H-GaN in Fig. 1 follow from an average of phonon dispersion curves calculated directly from rhombohedral supercell. It is, however, important to average them in the above indicated way, which guaranties the correct degeneracy of the phonon modes.

TABLE III. Calculated phonon freqencies [in THz] of modes in hexagonal 2H-GaN at the *M*, *K*, *A*, *H* and *L* points of the Brillouin zone. The dimensionality of mode degeneracy is given in brackets. Phonons at *M* point are commensurate with the rhombohedral supercell.

M	*K*	*A*	*H*	*L*
4.17 (1*d*)	6.37 (2*d*)	3.35 (4*d*)	4.77 (2*d*)	5.33 (2*d*)
5.75 (1*d*)	6.42 (1*d*)	6.94 (2*d*)	7.58 (2*d*)	5.36 (2*d*)
5.97 (1*d*)	7.90 (1*d*)	17.69 (4*d*)	9.74 (2*d*)	10.32 (2*d*)
7.36 (1*d*)	8.69 (2*d*)	19.29 (2*d*)	17.29 (2*d*)	18.03 (2*d*)
9.17 (1*d*)	17.74 (2*d*)		20.02 (2*d*)	18.11 (2*d*)
9.50 (1*d*)	19.00 (1*d*)		20.23 (2*d*)	21.53 (2*d*)
17.24 (1*d*)	19.06 (2*d*)			
17.40 (1*d*)	20.55 (1*d*)			
18.31 (1*d*)				
19.02 (1*d*)				
20.19 (1*d*)				
20.93 (1*d*)				

In Table II the zone-center phonon frequencies are compared with other *ab initio* calculations[5,6,8,4,19] and experimental data.[20–24] They show an overall good agreement. In Table III we give the phonon frequencies at all high-symmetry points in the Brillouin zone. We remind that the wave vectors at Γ and *M* points are commensurate with the rhombohedral supercell. For completeness of the lattice dynamics we show in Fig. 2 the total and partial phonon density of

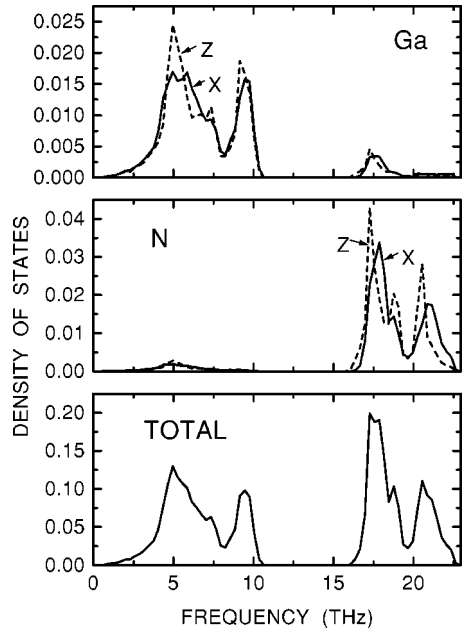

FIG. 2. Partial phonon density of Ga and N atoms along *x* and *z* directions, and total density of states of 2H-GaN.

states for Ga and N atoms in x and z directions. The spectra are normalized to 1 and 1/12 for total and partial density of states, respectively.

In conclusion, we have presented *ab initio* calculations of structural and lattice dynamical properties of GaN in hexagonal wurtzite structure. The results for the lattice constants and Raman frequencies are in good agreement with experimental data and previous calculations. The direct method could have been used because of the selection of the rhombohedral supercell. Due to periodic bondary conditions this supercell imposes a field that breaks the symmetry of the wurzite structure. The symmetry is reestablished by symmetry controlled renormalization of force constants.

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