Electronic structure of GaN with strain and phonon distortions

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The full-potential linear muffin-tin orbital method is used to study the electronic and structural properties of zinc-blende GaN. The total energy and electronic band structures under uniaxial strain and zone-center TO phonon distortions were calculated. This yields the cubic elastic constants, the zone-center TO phonon frequency, and the internal-strain parameter ζ. The elastic constants of hexagonal GaN are obtained using the transformation method of Martin [Phys. Rev. B **6**, 4546 (1972)]. The corresponding deformation potentials are calculated for some of the important eigenvalues.

Gallium nitride is considered as a promising material for short-wavelength electroluminescent devices.[1,2] In spite of their importance for adequate modeling of device applications, experimental data on the properties of GaN under deformations are not available due to the difficulty in obtaining good single crystals. Although there have been several first-principles calculations on GaN,[3–10] a comprehensive study of the elastic properties has not been reported to the best of our knowledge. In this work, we report calculations of the equilibrium and elastic properties of this material in the zinc-blende (ZB) structure. The calculations were performed *ab initio* within the local density approximation to the density functional theory[11] using the Hedin-Lundqvist parametrization of exchange-correlation[12] and the full-potential linear muffin-tin-orbital (FP-LMTO) method.[13] This method has been shown previously to provide accurate elastic constants for Si and diamond[14] and 3C-SiC.[15] Also, we determine the elastic constants for hexagonal (wurtzite) GaN from our zinc-blende elastic constants using the transformation method of Martin.[16] Finally, we present the strain-induced changes of the band structure and calculate the corresponding deformation potentials.

The details of our computational procedure are as follows. A multiple-κ muffin-tin-orbital basis set is used, where κ^2 is the kinetic energy of the envelope function. Three augmented Hankel functions with decay energies κ^2 of $-0.01, -1.0$, and -2.3 Ry were used for each angular momentum s, p, and d. (Calculations including f orbitals did not change the results appreciably.) The basis functions are centered on the Ga and N muffin-tin spheres only, giving a total of 27 orbitals per atom, but were augmented also in empty spheres at the usual tetrahedral interstices and including an angular momentum cutoff of $l = 4$. The 2s and 2p states of N and the 3d, 4s, and 4p states of Ga are treated as bands. The importance of treating the Ga 3d band dispersion and hybridization with N 2s has been emphasized before by Lambrecht and Segall[7] and Fiorentini *et al.*[9] The radii of the muffin-tin spheres were chosen so that they stay fixed and nonoverlapping under the considered distortions. (Radii were chosen as 97% of touching.) The charge density and po-

tential in the remaining interstitial region are expressed as expansions in a separate set of Hankel functions.[13] We used a set of Hankel functions with two decay energies ($\kappa^2 = -1.0$ and -3.0 Ry) centered on all spheres with angular momentum up to $l = 4$. The results were obtained nonrelativistically. The Brillouin zone summations were performed with a set of 10 special points.[17]

To calculate elastic constants, the total energies under hydrostatic, tetragonal, and trigonal strains were calculated using strains up to 6%. For each strain the total energy difference between the strained and the unstrained states are fitted to a parabolic curve. In effect, this means that the elastic constants are obtained from numerical second derivatives of the total energy differences. A frozen phonon calculation yields the zone-center phonon frequency in a similar way. For the trigonal strain, the relative position of the two sublattices is not determined by symmetry alone and was thus determined by total energy minimization. It is described by the so-called Kleinman internal strain parameter ζ.[18]

The calculated equilibrium properties, which are given in Table I, agree well with available previous calculations. The values reported for the bulk modulus measured on single-crystals range from 188–245 GPa.[20–22] Our result is in excellent agreement with other calculations using the FP-LMTO method[9] and with the atomic-sphere approximation (ASA) calculations of Lambrecht and Segall.[7] The apparent discrepancy of our results with the earlier ASA-LMTO result of 239 GPa for wurtzite GaN reported by Gorczyca and Christensen[4] has been resolved by recent refined calculations by these authors, who now obtain 200 GPa.[24] Our result for B is also in fair agreement with the pseudopotential calculations,[3,5,6,8,10] which differ among each other by as much as do the experimental values.

The calculated frequency of the zone-center TO phonon, 18.1 THz or 603 cm^{-1}, agrees very well with the calculation of Ref. 9 and reasonably well with the calculation of Ref. 10. As for the elastic constants, we note that the main discrepancy with the experimental data of Sherwin and Drummond[23] is our much larger value of C_{44}. We note that the values of Sherwin and

Drummond[23] were derived from data on hexagonal crystals. We thus prefer to make our comparison directly for the hexagonal tensor.

The relations between the elastic constants of the wurtzite and ZB structures were derived by Martin[16] assuming that the local tetrahedra extending to second neighbors about each atom are rotated but otherwise identical in the two structures. The procedure involves applying rotations to the elastic tensor and then adding corrections due to the internal strain (IS) between two inequivalently oriented tetrahedra in the wurtzite structure to the resulting tensor. We applied this procedure to our calculated cubic elastic constants. The resulting hexagonal elastic constants are given in Table II. We first note that the results of Martin's procedure[16] differ only slightly from those obtained by simply rotating the tensor without taking the internal rotation of the tetrahedra into account. This was also reported to be the case for SiC by Martin.[16] The only experimental data known to

TABLE I. Equilibrium properties, zone-center optic phonon, elastic properties of cubic GaN.

Property	Present	Other Calc.	Expt.[a]
a (Å)	4.46	4.46[b], 4.5[c,d], 4.42[e] 4.30[h], 4.45[i,j]	4.5[f], 4.50[g]
E_{coh}	10.8	10.9[b], 9.9[c], 8.2[h] 13.45[i]	9.0[i]
B (GPa)	201	198[b], 200[c], 173[e], 240[h] 176[i], 195[j], 239[m], 179[d]	245[k], 237[l] 188[n]
B'	3.9	4.4[c], 3.64[e], 2.66[i] 3.93[d]	3.2[n], 4.3[l]
ν_{Γ}^{TO} (cm^{-1})	603	600[b], 558[j]	
ζ	0.5		
C_{11} (GPa)	296		264[o]
C_{12} (GPa)	154		153[o]
C_{44} (GPa)	206		68[o]
A^P	2.90		1.23[o]

[a] Data for wurtzite GaN.
[b] Reference 9.
[c] Reference 7.
[d] Reference 3.
[e] Reference 5.
[f] Average a_{eff} from wurtzite GaN. $a_{eff} = (\sqrt{3}a^2c)^{1/3}$. References 22 and 20.
[g] Data for epitaxially grown cubic GaN. Reference 19.
[h] Reference 6.
[i] Reference 8.
[j] Reference 10.
[k] Reference 20.
[l] Reference 21.
[m] Reference 4.
[n] Reference 22.
[o] Reference 23. These are obtained from the hexagonal elastic constants derived from x-ray measurement of thermal expansion of GaN polycrystals (Ref. 25) which in turn were transformed into the cubic constants using Martin's method (Ref. 16).
[p] $A = 2C_{44}/(C_{11} - C_{12})$.

TABLE II. Elastic constants of wurtzite GaN transformed from values for zinc-blende GaN.

Elastic constant	Rotation only	With IS	Expt.[a]
C_{11} (GPa)	431	396	296
C_{12} (GPa)	109	144	130
C_{13} (GPa)	64	64	158
C_{33} (GPa)	476	476	267
C_{44} (GPa)	126	91	24
C_{66}[b] (GPa)	161	126	83

[a] From thermal expansion data. Reference 25.
[b] $C_{66} = (C_{11} - C_{12})/2$.

us were derived by using root mean square dynamic displacements (RDD) of atoms measured on GaN powder by the x-ray diffraction method and a theoretical bulk modulus of 200 GPa.[25] Overall, they are significantly smaller than our calculated values. This is not too surprising, because the data were taken on powders which tends to underestimate the elastic constants because of porosity. Significant uncertainties are also related to the method of extracting the full set of elastic constants from these measurements. Basically, the displacements of the atoms from the equilibrium are determined by the forces between them and thereby related to the elastic constants. The elastic constants of Ref. 25 were obtained using these relations and seeking solutions in a limited numerical range from the values of the Debye characteristic temperatures, RDD, the bulk expansion coefficient, and the bulk modulus. In a test on zinc, their method predicted much smaller values of C_{12} and C_{44} than those from ex-

TABLE III. Deformation potentials[a] of cubic GaN for [001] and [111] strains and optical phonon distortion in units of eV.

State	Strain	d		State	Strain	d	
Γ_{15}^v	[001]	d_3	-2.8	Γ_{15}^c	[001]	d_3	1.5
	[111]	d_5'	-3.4		[111]	d_5'	-20.7
		d_5	-5.3			d_5	-19.2
	optic	d_{5o}	14.6		optic	d_{5o}	-11.3
L_3^v	[001]	d_3^3	4.8	L_1^c	[111]	$d_1^{5'}$	14.4
	[111]	$d_1^{5'}$	8.1			d_1^5	15.9
		d_1^5	8.1		optic	d_{1o}^5	-11.0
		$d_3^{5'}$	1.0				
		d_3^5	4.4				
	optic	d_{1o}^5	0.4				
		d_{3o}^5	-27.0				
X_5^v	[001]	d_1^3	6.4	X_1^c	[001]	d_1^3	5.6
		d_3	0.3				
	[111]	d_4'	12.7				
		d_4	14.3				
	optic	d_{4o}	-12.6				

[a] We adopt the notation of Kane (Ref. 27), which is related to that of Pikus and Bir (Ref. 28) by $d_3 = \sqrt{3}b$, $d_5 = \sqrt{2}d$ and to that of Herring and Vogt (Ref. 29) by $d_1^5 = \Xi_u/\sqrt{3}$, $d_1^3 = \sqrt{2}\Xi_u/\sqrt{3}$.

periments using sound velocity measurements. (For C_{12} and C_{44}, they obtained a 60% underestimate.) In view of this and the demonstrated accuracy of the computational method, we consider our present values to be more accurate than those experimental values. We hope that our calculated results will provoke a renewed interest for carrying out high precision sound velocity measurements on sufficiently large single crystals of GaN. We note that recently important progress has been made in growing single crystals of wurtzite GaN.[26]

From the self-consistently calculated potential at each strain or phonon-distorted state, we calculate the band structure along some symmetry lines of the Brillouin zone. Figure 1 shows the bands structures for 2% tetrag-

onal (a), and 2% trigonal strain (b), and a phonon amplitude of $u = 0.01a$ (c), each compared to the equilibrium undistorted band structure. [Note that in the phonon distortion the Ga and N are displaced by $\pm(1/2)u(1,1,1)$.] The deformation potentials are defined as suitably symmetrized linear strain coefficients of the band-structure eigenvalues. We follow the notation of Kane[27] (d_3 and d_5) which is related to that of Pikus and Bir[28] (b and d) by $d_3 = \sqrt{3}b$, $d_5 = \sqrt{2}d$ for the deformation potentials of the Γ_{15} eigenstate. The splittings under [001] and [111] strains for the Γ_{15}, X, and L states are given in Kane[27] Eqs. (3.39)–(42) and Tables II, III, VI, and VII. The relation to different notations are given in Kane[27] Table XI. For the splitting of the Γ_{15} state, the d_5' corresponds
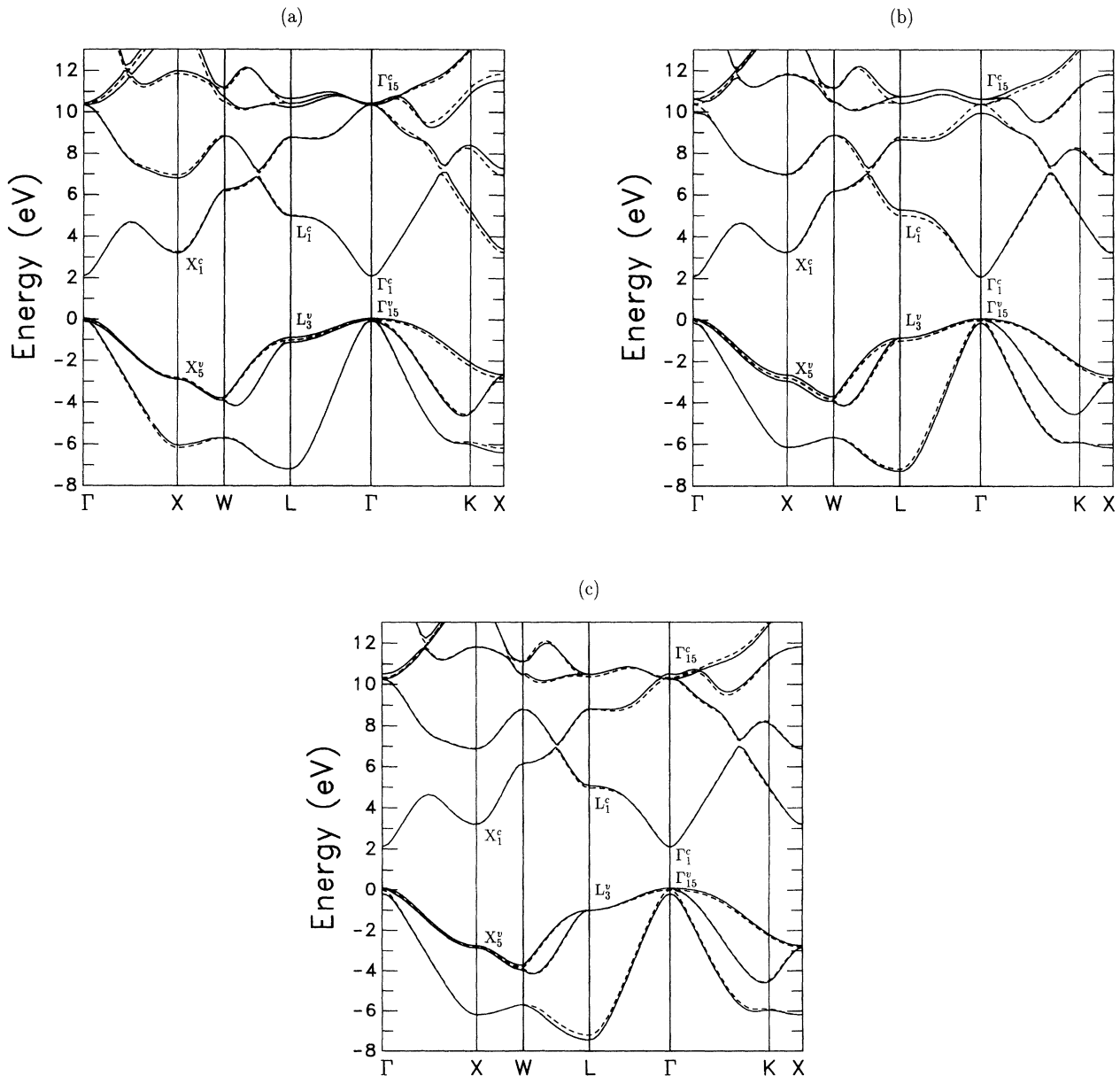

FIG. 1. Energy bands of zinc-blende GaN (full lines) under (a) tetragonal strain of 2%, (b) trigonal strain of 2%, and (c) Γ_{TO} phonon distortion with amplitude $u = 0.01a$; the dashed lines represent the undistorted band structure.

to uniform trigonal strain without the internal displacement, the unprimed d_5 includes the internal displacement effect and d_{5o} corresponds to the optical mode deformation potential. They are related by $d_5 = d'_5 - \zeta d_{5o}/4$. A similar decomposition is used for d_1^5, d_3^5, and d_4.

The calculation of deformation potentials by the present method was tested for Silicon. Our results are found to be in good agreement with the available experimental data and will be given elsewhere. The deformation potential results for GaN are given in Table III. These are essentially predictions since no experimental data or other calculations are known to us for these quantities. We note that for GaN the Γ_{15}^c state is not the lowest conduction band state; that is the Γ_1 state. The latter, however, is only subject to hydrostatic strain shifts. The calculation of these shifts differ in a significant way from the ones reported here which correspond to traceless (i.e., volume preserving) shear strains. The reason for this is that while for a traceless strain the average electrostatic potential remains unshifted, this is not the case when the volume changes. To account for and even properly define it one needs an interface-type calculation between two regions of the material experiencing different hydrostatic strains.[30,31] The determination of these "absolute" deformation potentials will be the subject of future work.

In summary, the full-potential LMTO calculations carried out here for zinc-blende GaN were found to provide groundstate properties (lattice constant, bulk modulus, and its pressure derivative) in excellent agreement with experiment and previous calculations. The same method was used here to calculate the full set of cubic elastic constants. These values along with Martin's transformation method[16] also provide the first *ab initio* determination of the full set of hexagonal elastic constants of wurtzite GaN. We believe these to be more accurate than the only set of experimental values reported today, which were based on a rather intricate analysis of x-ray data on powder samples. The TO-phonon frequency at the zone center was also determined and found to be in close agreement with experimental data and previous calculations of the corresponding phonons in wurtzite GaN. The strain-induced changes in the band struture were determined and the deformation potentials for the Γ, L, and X eigenvalues are reported.

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