

# Predictions of electronic, structural, and elastic properties of cubic InN

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We present theoretical predictions of electronic, structural, and elastic properties of cubic indium nitride in the zinc-blende structure (*c*-InN). Our *ab initio*, self-consistent calculations employed a local density approximation potential and the Bagayoko, Zhao, and Williams implementation of the linear combination of atomic orbitals. The theoretical equilibrium lattice constant is 5.017 Å, the band gap is 0.65 eV, and the bulk modulus is 145 GPa. The band gap is 0.74 eV at an experimental lattice constant of 4.98 Å. © 2004 American Institute of Physics. [DOI: 10.1063/1.1790064]

## I. INTRODUCTION AND MOTIVATIONS

Several review papers<sup>1-4</sup> have discussed the properties and applications of wurtzite and zinc-blende indium nitride (*c*-InN). In particular, the value of the band gap of wurtzite InN (*w*-InN) has recently attracted much interest<sup>3-5</sup> due to seemingly conflicting findings from experimental investigations. The current and potential applications of InN based semiconductor devices certainly warrant a rapid resolution of the unsettled issues relative to these important materials.<sup>1-5</sup> Indeed, light emitting diodes (LEDs), laser diodes (LDs), and photodiodes (PDs), over a wide range of energy, from ultraviolet to infrared wavelengths, are some of these applications of InN based semiconductors. The direct band gaps of high quality wurtzite InN films are reported<sup>3-5</sup> to be from 0.65 to 1 eV, depending on carrier concentration and other sample characteristics. The band gap of cubic InN (*c*-InN) is expected to be in this range or slightly below it. Hence, InN films could be critical for the fabrication of high speed LDs and PDs for optical communication systems.<sup>3</sup> Unlike *w*-InN, the most stable phase of InN in ordinary conditions, much remains to be known about *c*-InN. This situation is partly due to the serious difficulties associated with the growth of *c*-InN.<sup>3,4</sup>

These difficulties are apparent in the work of Yamamoto *et al.*<sup>6</sup> who grew *c*-InN on GaAs and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates. They reported the appearance of *w*-InN when the film thickness was over 0.05  $\mu$ m, and at thicknesses over 0.2  $\mu$ m, the *c*-InN films grown on GaAs were completely covered by hexagonal indium nitride. The films grown on sapphire contained columnar, fibrous structures. Unlike Yamamoto *et al.*<sup>6</sup> who utilized metalorganic vapor-phase epitaxy (MOVPE) Tabata *et al.*,<sup>7</sup> Chandrasekhar *et al.*,<sup>8</sup> and Cimalla *et al.*<sup>9</sup> employed molecular beam epitaxy (MBE) to grow *c*-InN films. These authors reported values of the lattice constant of *c*-InN of 4.97 $\pm$ 0.01, 4.980, and 4.986 Å, respectively. We are unaware of reports of experimental investigations of the electronic and elastic properties of *c*-InN. Hence, an aim of this work is to predict electronic and related properties of *c*-InN, including the band gap.

The need for this work is partly underscored by the disagreement between previous theoretical findings.<sup>10-22</sup> Previous local density approximation (LDA) calculations that em-

ployed the pseudopotential (PP) method produced negative band gaps ranging<sup>10,11,13-15,19</sup> from -0.18 to -0.40 eV. Other LDA calculations,<sup>11,12,16,19</sup> using variations of the linearized augmented plane wave (LAPW),<sup>11,12</sup> linear muffin-tin orbital (LMTO),<sup>16</sup> and the atomic sphere approximation (ASA) (Ref. 19) obtained *c*-InN band gaps of 0.08–0.48 eV. The generalized gradient approximation (GGA),<sup>11,13</sup> within the pseudopotential approach, led to a gap value<sup>13</sup> of -0.55 eV. Self-interaction corrections to LDA, quasiparticle (QP) approaches, and exact exchange calculations reported *c*-InN band gaps of 0.43–1.40 eV as shown in Table I below. The very recent empirical pseudopotential result of Fritsch *et al.*<sup>22</sup> is 0.592 eV for the band gap of *c*-InN. Our focus here is mainly on the LDA results that are very small or negative for the band gap of *c*-InN. This situation constitutes another motivation for this work, besides the lack of experimental data on the electronic and related properties of *c*-InN. Our LDA calculations recently resolved the controversy that was surrounding the band gap of wurtzite InN.<sup>23</sup> In particular, our LDA calculations, within the Bagayoko, Zhao, and Williams (BZW) implementation of the linear combination of atomic orbitals (LCAO) method, obtained a *w*-InN band gap of 0.88 eV, in very good agreement with measurements from a recent series of experimental investigations.<sup>23</sup>

Further, utilizing features of the calculated density of states (DOS), we showed<sup>23</sup> the possibility of obtaining a gap as large as 2 eV if optical absorption is the only measurement technique utilized. Difficulties in precisely determining the band edge, analysis techniques, and related uncertainties explain this assertion. Our work on *w*-InN added to a series of articles according to which it is no longer correct to state that local density approximation woefully underestimates the band gaps of semiconductors. Hence, and in the light of the mostly negative values of the band gap of *c*-InN, there exists a compelling rationale for an implementation of the LDA that does not suffer from an effect<sup>24-26</sup> believed to be mostly responsible of the dismal underestimation of band gaps. Incidentally, the band gap problem was actually a symptom of a more general and unrecognized problem stemming from unoccupied levels or bands that are affected by the effect referenced above and recalled below.

TABLE I. Experimental and theoretical lattice constants ( $a$ , in angstroms) for  $c$ -InN, along with the calculated values of the bulk modulus gigapascal and of the fundamental band gap (eV). Results in the last three columns, for a given row, are from the reference cited in that row.

	Computational Method	$a$ (Å)	$B$ (GPa)	$E_g$ (eV)	
Local Density Approximation (LDA) Potentials	LCAO-BZW (Present work)	5.017	145	+0.65	
		4.98		+0.74	
		4.95	145	-0.36 <sup>a</sup>	
		5.004	140	-0.40 <sup>b</sup>	
	Pseudopotential Method (PP)	4.95	145 <sup>c</sup>		
		4.97 <sup>d</sup>			
		4.932	140	-0.35 <sup>e</sup>	
		4.788	155 <sup>f</sup>		
	Generalized gradient approximation (GGA)	LAPW	4.94	145 <sup>c</sup>	-0.18 <sup>g</sup>
			5.03	138	-0.11 <sup>h</sup>
Full potential LAPW				-0.48 <sup>h</sup>	
				-0.4 <sup>i</sup>	
Full Potential LMTO	4.92	139 <sup>j</sup>			
	Atomic sphere approximation (ASA)			-0.1 <sup>i</sup>	
Generalized gradient approximation (GGA)	PP	5.06	120 <sup>c</sup>	+0.02 and +0.08 <sup>k</sup>	
		5.109	118	-0.55 <sup>b</sup>	
LDA plus self-interaction correction (SIC)		5.05 <sup>d</sup>		+0.43 <sup>a</sup>	
QP Calculation	PP			+0.52 <sup>a</sup>	
QP+SIC	PP			+1.31 <sup>a</sup>	
DFT Exact Exchange				+1.4 <sup>g</sup>	
DFT, SX	ASA			+1.3 <sup>i</sup>	
Estimate of the bulk modulus of zinc-blende indium nitride ( $c$ -InN) using elastic properties of wurtzite InN			137 <sup>l</sup>		
Empirical Pseudopotential Calculations (EMP)				+0.592 <sup>m</sup>	
Experimental: Measured lattice constants		4.97±0.01 <sup>n</sup>			
		4.98 <sup>o</sup>			
		4.986 <sup>p</sup>			

<sup>a</sup>Reference 10.<sup>b</sup>Reference 13.<sup>c</sup>Reference 11.<sup>d</sup>Reference 15.<sup>e</sup>Reference 18.<sup>f</sup>Reference 21.<sup>g</sup>Reference 14.<sup>h</sup>Reference 12.<sup>i</sup>Reference 16.<sup>j</sup>Reference 17.<sup>k</sup>Reference 19.<sup>l</sup>Reference 20.<sup>m</sup>Reference 22.<sup>n</sup>Reference 7.<sup>o</sup>Reference 8.<sup>p</sup>Reference 9.

## II. METHOD AND COMPUTATIONAL DETAILS

We performed zero temperature, nonrelativistic calculations of the electronic and related properties of  $c$ -InN. Our *ab initio*, self-consistent calculations employed the local density approximation potential of Ceperley and Alder<sup>27</sup> as parametrized by Perdew and Zunger.<sup>28</sup> As stated above, we used the LCAO. The feature distinguishing our computational method from the previous investigations noted above consists of our implementation of the BZW procedure. In so doing, we started the calculations for  $c$ -InN with a minimal basis set. We subsequently performed several other self-consistent calculations with larger and larger basis sets. The basis set for any of these calculations was obtained by augmenting the one for the previous calculation with the orbital describing the next excited level of the atomic or ionic species present in the system. The occupied bands of a given calculation are compared to those of the previous. These comparisons, particularly for the first two calculations, often show differences (in numerical values, branching, or curvature). This process continues until the occupied energies

from a calculation are equal, within computational uncertainties, to their corresponding ones from the calculation that follows it. Then, the output of the former calculation provides the physical description of the material under study and the related basis set is dubbed the optimal basis set. According to the Rayleigh theorem,<sup>26</sup> some of the *unoccupied bands* from the latter may be lower than their counterpart from the former.<sup>24-26,29,30</sup>

The above additional lowering is the *basis set* and *variational* effect inherently associated with variational calculations of the Rayleigh-Ritz type. In the iterative process, the use of the wave functions for the occupied states *only* in the construction of the charge density, and hence the potential and the Hamiltonian, ensures the exhaustion of the accounting for the physical interactions when the occupied energies converge vis-a-vis the size of the basis set. As fully explained elsewhere,<sup>24-26,29</sup> however, some unoccupied energies will continue to be lowered as the basis set is increased beyond the optimal one. The sizes of the minimal and optimal basis sets vary vastly with the type of functions in the

TABLE II. Eigenvalues (eV), along high symmetry points, for zinc-blende indium nitride (*c*-InN) as obtained from LDA-BZW calculations for  $a = 5.017 \text{ \AA}$ , the theoretical equilibrium value. The Fermi energy of  $-0.21687 \text{ eV}$  is set to zero in the table.

L	$\Gamma$	X	K
-15.5192	-14.8427	-15.6493	-15.5949
-14.7559	-14.8427	-14.7301	-14.7034
-14.7559	-14.8427	-14.5254	-14.5837
-14.4740	-14.5336	-14.5254	-14.5739
-14.4740	-14.5336	-14.4463	-14.4865
-11.7624	-14.1793	-11.3085	-11.2078
-5.5713	0.0000	-4.7495	-4.5900
-0.8335	0.0000	-2.2093	-3.3631
-0.8335	0.0000	-2.2093	-1.7848
4.0316	0.6536	4.1816	5.6110
8.4339	9.7615	6.8978	7.1493
10.6892	9.7615	11.8922	10.5553
10.6892	9.7615	11.8922	11.6130

atomic orbitals (i.e., exponential, Gaussian, plane wave functions) and with other features of the calculations (i.e., pseudopotential, LAPW, etc). As described above, the BZW method is applicable in most computations that utilize the LCAO formalism. The LCAO program package we employed in this work was developed many years<sup>31-33</sup> before the introduction of the BZW method in 1998. We provide below computational details germane to a replication of our calculations.

Zinc-blende InN is a member of the III-V family. The atomic wave functions of the ionic states of  $\text{In}^{1+}$  and  $\text{N}^{1-}$  were obtained from self-consistent *ab initio* calculations. The radial parts of the atomic wave functions were expanded in terms of Gaussian functions. A set of even-tempered Gaussian exponents was employed for In with a minimum of 0.1400 and a maximum of  $0.2300 \times 10^6$ , with 16 Gaussian functions for the *s* and *p* states and 14 for the *d* states of  $\text{In}^{1+}$ . The two largest exponents were not included in the description of the *d* state. Similarly, a set of even-tempered Gaussian exponents was utilized to describe  $\text{N}^{1-}$ , with a minimum of 0.1242 and a maximum of  $0.1365 \times 10^5$ . Both the *s* and *p*

TABLE III. Eigenvalues (eV), along high symmetry points, for zinc-blende indium nitride (*c*-InN), as obtained from LDA-BZW calculation for  $a = 4.98 \text{ \AA}$ . The Fermi energy  $-0.21658 \text{ eV}$  is set to zero the table.

L	$\Gamma$	X	K
-15.5977	-14.8586	-15.7269	-15.6720
-14.7642	-14.8586	-14.7370	-14.7084
-14.7642	-14.8586	-14.5160	-14.5781
-14.4583	-14.5212	-14.5160	-14.5685
-14.4583	-14.5212	-14.4279	-14.4714
-11.7856	-14.3473	-11.3252	-11.2093
-5.7063	0.0000	-4.8350	-4.6807
-0.8675	0.0000	-2.2907	-3.4730
-0.8675	0.0000	-2.2907	-1.8515
4.1748	0.7383	4.2140	5.6870
8.5382	9.9148	7.1020	7.3237
10.8738	9.9148	12.1018	10.7467
10.8738	9.9148	12.1018	11.8177

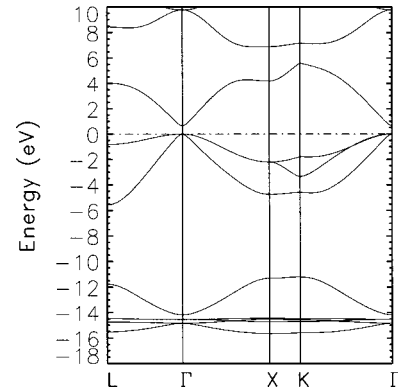


FIG. 1. Calculated LDA-BZW band structure of zinc-blende Indium Nitride (*c*-InN) at the theoretical equilibrium lattice constant of  $5.017 \text{ \AA}$ , as obtained with BZW optimal basis set. The Fermi level ( $-0.21687 \text{ eV}$ ) is set to zero in the figure.

functions were expanded in terms of 13 Gaussian orbitals. The minimal basis set comprised atomic orbitals representing  $\text{In}^{1+}$  ( $1s2s2p3s3p3d4s4p4d5s5p$ ) and  $\text{N}^{1-}$  ( $1s2s2p$ ). A mesh of  $28k$  points in the irreducible Brillouin zone, with proper weights, was used in the self-consistent iterations. The computational error for the valence charge was about  $-0.00144979$  for 36 electrons. The self-consistent potentials converged to a difference around  $10^{-5}$  after about 60 iterations.

### III. RESULTS AND DISCUSSIONS

Table I shows our calculated, theoretical equilibrium band gap of  $0.65 \text{ eV}$ , at a lattice constant of  $5.017 \text{ \AA}$ , and the value of  $0.74 \text{ eV}$  at an experimental lattice constant of  $4.98 \text{ \AA}$ . Tables II and III contain the calculated energies, at some high symmetry points in the Brillouin zone, for the two lattice constants given above. Figures 1–3 exhibit the energy bands, for the theoretical equilibrium lattice constant ( $5.017 \text{ \AA}$ ), and the related total (DOS) and partial (pDOS) densities of states. The curve of the total energy versus the lattice constant is shown in Fig. 4.

The lack of experimental data, except for the lattice constant, precludes an extensive discussion of these results. Our predicted equilibrium lattice constant is within 0.6% from

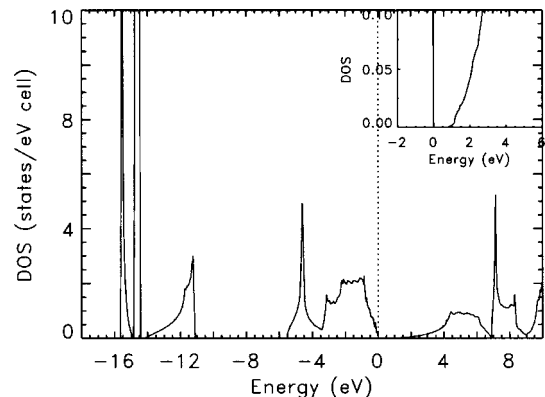


FIG. 2. Total DOS for zinc-blende indium nitride (*c*-InN) as obtained with the bands shown in Fig. 1. The inset illustrates our definition of a “practical band gap.”

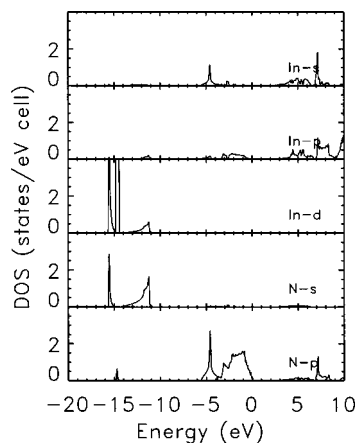


FIG. 3. pDOS for zinc-blende indium nitride (*c*-InN) as obtained with the bands shown in Fig. 1. The dominance of nitrogen *p* at the top of the valence band is obvious in this graph.

the latest experimental one of 4.986 Å. Our calculated bulk modulus of 145 GPa is close to the results from some other LDA calculations<sup>10,11</sup> and disagrees with findings around 120 GPa from GGA calculation<sup>11,13</sup> as shown in Table I. The tables for the calculated energies are expected to provide useful comparisons for future experimental investigations. Our calculated LDA-BZW band structure is drastically different from the findings of most of the previous calculations—as far as the unoccupied bands are concerned. The large differences between our calculated band gaps and previous LDA results in Table I are a direct consequence of the differences between the respective *unoccupied* bands.

The empirical pseudopotential (EMP) result<sup>22</sup> of 0.592 eV is relatively close to our findings of 0.65 and 0.74 eV. We cannot draw much fundamental significance from this fact, however, given that this EMP result was obtained using model potential parameters whose derivation entailed fitting to data that included a band gap of 0.59 eV. For the purposes of application, however, this closeness portends much importance. Indeed, we expect potential parameters derived from fitting to our data to lend themselves to credible and practical descriptions of electronic, optical, elastic, and structural properties of materials. This assertion is partly supported by the versatility and relative ease of empirical pseudopotential calculations.

As in the case of *w*-InN,<sup>23</sup> our results do not show any indication of an overestimation of the *p*-*d* repulsion by LDA potentials. This overestimation was believed<sup>10</sup> to be the source of the very small or negative band gaps by pushing the top of the valence band, dominated by *p* states, to higher energies. According to our findings, it is rather the extra lowering of the bottom of the conduction band that produces LDA band gaps that are negative or very small<sup>23,25</sup> if LCAO type computations do not utilize the BZW approach to avoid it while ensuring the adequacy (or convergence) of the basis set for the description of occupied states. In fact, the basic derivation of the ground state theory that is the original density functional theory<sup>34,35</sup> implicitly suggests such an approach, notwithstanding the need to account for the redistribution of electrons in molecular to solid environments with judicious polarization and diffuse orbitals.<sup>36</sup>

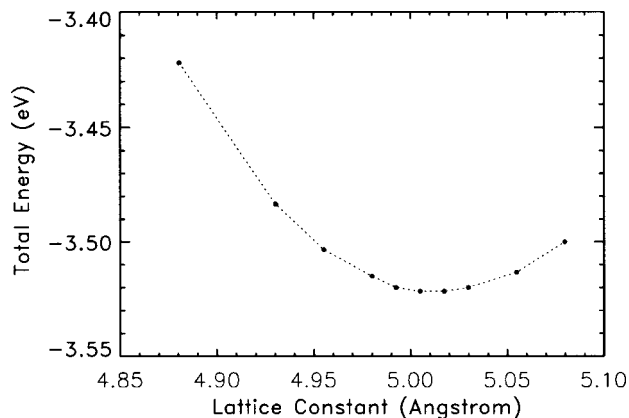


FIG. 4. Total energy of (*c*-InN) vs the lattice constant. The total energy at the equilibrium lattice constant of 5.017 Å is 1949.4215 eV.

As per their definition, effective masses provide a measure of the quality (i.e., curvature) of band structures. Our LDA-BZW calculations found electron effective masses, at the bottom of the conduction band, of  $0.065m_0$ ,  $0.066m_0$ , and  $0.066m_0$  in the  $\Gamma$ -L,  $\Gamma$ -X, and  $\Gamma$ -K directions, respectively, for the equilibrium lattice constant. For a lattice constant of 4.98 Å, the corresponding effective masses for the electrons are  $0.076m_0$ ,  $0.073m_0$ , and  $0.073m_0$  in the  $\Gamma$ -L,  $\Gamma$ -X, and  $\Gamma$ -K directions, respectively. Our calculated, equilibrium, electron effective masses are very close to the  $0.066m_0$  from the EMP calculations of Fritsch, Schmidt, and Grundmann.<sup>22</sup> This agreement supports our comment above relative to the potential use of EMP calculations when the potential parameters are derived in part by fitting to LDA-BZW results.

#### IV. CONCLUSION

In lieu of a conclusion, we contend that our *ab initio*, self-consistent LDA-BZW calculations have predicted electronic, structural, and elastic properties of cubic InN (*c*-InN) in the zinc-blende structure. It is hoped that experimental investigations will follow in the near future. It emerges from this work that theoretical efforts should be directed to the determination of actual limitations of LDA and of other approaches as opposed to echoing the chorus now known to be untenable, as per the physical interactions, and that ascribes to LDA a woeful underestimation of band gaps that is, as per the Rayleigh theorem, straightforwardly a consequence of a basis set and variational effect.

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