

First-principles prediction of structure, energetics, formation enthalpy, elastic constants, polarization, and piezoelectric constants of AlN, GaN, and InN: Comparison of local and gradient-corrected density-functional theory

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A number of diverse bulk properties of the zinc-blende and wurtzite III-V nitrides AlN, GaN, and InN, are predicted from first principles within density-functional theory using the plane-wave ultrasoft pseudopotential method, within both the local density approximation (LDA) and generalized gradient approximation (GGA) to the exchange-correlation functional. Besides structure and cohesion, we study formation enthalpies (a key ingredient in predicting defect solubilities and surface stability), spontaneous polarizations and piezoelectric constants (central parameters for nanostructure modeling), and elastic constants. Our study bears out the relative merits of the two density-functional approaches in describing diverse properties of the III-V nitrides (and of the parent species N₂, Al, Ga, and In). None of the two schemes gives entirely successful results. However, the GGA associated with the multiprojector ultrasoft pseudopotential method slightly outperforms the LDA overall as to lattice parameters, cohesive energies, and formation enthalpies of wurtzite nitrides. This is relevant to the study of properties such as polarization, vibrational frequencies, elastic constants, nonstoichiometric substitution, and absorption. A major exception is the formation enthalpy of InN, which is underestimated by the GGA (~ 0 vs -0.2 eV).

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I. INTRODUCTION AND METHOD

The III-V nitride semiconductors AlN, GaN, and InN and their alloys are by now well established as a strategic material system¹ for applications in high-frequency optoelectronics (light-emitting diodes and lasers), and high-power electronics (e.g., high-electron-mobility transistors). Most of their potential in these fields is due, respectively, to the large tunability of band gaps with alloy composition (in principle, 1.9 to 6.2 eV), and to their high peak and saturation drift velocity, coupled with polarization-induced effects allowing for the realization of high-density low-dimensional charge gases.²

Nitride physics posed a number of puzzles to (and profited considerably from) *ab initio* studies of various properties and subsystems, ranging from surfaces³ to defects,⁴ and polarization-related properties.⁵ Heralding the unusual nature of these materials, the standard study of the structural properties of bulk materials gave unexpected results in early studies. For instance, since some of the earliest papers,⁶ quite unusually for III-V semiconductors, the semicore 3*d* electrons of Ga were found to behave as valence electrons and to be essential to describe accurately the structural properties.

A major source of uncertainty, both technical and ideological in nature, in density-functional theory (DFT) calculations is the choice of the exchange-correlation functional. While the local density approximation (LDA) is used most commonly, the generalized gradient approximation (GGA) has become a close competitor in recent years. In this work, we study the effects of using either LDA or GGA in the

prediction of the properties of III-V nitrides. Such a comparison has been attempted only once previously for III-V nitrides,⁷ and restricted to structural and cohesive properties.⁸

In this paper, we add a number of aspects to the theme of GGA versus LDA comparison for the nitrides. *First*, we use ultrasoft pseudopotentials, which should in principle⁹ improve over norm-conserving potentials.⁷ *Second*, we calculate formation enthalpies, which are a cornerstone for predictions on nonstoichiometric systems relevant to surface reconstruction and impurity solubility. This calculation requires the study of the metallic phases of Al, Ga, and In, the N₂ molecule, and solid nitrogen (a molecular solid comprising N₂ dimers on an hcp lattice). *Third*, we evaluate the spontaneous polarization and the piezoelectric constants of the wurtzite phase¹⁰ in both the GGA and LDA. We find that these quantities are moderately affected by the choice of exchange correlation, unlike most others properties. *Fourth*, we evaluate a subset of the elastic constants in LDA and GGA.

The calculations have been done using VASP (Vienna *ab initio* simulation package),¹¹ which implements the DFT scheme within both the LDA and GGA approximations: we adopted the well established Perdew-Wang (PW91) version of the GGA¹² and the Ceperley-Alder LDA.¹³ Ultrasoft pseudopotentials⁹ describe the electron-ion interaction. As usual, the potentials provided with VASP are generated for the free atom using the appropriate (LDA or GGA) functional. The pseudopotentials for Ga and In include, respectively, the semicore 3*d* and 4*d* states in the valence. A plane wave basis is used to expand the wave functions. We use a

TABLE I. Bond length, vibrational frequency, and binding energy (not including zero-point energy) of the N₂ dimer.

	d (Å)	ω (THz)	E_b (eV)
LDA	1.107	464.3	-11.332
GGA	1.113	442.8	-10.558
Experiment ^a	1.10	444.8	-9.9

^aReference 7.

cutoff of 350 eV, which is sufficient to fully converge all properties of relevance. For k -space summation, we use at least a Monkhorst-Pack (888) grid, except for the N₂ molecule. Lattice constants and internal parameters are calculated using standard total energy calculations. Polarizations and related quantities are obtained using the Berry-phase approach¹⁴ as in previous work.¹⁰ The elastic constants are calculated numerically as derivatives of the stress tensor, the stress values being taken at strains of about $\pm 1\%$ along the c and a axis, for C_{33} and C_{31} , respectively. Cohesive energies are calculated relative to spin-polarized free atoms. The formation enthalpies ΔH_{XN} per atom pair of the XN crystals are calculated as

$$\Delta H_{XN} = E_{XN} - E_X - E_N, \quad (1)$$

where E_{XN} is the total energy per atom pair of the compound XN, E_X the energy per atom of bulk $X = \text{Al, Ga, and In}$, and E_N is the energy per N atom in the N₂ dimer or the condensed N₂ phase. We compare our results for the structure of the nitrides mostly with the LDA and GGA calculations by Stampfl and van de Walle.⁷ Many more theoretical data on structure are collected in Ref. 7.

II. PARENT SPECIES

A. Nitrogen: Molecule and solid

The nitrogen dimer is studied in artificial periodic conditions in a cubic box of side 10 Å, using the Γ point for k summation. The results, listed in Table I, agree well with other LDA and GGA calculations. GGA shows an overall better agreement with experiment. The binding energy is evaluated including the spin-polarization energy of the N atom (-2.89 eV), calculated with a local-spin-density all-electron scalar-relativistic atomic code.¹⁵ Here, and below, we neglect the difference of spin-polarization energy in GGA and LDA. We checked that this causes an error per atom in the cohesive energy, of at most 10 meV (40 meV for N₂).

TABLE II. Structural parameters and binding energy per molecule (not including zero-point energy) of hexagonal solid N₂.

	a (Å)	c/a	E_b (eV)
LDA (present)	4.0205	1.3311	-11.660
GGA (present)	4.0633	1.7929	-10.701
Experiment ^a	4.039	1.6514	

^aReference 16.

TABLE III. Lattice constant, binding energy, and bulk modulus of bulk fcc Al.

	a (Å)	E_b (eV)	B (Mbar)
LDA (present)	3.9809	-4.064	0.766
GGA (present)	4.0491	-3.561	0.689
Experiment ^a	4.05	-3.39	0.773

^aReference 18.

Solid nitrogen is a condensate of N₂ molecules. We consider the stable phase, with vertically oriented N₂ molecules centered at the lattice points of a close packed hexagonal lattice. The (888) grid is used for k -space summation. We compare our results with experimental data from Ref. 16 in Table II. From the data in Tables I and II, the binding energy per molecule in the condensed phase is 0.328 eV in the LDA and 0.143 eV in the GGA. While performing well with respect to the in-plane lattice constant (about $\pm 0.5\%$ relative deviation), both functionals fail to some extent with the axial lattice parameter: LDA underestimates it strongly ($\sim 20\%$) and GGA overestimates it ($\sim 9\%$). The vertical center-to-center intermolecular distances are 3.33 Å experimentally, 3.64 Å in GGA, and 2.68 Å in LDA. This system is indeed a severe test for both functionals because of its weak dipolar binding. GGA performs slightly better, as expected. The binding of the N₂ system, already extremely large in reality, is overestimated appreciably in both approaches.

Our calculated zero-point energies for N₂ are 0.153 eV in the LDA, and 0.146 in the GGA. This reduces the binding of N₂, and accordingly makes the formation enthalpies of the nitrides more negative by about 0.07 eV in both cases. In the tables below, we will report the enthalpies *without* this additional energy. (We assume, as plausible, that the zero-point energy is the same for free and bound N₂ molecules.)

B. Bulk Al, Ga, and In

Metallic Al, Ga, and In are a necessary ingredient to calculate formation enthalpies. Al is a good free-electron metal, and has fcc structure. Ga is a mixed-bonding marginal metal (see, e.g., Ref. 17). At ambient conditions, its stable phase is a dimerized structure known as α -Ga, a face-centered orthorhombic lattice with crystallographic vectors $\mathbf{a}_1 = a\hat{x}$, $\mathbf{a}_2 = \frac{1}{2}(b\hat{y} + c\hat{z})$, $\mathbf{a}_3 = \frac{1}{2}(-b\hat{y} + c\hat{z})$ and eight atoms per primitive cell, whose positions are defined by two additional internal parameters u and v .^{16,17} Indium crystallizes in the

TABLE IV. Lattice constant, binding energy, axial ratios, and internal parameter (units of c) of α -Ga.

	a (Å)	b/a	c/a	u	v	E_b (eV)
LDA (present)	4.4365	0.9985	1.6856	0.0816	0.1577	-3.484
LDA ^a	4.377	0.994	1.688	0.0803	0.1567	
GGA (present)	4.5962	0.9917	1.6961	0.0834	0.1559	-2.796
Experiment ^a	4.51	1.0013	1.695	0.0785	0.1525	

^aReference 17.

TABLE V. Lattice constant, axial ratio, and binding energy of bulk In.

	a (Å)	c/a	E_b (eV)
LDA (present)	3.1861	1.5348	-3.116
GGA (present)	3.2958	1.5448	-2.470
Experiment ^a	3.244	1.5222	

^aReference 16.

monatomic body-centered tetragonal lattice, with lattice constants a and c , and primitive vectors $\mathbf{a}_1 = a\hat{\mathbf{x}}, \mathbf{a}_2 = a\hat{\mathbf{y}}, \mathbf{a}_3 = \frac{1}{2}(a\hat{\mathbf{x}} + a\hat{\mathbf{y}} + c\hat{\mathbf{z}})$.

We report our results for Al in Table III, for Ga in Table IV, and for In in Table V. In these calculations we use a cutoff of 350 eV, an (888) k -space mesh for Al and In, and a (12 12 12) mesh for Ga. The cohesive energy includes the atomic spin-polarization energy (-0.136 eV for Al, -0.134 eV for Ga, and -0.117 eV for In). The GGA improves appreciably the lattice constant and binding energy of Al. For Ga, both approaches are off by about the same amount in opposite directions for a . In both cases, axial ratios and internal parameters are excellent. Our LDA results are improved somewhat over those of Ref. 17, presumably because of the explicit treatment of $3d$ electrons. For In, LDA and GGA are again off the mark by equal and opposite amounts for a . The LDA axial ratio is slightly better than that from the GGA. In short, the usual trend is obtained for the expanded and softer lattice as produced by GGA compared to LDA. If one is forced to choose, GGA generally performs better, especially in terms of cohesive energies. In any case, the deviations typically are below $\pm 1\%$, so both approaches are quite legitimate.

III. THE NITRIDES

Binary III-V nitrides occur in nature in the wurtzite structure. Zinc-blende nitrides have a slightly higher energy. It is possible to grow epitaxially, e.g., zinc-blende GaN on cubic substrates. We first analyze zinc-blende (Sec. III A), then wurtzite (Sec. III B). Our results are compared with those of Ref. 7, where numerous other theoretical values are provided.

TABLE VI. Lattice constant, binding energy, and formation enthalpy ΔH of zinc-blende AlN.

	a (Å)	E_b (eV)	ΔH (eV)
LDA (present)	4.332	-13.347	-3.449
LDA ^a	4.310	-13.242	
GGA (present)	4.390	-11.907	-2.975
GGA ^a	4.394	-11.361	
Experiment ^b	4.37		

^aReference 7.^bReference 7.TABLE VII. Lattice constant, binding energy, and formation enthalpy ΔH of zinc-blende GaN.

	a (Å)	E_b (eV)	ΔH (eV)
LDA (present)	4.446	-10.982	-1.689
LDA ^a	4.518	-10.179	
LDA ^b	4.466	-10.880	
GGA (present)	4.538	-9.249	-1.102
GGA ^a	4.590	-8.253	
Experiment ^c	4.519		

^aReference 7.^bReference 6.^cReference 7.

A. Zinc-blende AlN, GaN, InN

For zinc-blende nitrides we used the usual 350 eV cutoff and (888) k grid. To estimate the cohesive energy, we use the atomic spin polarizations indicated previously. Our results are reported in Tables VI, VII, and VIII, for AlN, GaN, and InN, respectively. The results confirm the by now usual behavior of GGA versus LDA, consisting of a softening of the lattice, which improves lattice constant and binding energy, and worsens slightly the bulk modulus. Comparing the cohesive energy with that of the wurtzite phase as discussed below, we find that zinc blende is disfavored over wurtzite.

B. Wurtzite AlN, GaN, InN

Wurtzite is a hexagonal close-packed lattice, comprising vertically oriented X-N units at the lattice sites. The basal lattice parameter is a , the axial lattice parameter is c . The interatomic distance in the basic unit is described by an internal parameter u expressed in units of the axial ratio c/a . The ideal (i.e., for touching hard spheres) values of the axial ratio and internal parameter are, respectively, $c/a = \sqrt{8/3}$ and $u = 3/8$. The crystallographic vectors of wurtzite are $\mathbf{a} = a(1/2, \sqrt{3}/2, 0)$, $\mathbf{b} = a(1/2, -\sqrt{3}/2, 0)$, and $\mathbf{c} = a(0, 0, c/a)$. The Cartesian coordinates of the basis atoms are $(0, 0, 0)$, $(0, 0, uc)$, $a(1/2, \sqrt{3}/6, c/2a)$, and $a(1/2, \sqrt{3}/6, [u + 1/2]c/a)$.

Our results are reported in Tables IX, X, and XI, for AlN, GaN, and InN, respectively. For comparison, experimental data, and the results of Ref. 7 are also listed. As to structure, in all cases both the axial ratio and the internal parameter are nonideal. Deviation from ideality increases from GaN to InN

TABLE VIII. Lattice constant, binding energy, and formation enthalpy ΔH of zinc-blende InN.

	a (Å)	E_b (eV)	ΔH (eV)
LDA (present)	4.964	-9.232	-0.282
LDA ^a	5.004	-8.676	
GGA (present)	5.067	-7.680	0.140
GGA ^a	5.109	-6.855	
Experiment ^b	4.98		

^aReference 7.^bReference 7.

TABLE IX. Lattice constant, axial ratio, internal parameter, and formation enthalpy of wurtzite AlN.

	a (Å)	c/a	u	E_b (eV)	ΔH (eV)
LDA (present)	3.0698	1.5995	0.3821	-13.536	-3.642
LDA ^a	3.057	1.617	0.3802	-13.286	
GGA (present)	3.1095	1.6060	0.3819	-12.071	-3.142
GGA ^a	3.113	1.6193	0.3798	-11.403	
Experiment ^b	3.1106	1.6008	0.3821 ^c	-11.669 ^a	-3.13 ^d

^aReference 7.^bReference 20.^cReference 21.^dReference 19.

to AlN. As usual GGA improves considerably the binding energy, and occasionally the lattice constant, at the cost of a slight overestimate of the axial ratio. The internal parameter u (alias the axial bond length) is well reproduced in all the various combination of materials and approximations. The experimental values of the lattice mismatch between the nitrides are well reproduced both by LDA and GGA. The maximum deviation from experimental mismatch is 0.3% for AlN/GaN, 1% for GaN/InN, and 1.3% for AlN/InN.

The GGA calculations produce lattice constants and internal parameters with maximum deviations from experiment below 0.3% for AlN, 0.9% for GaN, and 1.7% for InN (+1.3% for a and +1.7% for c). In this respect, these are probably the best DFT pseudopotential results so far for these materials. The improvement over previous GGA results is to be attributed to the use of ultrasoft, multiprojector pseudopotentials.⁹ By the same token, it is quite likely that all-electron calculations using the same GGA parametrization may improve the agreement further, especially for InN.

Calculated cohesive energies generally overestimate, as usual, the experimental value. GGA corrects in part the LDA overbinding, and exhibits better agreement. Comparing the cohesive energies of the zinc-blende and wurtzite phases, as already mentioned, we find wurtzite to be energetically favored over zinc blende. The predicted difference per atom pair between the two phases is 189 meV (LDA) and 164 meV (GGA) for AlN, 17 meV (LDA) and 16 meV (GGA) for GaN, and 17 meV (LDA) and 15 meV (GGA) for InN.

Good results are also achieved for the formation enthalpies. The values in the tables, referred to an atom pair, were

TABLE X. Lattice constant, axial ratio, internal parameter, and formation enthalpy of wurtzite GaN.

	a (Å)	c/a	u	E (eV)	ΔH (eV)
LDA (present)	3.131	1.6301	0.3768	-10.999	-1.685
LDA ^a	3.193	1.634	0.376	-10.187	
GGA (present)	3.1986	1.6339	0.3772	-9.265	-1.118
GGA ^a	3.245	1.632	0.3762	-8.265	
Experiment ^b	3.1890	1.6263	0.377	-9.058 ^a	-1.08 ^c

^aReference 7.^bReference 21.^cReference 19.

TABLE XI. Lattice constant, axial ratio, internal parameter, and formation enthalpy of wurtzite InN.

	a (Å)	c/a	u	E_b (eV)	ΔH (eV)
LDA (present)	3.509	1.6121	0.3791	-9.249	-0.303
LDA ^a	3.544	1.626	0.377	-8.694	
GGA (present)	3.5848	1.6180	0.37929	-7.695	0.125
GGA ^a	3.614	1.628	0.377	-6.872	
Experiment ^b	3.538	1.6119		-7.970 ^c	-0.21 ^d

^aReference 7.^bReference 22.^cReference 7.^dReference 19.

obtained using the energy per N atom in the solid-N₂ phase. If the N₂ molecule is assumed as the reference instead, as is plausible in high-temperature growth techniques, the formation enthalpy becomes more negative by one-half of the binding energy of solid N₂—that is, 0.164 eV and 0.071 eV, respectively, must be subtracted to the LDA and GGA values in the tables. To account for the zero-point motion of N₂, half the zero-point energy of N₂ (≈ 0.07 eV) should be subtracted from the values in the tables.

The calculated GGA formation enthalpies are in general agreement with experiment for AlN and GaN. For InN, GGA overcorrects the LDA overbinding and gives a positive value. Using the free N₂ molecule as the N reservoir, and including the zero-point energy, the GGA formation enthalpy of InN improves slightly, becoming essentially zero (in fact, barely negative but at the limit of our numerical accuracy). This problem is probably due to InN itself, and only marginally to the In or N parent phases. Indeed, quite unusually, even the calculated cohesive energy underestimates the experimental value. This was observed also in the pseudopotential study of Ref. 7 and in unpublished full-potential linearized augmented plane wave calculations.²⁴ We are not aware of other formation enthalpy calculations for InN. The issue is open to further investigation.

In Table XII, we report for each of the nitrides the spontaneous polarization in the equilibrium structure, the dynamical effective charges, the piezoelectric constants, and a subset of elastic constants relevant to symmetry-conserving strains. The reason for collecting these data in one table is that they provide an almost self-contained set of input data for the simulation of nanostructures made of wurtzite nitrides. The only additional data needed are the static dielectric constants, which were reported elsewhere.²⁵ In the last column we report the proper piezoelectric constant e_{31}^p . As discussed recently,^{26,27} this value should be compared with experiments involving current flow across the sample, whereas the “improper” constant e_{31} is relevant to systems in depolarizing fields such as nitride nanostructures.⁵

It is not infrequent to hear the incorrect statement that the spontaneous polarization is nonvanishing in wurtzite because of structural nonideality. In actuality, a nonvanishing polarization is allowed on symmetry grounds²⁸ in the *ideal* wurtzite structure as well. Indeed, we find that the calculated Berry-phase polarization in the ideal structure is

TABLE XII. Spontaneous polarization (C/m^2), piezoelectric constants (C/m^2), dynamical charges, elastic constants (GPa), and the ratio $R = -2C_{31}/C_{33}$ (see text) of wurtzite nitrides, as obtained in the LDA and GGA approximation. The last column reports the proper e_{31} piezoelectric constant.

	P	Z^*	e_{33}	e_{31}	C_{33}	C_{31}	R	e_{31}^p
AlN								
LDA	-0.100	2.652	1.80	-0.64	384	111	-0.578	-0.74
LDA ^a					373	108	-0.579	
GGA	-0.090	2.653	1.50	-0.53	377	94	-0.499	-0.62
GaN								
LDA	-0.032	2.51	0.86	-0.44	415	83	-0.400	-0.47
LDA ^a					405	103	-0.508	
GGA	-0.034	2.67	0.67	-0.34	354	68	-0.384	-0.37
InN								
LDA	-0.041	3.045	1.09	-0.52	233	88	-0.755	-0.56
LDA ^a					224	92	-0.821	
GGA	-0.042	3.105	0.81	-0.41	205	70	-0.683	-0.45

^aReference 23.

-0.032 C/m^2 in AlN, -0.018 C/m^2 in GaN, and -0.017 C/m^2 in InN. These values are smaller (by a factor of 2 to 3) than the actual ones for nonideal structures (Table XII). This confirms the intuitive idea that nonideality, and especially changes in u , can increase polarization substantially, and indicates that an accurate determination of the structure is mandatory to obtain reliable polarization values.²⁷

Theoretical predictions on polarization properties were shown to compare quite favorably with experimental evidences in various papers (see, e.g., Refs. 2, 5, and 29). It should be noted, however, that the link between polarization and the observed quantities, typically optical shifts or densities of mobile charge, is rather indirect and affected by uncertainties due to issues of nanostructure design, material quality, and reverse modeling. Thus, comparison with experiment does not yet allow a clear-cut evaluation of the performance of LDA versus GGA. The recently discovered³⁰ nonlinear behavior of the polarization in nitride alloys is an additional source of uncertainty.

The LDA elastic constants are in fair agreement with those of Wright.²³ The GGA constants are smaller, as is to be expected given the general tendency of GGA to produce a softer lattice. According to elasticity theory, the axial strain induced in wurtzite by an in-plane (e.g., epitaxial) strain ϵ_1 is $\epsilon_3 = -2 \epsilon_1 C_{31}/C_{33} = R \epsilon_1$. The quantity R is thus relevant to epitaxial nitride systems, and it is reported in Table XII. Several experimental data for the elastic constants and R are

compiled in Ref. 23. The considerable spread of those data does not allow a definite conclusion about whether GGA produces a systematically improved agreement with experiment over LDA in this respect.

IV. SUMMARY

In conclusion, the present calculations suggest an overall improvement of the predicted properties of wurtzite III-V nitrides through the GGA compared to the LDA. In particular, in the former approach, the structural parameters exhibit deviations from experiment below 0.3% for AlN, 0.9% for GaN, and 1.7% for InN. GGA cohesive energies and formation enthalpies are in fair to excellent agreement with experiment, and improve over LDA values; the only clear-cut GGA failure is the formation enthalpy of InN. Elastic properties follow the expected trends of GGA versus LDA behavior; due to uncertainties in the experimental data, comparison with experiment does not provide definite support to one or the other approximation. Polarization properties are moderately sensitive to the exchange-correlation functional, as long as the latter predicts the correct structure (especially, the correct internal parameter u). For these properties too, comparison with experiment is indirect and affected by many sources of uncertainty, and does not support one or the other approach. Concerning the cohesion and structure of the parent species (N_2 , Ga, Al, In), only in the case of condensed N_2 do we find major discrepancies with experiment.

In light of the present results, our conclusion is that the choice of either the GGA or LDA will depend on the specific problem being addressed. The GGA outperforms slightly the LDA overall with respect to cohesive energies and formation enthalpies of wurtzite nitrides (except for InN), and usually also as to lattice and internal parameters in comparison with recent accurate experiments. We thus presume that the GGA might be preferred in density-functional studies of III-V nitrides for quantities such as macroscopic polarization, piezoelectricity, lattice dynamics, and possibly elastic constants, which depend critically on the accuracy of the equilibrium structure.

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