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 zincblende 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 LDA (local density) and GGA (generalized gradient) approximations 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 N$_2$, Al, Ga, and In), and leads us to conclude that the GGA approximation, associated with high-accuracy techniques such as multiprojector ultrasoft pseudopotentials or modern all-electron methods, is to be preferred in the study of III-V nitrides.

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 system for applications in high-frequency optoelectronics (LED and LASER), and high-power electronics (e.g. HEMTs). 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.

Nitrides physics posed a number of puzzles to (and profited considerably from) ab initio studies of various properties and subsystems, ranging from surfaces to defects and polarization-related properties. Herding the unusual nature of these materials, the standard study of the structural properties of bulk materials was a source of surprises in early studies. For instance, since some of the earliest papers 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 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 LDA is used most commonly, the generalized gradient approximation, or 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. Similar calculations have been performed only once previously, and were concerned with structural and cohesive properties. In this paper, we add several new aspects to this theme. First, we use ultrasoft pseudopotentials, which should in principle improve over norm-conserving potentials. Second, we carefully calculate formation enthalpies, which are the cornerstone of predictions on non-stoichiometric systems relevant to surface reconstruction and impurity solubility. This calculation requires us to study the metallic phases of Al, Ga, and In, the N$_2$ molecule, and solid nitrogen (a molecular solid comprising N$_2$ dimers on an hcp lattice). Third, we evaluate the spontaneous polarization and the piezoelectric constants of the wurtzite phase 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), which implements the DFT scheme within both the LDA and GGA approximations: we adopted the well established PW91 version of the GGA and Ceperley-Alder LDA. Ultrsoft pseudopotentials 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 cut off 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 N$_2$ molecule. Lattice constants and internal parameters are calculated using standard total energy calculations. Polarizations are obtained using the Berry phase approach, as in previous work. Cohesive energies are calculated relative to spin-polarized free
atoms. The formation enthalpies $\Delta H_{\text{XN}}$ per atom pair of the XN crystals are calculated as

$$\Delta H_{\text{XN}} = E_{\text{XN}} - E_{\text{X}} - E_{\text{N}},$$  \hspace{1cm} (1)$$

where $E_{\text{XN}}$ is the total energy per atom pair of the compound XN, $E_{\text{X}}$ the energy per atom of bulk $\text{X} = \text{Al, Ga, and In}$, and $E_{\text{N}}$ is the energy per N atom in the $\text{N}_2$ dimer or the condensed $\text{N}_2$ phase.

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 $\Gamma$ 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 functional. The GGA performs slightly better, as expected. The binding energy is obtained of 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 ±1%, so both approaches are quite legitimate.

III. THE NITRIDES

Binary III-V nitrides occur in nature in the wurtzite structure (the $\beta$ phase). Zinc-blende nitrides (the $\alpha$ phase) have a slightly higher energy. It is possible to grow epitaxially, e.g., $\alpha$-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. [1], where numerous other theoretical values are provided.

A. Zinc-blende $\text{AlN, GaN, InN}$

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 LDA results improve somewhat over those of Ref. 15, 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 $\alpha$. The LDA axial ratio is slightly better than GGA’s. In short, the usual trend is obtained of expanded and softer lattice as produced by GGA compared to LDA. If one is forced to choose, LDA generally performs better, especially in terms of cohesive energies. In any case, the deviations typically are below ±1%, so both approaches are quite legitimate.

B. Wurtzite $\text{AlN, GaN, InN}$

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 packed hard spheres) values of the axial ratio and internal parameter are respectively...
energy of solid-N

sumed as reference instead, one half of the binding energy is calculated at the cost of a slight overestimate of the axial ratio. The present GGA calculations improve considerably lattice constant and binding energy, 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 present 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. By the same token, it is quite likely that all-electron calculations using the same GGA parameterization may improve the agreement further, especially for InN.

Calculated cohesive energies 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 zincblende. 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, 17 meV (LDA) and 15 meV (GGA) for InN.

Good results are also achieved for the formation enthalpies. These were obtained using the energy per N atom in the solid-N$_2$ phase: if the N$_2$ molecule is assumed as reference instead, one half of the binding energy of solid-N$_2$ (i.e. 0.164 eV in LDA, and 0.071 eV in GGA) must be added to the values in the Tables. The reported values are referred to an atom pair. The available formation enthalpy measurements for the nitrides are not very recent and their spread is considerable (this is presumably also the case for cohesive energies, which are measured as heats of vaporization). 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. This problem is due to InN itself, and not to In or N parent phases: indeed, quite unusually, the calculated cohesive energy *underestimates* the experimental value. We are not aware of other formation enthalpy calculations for InN. The issue is open to further investigation, especially by all-electron methods.

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. In the last column we report the proper piezoelectric constant $e_{31}^P$. As discussed recently, 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.

It is not infrequent to hear the incorrect statement that the spontaneous polarization is non vanishing in wurtzite because of structural non-ideality. In actual fact, a non-vanishing polarization is allowed on symmetry grounds in the ideal wurtzite structure as well. Indeed, we find that the calculated Berry-phase polarization in the ideal structure is indeed non-zero: $-0.032$ 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 non-ideal structures (Table XII). This confirms the intuitive idea that non-ideality, 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.

Theoretical predictions on polarization properties were shown to compare quite favorably with experimental evidences in various papers (see e.g. Refs. 2, 3, 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 vs GGA. The recently reported non-linear 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. 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 $\epsilon_1$ 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. 24. 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, GGA and LDA calculations for III-V nitrides suggest an overall improvement of the predicted properties in the former approximation. In particular, the structural parameters are extremely accurate, with deviations from experiment below 0.3 % for AlN, 0.9 % for GaN, and 1.7 % for InN. Cohesive energies and formation enthalpies are in fair to excellent agreement with experiment; the only clear-cut failure (in the GGA approximation) is the positive formation enthalpy of InN. Elastic properties follow the expected trends of GGA vs 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 LDA behavior; due to uncertainties in the experimental data, comparison with experiment does not provide definitive support to one or the other approach. Concerning the cohesion and structure of parent species (N₂, Ga, Al, In), only in the case of condensed N₂ do we find major discrepancies with experiment. In the light of the present results, our conclusion is that the GGA approximation should be preferred in density-functional studies of III-V nitrides. Of course, the choice of one or the other approximation may depend on the specific problem being addressed.

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TABLE I. Bond length, vibrational frequency, and binding energy of the N$_2$ dimer.

|           | $d$ (Å) | $\omega$ (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       |

*Ref. [7]*

TABLE II. Structural parameters and binding energy per molecule of hexagonal solid N$_2$

|           | $a$ (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|            |

*Ref. [15]*

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      |

*Ref. [17]*

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     |
| GGA$^a$  | 4.51    | 1.0013| 1.695 | 0.0785| 0.1525|            |

*Ref. [16]*

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|            |

*Ref. [15]*

TABLE VI. Lattice constant, binding energy, and formation enthalpy $\Delta H$ of zinc-blende AlN.

|           | $a$ (Å) | $E_b$ (eV) | $\Delta H$ (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    |            |                |

*Ref. [7]  
$^b$Ref. [19]*

TABLE VII. Lattice constant, binding energy, and formation enthalpy $\Delta H$ of zinc-blende GaN.

|           | $a$ (Å) | $E_b$ (eV) | $\Delta H$ (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   |            |                |

*Ref. [7]  
$^b$Ref. [6]  
$^c$Ref. [19]*

TABLE VIII. Lattice constant, binding energy, and formation enthalpy $\Delta H$ of zinc-blende InN.

|           | $a$ (Å) | $E_b$ (eV) | $\Delta H$ (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    |            |                |

*Ref. [7]  
$^b$Ref. [19]*

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

|           | $a$ (Å) | $c/a$ | $u$ | $E_b$ (eV) | $\Delta H$ (eV) |
|-----------|---------|-------|-----|------------|-----------------|
| LDA (present) | 3.1861  | 1.5348| 0.3821| −13.536    | −3.642          |
| LDA$^a$  | 3.0798  | 1.5995| 0.3821| −13.536    | −3.642          |
| GGA (present) | 3.057   | 1.617 | 0.3802| −13.286    |                |
| GGA$^a$  | 3.1095  | 1.6066| 0.3819| −12.071    | −3.142          |
| GGA$^a$  | 3.113   | 1.6195| 0.3798| −11.403    |                |
| Experiment$^b$ | 3.1106  | 1.6008| 0.3821| −11.669$^b$ | −3.13$^d$ 2.53$^e$|

*Ref. [7]  
$^b$Ref. [20]  
$^c$Ref. [21]  
$^d$Ref. [18]  
$^e$Ref. [19]*
### 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) | 3.1461 | 1.6273 | 0.3768 | -10.999 | -1.685  |
| LDA       | 3.193  | 1.634  | 0.376 | -10.187 |
| GGA (present) | 3.1986 | 1.6339 | 0.3772 | -9.265  | -1.118  |
| GGA       | 3.245  | 1.632  | 0.3762 | -8.265  |
| Experiment b | 3.1890 | 1.6263 | 0.377 | -9.058 a | -1.08 c | -1.91 d |

aRef. 7  
bRef. 21  
cRef. 18  
dRef. 19

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

|          | a (Å) | c/a   | u    | E(eV) | ΔH (eV) |
|----------|-------|-------|------|-------|---------|
| LDA (present) | 3.5218 | 1.6121 | 0.3791 | -9.249 | -0.303  |
| LDA       | 3.544  | 1.626  | 0.377 | -8.694 |
| GGA (present) | 3.5848 | 1.6180 | 0.37929 | -7.695 | 0.125   |
| GGA       | 3.614  | 1.628  | 0.377 | -6.872 |
| Experiment b | 3.538  | 1.6119 |       | -7.970 e | -0.21 d | -1.36 e |

aRef. 7  
bRef. 22  
cRef. 18  
dRef. 19  
eRef. 23

### TABLE XII. Spontaneous polarization (C/m²), piezoelectric constants (C/m²), dynamical charges, elastic constants (GPa), and the ratio $R = -\frac{2C_{31}}{C_{33}}$ (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 | 0.85 | -0.44 | 415 | 83 | -0.400 | -0.47 |
|          | LDA a | 405 | 103 | -0.508 |
|          | GGA | -0.034 | 2.67 | 0.66 | -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 |

aRef. 24  
bRef. 22  
cRef. 19  
dRef. 18  
eRef. 23

TABLE XII. Spontaneous polarization (C/m²), piezoelectric constants (C/m²), dynamical charges, elastic constants (GPa), and the ratio $R = -\frac{2C_{31}}{C_{33}}$ (see text) of wurtzite nitrides, as obtained in the LDA and GGA approximation. The last column reports the proper $e_{31}$ piezoelectric constant.