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LETTER TO THE EDITOR

Classical simulations of the properties of group-III nitrides

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Abstract. We present interatomic pair potential parameters derived for the GaInAlN system. Potentials are fitted to bulk material properties, such as lattice constants and elastic and dielectric constants, and are then employed to calculate Schottky and Frenkel defect energies in GaN, InN and AlN. Schottky defects are found to be lower in energy than Frenkel defects, suggesting that vacancies are more readily formed in the group-III nitrides. The formation energies of both Schottky and Frenkel defects in all the nitrides are found to depend on the size of the cation. Solution energies indicate that InN readily dissolves in both GaN and AlN, at least at low concentration.

In recent years, there has been much interest in the group-III nitrides GaN, AlN and InN. Research has been stimulated by the marketability of these direct band gap semiconductors and the prospect of fabricating electronic devices such as high brightness, efficient blue and green light emitting diodes (LEDs), high temperature, high frequency field effect transistors and also ultraviolet and blue laser diodes (LDs). For example, the band gap of GaN (3.4 eV) can be tailored by alloying with InN (1.9 eV) and AlN (6.3 eV) which allows control over the wavelength of emission. Alloying is also employed to make single and multiple quantum well structures, which further improves the efficiency of LDs and LEDs. Such potential application makes it important to understand the underlying atomic and electronic structure of the group-III nitrides. Already much work has been carried out, especially using *ab initio* calculations, to model bulk material properties and to characterize the electronic structure of native and extended defects. However, because of the computational effort involved, these calculations are often restricted to small models which usually contain under 100 atoms. The use of classical pair potential models lifts this restriction and allows one to model cells containing thousands of atoms although, of course, only the atomic structure and not the electronic structure can be simulated. As yet there have been few classical investigations into the group-III nitrides despite their success in predicting atomic structure and defect energies [1]. Recently, Zapol *et al* [2] presented short range pair potential parameters within the shell model for GaN. Adopting a partial charge model, they successfully reproduced bulk material properties for the wurtzite, sphalerite and rocksalt phases. Cormack [3] has also presented a set of potential parameters for AlN using a formal charge model. In our study, we derive parameters which enable the entire GaInAlN system to be modelled. Again using a shell model we focus on the wurtzite phase for this system, which is the phase observed under normal experimental conditions. The model and methodologies are well established and only a summary is presented here.

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The long range electrostatic energy is evaluated through the Ewald summation [4]. The short range interaction between ions is described using a Buckingham pair potential which has the following form:

$$V_{ij} = A\exp(-r_{ij}/\rho) - Cr_{ij}^{-6}. \tag{1}$$

The parameters A, ρ and C are fitted to experimental lattice parameters, elastic constants and dielectric constants using a least squares fitting routine. For the nitrogen atom polarization effects are taken into account by the shell model [5] in which the electrons are modelled by a massless 'shell' with charge Y which is connected to the core by a spring with spring constant K. The polarizability is then given by $\alpha = Y^2/K$.

Similar to the approach of Zapol *et al* we have used partial charges in which the Ga, Al and In cores are attributed a charge of +2e, and the N atom an overall charge of −2e. Our own density functional theory calculations support the use of a partial over a formal charge model [6], with a Mulliken population analysis giving the following Mulliken charges: Ga +0.97e, N −0.97e in GaN; In +1.20e, N −1.20e in InN; and Al +1.30e, N −1.30e in AlN. All the classical calculations and the fitting procedure are performed using the GULP computer code, the methodology of which can be found in [7]. Parameters for all three structures were fitted simultaneously, with common N–N potentials, thus resulting in a self-consistent set of parameters suitable for future doping studies. Parameters are shown in table 1, and calculated and experimental bulk material properties are shown in table 2.

Table 1. Interatomic pair potential parameters for the group-III nitrides. The cutoff radius for the potentials is taken to be 16 Å. An 's' represents a shell and a 'c' represents a core.

Atom types	A (eV)	ρ (Å)	C (eV Å^6)	K (eV Å^{-9})	Y (e)
N s N s	5134.176	0.3140	283.8		
Ga c N s	782.107	0.3166	0.0		
Ga c Ga c	5902.871	0.3187	250.0		
In c N s	870.207	0.3263	0.0		
In c In c	6141.774	0.3567	258.0		
Al c N s	698.547	0.3224	0.0		
Al c Al c	5131.179	0.3040	248.0		
N c N s				16.200	−2.50

It can be seen that the derived parameters reproduce, within acceptable limits, the experimental values for lattice, elastic and dielectric constants. It is noted that in the literature there are various values of elastic constants to be found which vary by around 30% for all three nitrides. In addition, the difference in energy between the sphalerite and wurtzite forms of the three nitrides was computed, and the wurtzite form was found to be the most stable in each case, as experimentally observed. The energy differences were calculated to be 0.09 eV (GaN), 0.09 eV (InN) and 0.10 eV (AlN) per formula unit. To further test the potential parameters we have calculated native defect energies, and Schottky and Frenkel energies. The technique due to Mott and Littleton is used which allows the energy of a single isolated defect within an infinite lattice to be calculated [14]. An inner region, in which all atoms are treated explicitly, was taken to have a radius of 10 Å, and contained on average 350 atoms. The outer region responds to the electric field introduced by the charged defect, according to the continuum approach of Mott and Littleton, and in our calculations this was taken to have a radius of 26.5 Å. Defect energies for native defects such as vacancies, interstitials and antisites were calculated. However these energies are simply the difference between the energy of the initial and the defective structures and do not indicate the formation energy of the defect, since this

Table 2. Calculated and experimental material properties for wurtzite GaN, InN and AlN. References: [a] [8], [b] [9], [c] [10], [d] [11], [e] [12] and [f] [13].

Property	GaN	InN	AlN
Lattice constants (Å)			
a	3.20, (3.19)[a]	3.53, (3.54)[b]	3.11, (3.11)[b]
c	5.14, (5.19)[a]	5.69, (5.69)[b]	4.97, (4.98)[b]
Elastic constants (10^{11} dyn cm^{-2})			
c_{11}	41.04, (39.0)[c]	29.75, (19.0)[d]	41.74, (41.1)[e]
c_{12}	16.14, (14.5)[c]	10.74, (10.4)[d]	17.81, (14.9)[e]
c_{13}	14.17, (10.6)[c]	10.87, (12.1)[d]	15.20, (9.9)[e]
c_{33}	41.30, (39.8)[c]	25.05, (18.2)[d]	43.20, (38.9)[e]
c_{44}	12.28, (10.5)[c]	8.94, (1.0)[d]	12.46, (12.5)[e]
c_{66}	12.45, (12.3)[c]	9.51	11.97
Bulk modulus (GPa)	236, (210)[c]	165, (139)[d]	248, (210)[e]
Dielectric constants			
ϵ_0^{11}	8.64, (9.38)[f]	9.82, (15)[b]	8.07, (8.8)[b]
ϵ_0^{33}	12.64, (10.2)[f]	17.71	11.22
ϵ_∞^{11}	4.25, (5.35)[f]	3.50, (8.4)[b]	4.46, (4.7)[b]
ϵ_∞^{33}	4.58, (5.35)[f]	3.69	4.85

Table 3. Calculated Schottky and Frenkel defect energies, lattice energies per formula unit and solution energies for InN, GaN and AlN. Also shown are the relaxations of atoms surrounding anion and cation vacancies. The two values refer to the outward relaxation of equivalent and inequivalent nearest neighbour bond lengths respectively. References: [a] [2] and [b] [3].

	InN	GaN	AlN
Lattice energy (eV)	−38.82	−42.62	−43.50
Defect			
Schottky (eV)	3.39	4.74, (4.8)[a]	5.17, (8.45)[b]
Cation Frenkel (eV)	7.43	7.42, (6.9)[a]	6.62, (11.15)[b]
Anion Frenkel (eV)	4.76	6.66, (6.1)[a]	7.40, (19.77)[b]
Relaxations (%)			
N vacancy	15.3, 14.9	17.5, 16.8	19.7, 19.9
Cation vacancy	20.2, 25.0	9.6, 14.0	3.5, 7.5
Solution energies (eV)	0.09 ($\mathrm{Ga_{In}}$)	0.99 ($\mathrm{Al_{Ga}}$)	0.86 ($\mathrm{Ga_{Al}}$)
	1.00 ($\mathrm{Al_{In}}$)	−1.53 ($\mathrm{In_{Ga}}$)	−0.51 ($\mathrm{In_{Al}}$)

requires a knowledge of the chemical potential of the individual atoms. The defect energies can, nevertheless, be used to obtain Schottky and Frenkel defect energies which are shown in table 3. The Schottky energies are obtained using the calculated values for the lattice energy per formula unit E_{latt}. For example, for the case of GaN,

$$E_{Schottky} = \tfrac{1}{2}\{E(V_{\mathrm{Ga}}) + E(V_{\mathrm{N}}) + E_{latt}(\mathrm{GaN})\} \tag{2}$$

where $E(V_{\mathrm{Ga}})$ and $E(V_{\mathrm{N}})$ are the defect energies of a Ga and a N vacancy respectively.

For all three nitrides, the Schottky defect is found to have the lowest energy. This finding is in good agreement with that of Zapol and Cormack and confirms that the vacancies are the most readily formed defects in the group-III nitrides. The values obtained by Cormack are significantly higher than our values due to the use of a formal charge model. It is interesting to note the difference in energy between the nitrogen Frenkel defect and cation Frenkel defect in each material. These differences are 2.67 eV for InN, which has the largest cation, 0.76 eV for GaN, and −0.78 eV for AlN, which has the smallest cation. This indicates that, for InN and GaN, nitrogen vacancies and interstitials are more readily formed than cation vacancies and interstitials. For GaN, this result agrees with findings from *ab initio* calculations which, due to their ability to calculate chemical potentials, are able to calculate individual formation energies. In [15] the nitrogen interstitial is found to have a lower formation energy than the gallium interstitial and the nitrogen vacancy has a lower formation energy than the gallium vacancy, except under high n-type conditions. The picture is not so straightforward for AlN and InN [16]. Defects involving the small N atom may have lower formation energies but this very much depends on the charge state of the defect and also whether one considers nitrogen rich or gallium rich conditions.

The creation of native defects causes a significant relaxation of the surrounding atoms. Most notable in our study are the relaxations surrounding the nitrogen and cation vacancies which, similar to Schottky and Frenkel defect energies, are dependent on the size of the cation, as shown in table 3. It is noted that, in wurtzite, a vacancy is surrounded by three equivalent nearest neighbours and one inequivalent nearest neighbour. In table 3, the relaxations are given in terms of the percentage increase in the nearest neighbour bond lengths.

For all three nitrides, it is found that the octahedral interstitial site is energetically preferred over the tetrahedral site, for both the anion and the larger cation interstitials. As far as we know there are no *ab initio* comparisons available between tetrahedral and octahedral interstitial sites in AlN and InN. *Ab initio* calculations on wurtzite GaN show that the octahedral site is preferred for the gallium interstitial but that the nitrogen atom prefers a low symmetry split interstitial configuration [15]. Our current model shows such a split interstitial to be unstable.

The solution energies for doping one nitride with another were also calculated. This is the energy change on the inclusion of one mole of the dopant in the host material. Using the doping of GaN with InN as an example and assuming a substitutional mechanism as suggested by our calculations (table 3), the solution energy is given by

$$E_{sol} = E(\mathrm{In_{Ga}}) + E_{latt}(\mathrm{GaN}) - E_{Latt}(\mathrm{InN}) \tag{3}$$

where $E(\mathrm{In_{Ga}})$ is the defect energy for substitution of a gallium atom with indium, and E_{latt} is the lattice energy per formula unit. A negative solution energy indicates that the dopant readily dissolves in the host material and, as shown in table 3, this is found to be the case for the doping of GaN and AlN with InN. In the four other cases considered the inclusion of the dopant is less favoured although only marginally for GaN in InN. Experimentally it is known that all three materials dissolve in each other, at least for low concentrations, as is generally found here. Phase separation is observed at higher concentrations. This occurs, for example, when the concentration of InN in GaN exceeds 28 % [17].

In conclusion, we have derived a set of pair potential parameters which enables the entire GaInAlN system to be modelled. These potentials are successful in predicting bulk material properties, such as lattice parameters and elastic and dielectric constants. Mott Littleton defect calculations show that the Schottky defect is most readily formed in the group-III nitrides and that the relative formation energies of Schottky and Frenkel defects depends on the size of the cation. Solution energies indicate that InN readily dissolves in GaN and AlN at least for low concentrations. We are now considering the energetics of small indium and aluminium clusters in GaN.

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