

# Theoretical study of point defects in GaN and AlN; lattice relaxations and pressure effects

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## Abstract

Native defects and some common dopants (Mg, Zn, and C) in cubic GaN and AlN are examined by means of *ab initio* theoretical calculations using two methods: *i*) the Green's function technique based on the linear muffin-tin orbital method in the atomic-spheres approximation; *ii*) a supercell approach in connection with the full-potential linear muffin-tin-orbital method. We apply the first method to look mainly at the energetic positions of the defect and impurity states in different charge states and their dependence on hydrostatic pressure. The second method allows us to study lattice relaxations. Whereas small relaxations are found near vacancies and substitutional Mg and Zn, the calculations predict large atomic displacements around antisite defects and the substitutional carbon impurity on the cation site.

## 1. Introduction

The III-V nitrides are important materials for optoelectronic device applications. Their optical properties are strongly influenced by native and introduced defects. The nature of these defects is by far not yet fully understood, but intense experimental and theoretical research activity during the past few years provide constantly new data on these systems. Our work, described here, attempts to add some information by means of *ab initio* calculations of electronic structure properties of defects in GaN and AlN. This work is based on the density-functional theory (DFT), using two calculational methods. The first method is the linear muffin-tin orbital (LMTO) [1] Green's function (GF) method [2] It only allows us to study ideal substitutional defects without taking structural relaxations into account. The results are compared to those obtained by our *second method*, calculations using a supercell approach and the full-potential [3] LMTO method with lattice relaxation included.

In both methods we are using the local-density approximation (LDA) [4] to the DFT, by which exchange and correlation effects are accounted for by a simple local potential.

In the LMTO GF method the valence electronic structure of the impurity atom is obtained from the Green's function  $G$ , which is found by solving the Dyson equation with  $G_0$ , the Green's function of the pure crystal host, and  $\Delta V$ , the perturbation due to the impurity. In the LMTO method the host Green's function is calculated from the band structure of the pure crystal within the atomic sphere approximation (ASA), i.e., the crystal volume is approximated by slightly overlapping atom centered spheres, inside which the potential is made spherically symmetric. The fundamental gaps derived from the LDA bandstructures are generally 50-100% too small. To overcome this problem we have chosen to rigidly shift the conduction band upwards to match the experimental minimum gap. We are not able to include lattice relaxations in the GF calculation, so in order to study such structural effects we resort to the supercell method. Relaxations cannot be predicted from total-energy calculations using the ASA. Therefore, the full nonspherical shapes of potentials and charge distributions must be taken into account. We do this by combining the supercell approach with the full-potential version [3] of the LMTO scheme. Calculations are performed using 32-atom supercells.

In contrast to the LMTO GF method where defect states are characterized by a single energy level, in the supercell approach, large, but finite, cells, each containing a defect, are repeated *ad infinitum*, leading to impurity bands with finite widths. In that case we estimate the impurity levels in the band gap as the centre-of-gravity of the impurity band. The LMTO GF method gives a fast way to get both neutral and charged states of defects, and to derive pressure coefficients (or deformation potentials) for the impurity levels. However, the assumption that the host atoms remain in their ideal positions can lead to substantial errors in the level energies in cases with pronounced relaxations. Therefore we compare in the next sections, the GF LMTO results with the FP LMTO supercell calculations.

Both GaN and AlN can crystallize in two phases, the cubic (zincblende) and hexagonal (wurtzite) phases. We study here the cubic phase, believing that there is little difference in impurity level positions of the two phases. A comparison of defect properties for wurtzite and cubic GaN made by Neugebauer and Van de Walle [5] showed only minor deviations in formation energy and atomic relaxations between these two hosts, and energy level positions remained practically the same.

## 2. Native defect levels

There are very similar tendencies in the positions of native defect levels in GaN and AlN, but the absolute values are different mainly due to the different values of the energy gaps. The energy gap of AlN in the zinc-blende structure is 6.1 eV, almost twice that of GaN (3.25 eV). Comparing GaN and AlN, the same sequence of states is seen for all the native defects. The positions of the states in the gap are also similar, with the general rule that they are lying somewhat deeper in the energy gap in AlN. Especially, some states which are resonant with the conduction or valence band in GaN (as  $V_N$ ) have in AlN moved into the band gap.

### 2.1. Vacancies

Cation vacancies ( $V_{\text{cat}}$ ) create several acceptor states both in GaN and AlN ranging from 0.2 eV to 1.9 eV above the valence-band maximum (VBM), whereas nitrogen vacancies act as shallow donors.  $V_{\text{cat}}$  in the neutral charge state is a triple acceptor with a level close to the VBM. The  $V_{\text{Ga}}$  level position in GaN is 0.2 eV above the VBM, and in AlN  $V_{\text{Al}}$  lies 0.5 eV above the VBM, in agreement with the pseudopotential calculations by Boguslawski et al. [6] (0.3 eV in GaN and 0.4 eV in AlN).

Outward relaxation is found for cation vacancies. In GaN the nearest neighbors are shifted away by 4 % of the bond length, and in AlN a much larger shift of 11 % is found. This agrees with other theoretical results. For example, the same values were obtained by Neugebauer and Van de Walle [5] for GaN, and by Mattila et al. [7] for AlN. We notice that in the case of AlN the relaxations induce a downshift of the  $V_{\text{Al}}$  level by  $\approx 0.2$  eV (from the 0.7 eV from LMTO GF to  $\approx 0.5$  eV as estimated from the supercell calculation.)

While the cation vacancy level positions are very similar in GaN and AlN, the nitrogen vacancy behaves quite differently in the two compounds. In GaN the  $a_1$  (s-like) state of  $V_N$  forms a resonance below the VBM, whereas the  $t_2$  (p-like) state appears as a resonance in the conduction band. For the neutral charge state one electron is bound by the positive potential in a shallow donor level characterized by the effective mass of the conduction band minimum (CBM), i. e., the nitrogen vacancy acts as a single donor. In contrast, the  $V_N$  levels in AlN are moved into the band gap. As results from the LMTO GF calculations the  $a_1$  (s-like) state of  $V_N$  lies 1.7 eV above the VBM, whereas the  $t_2$  (p-like) state is found to be 0.4 eV below the CBM.

Lattice relaxations are small near the nitrogen vacancy, both in GaN and AlN. In GaN we find that the nearest neighbor Ga atoms relax inwards by 4 % of the bond length. This is in agreement with pseudopotential calculations [8] (inward relaxation  $\approx 3$  % of the bond length). The relaxations in AlN were found to be vanishingly small.

### 2.2. Antisites

Antisite defects introduce deep levels both in GaN and AlN. Lattice relaxations connected with these defects are very pronounced, but quite different for cation and nitrogen antisites.

In their neutrally charged states, the cation antisite defects  $\text{Ga}_N$  and  $\text{Al}_N$ , are double acceptors. In GaN, the Ga

$N_{\text{N}}$  level is about 1.0 eV above the VBM according to our supercell calculation. This is a little lower than the position ( $\approx 1.5$  eV) of the same state obtained by the pseudopotential calculations. [6] In AlN the  $Al_{\text{N}}$  energy level is close to the midgap; i.e.  $\approx 3$  eV above the VBM.

For both compounds we find an outward relaxation around the cation antisite. In GaN the distance to the nearest neighbors is increased by 12 % of the ideal bond length, in AlN by 18 %. The result for GaN is in agreement with the pseudopotential calculations [6] (11 % outward relaxation).

The nitrogen antisite defect behaves almost identically in GaN and AlN. The neutral nitrogen antisite defect,  $N_{\text{Ga}}$ , introduces a doubly occupied  $a_1$  state just above the VBM and an empty triplet close to the CBM.

Assuming for the nitrogen antisite the full  $T_d$  symmetry, we find a small 1 % outward displacement of the nearest neighbor nitrogen atoms. But, if on the other hand, we allow for symmetry changes, we find that the nitrogen antisite distorts strongly along a three-fold symmetry axis. In the case of  $N_{\text{Ga}}$  the bond distance to the nearest neighbor atom is reduced by 30 % (in agreement with pseudopotential calculations [6]). Supercell calculations for  $N_{\text{Al}}$  yield a similar result; a reduction of the bond length to the nearest nitrogen atom by 29 %, and this agrees with the result obtained by Mattila et al. [7] Note that the shortest N-N distance ( $\approx 1.3$  Å) in this relaxed structure is closer to the interatomic distance (1.1 Å) in the free  $N_2$  molecule than to the bond length of AlN (1.89 Å) or GaN (1.94 Å). These large relaxations imply that the energy levels determined by means of our GF calculations (no relaxation) differ from those obtained by the supercell approach. Indeed, in both compounds we observe a downward shift of energy levels due to relaxation effects. In GaN from 0.7 eV above the VBM to a position close to the VBM. The corresponding state in AlN shifts from  $\approx 2.5$  eV ( $a_1$  state) to  $\approx 1.4$  eV above the VBM.

We have also investigated the metastability of the nitrogen antisite reported previously by Mattila. [7] When the antisite is displaced along the (111) axis away from the nearest neighbor atom a second energy minimum occurs. We find this at a displacement equal to 49 % of the bond length for AlN and 45 % for GaN. The relaxation of the remaining atoms at the displaced site is spherically symmetric - the three atoms surrounding the antisite relax inwards. In AlN they relax by 8 % of the bond length, in GaN they relax by 12 % of the bond length. The results above are in good agreement with the pseudopotential calculation by Mattila. [7]

### 3. Impurity levels

In the present work we study the substitutional C, Zn and Mg impurities. The importance of the C impurity follows from the fact that carbon atoms may be unintentionally incorporated in nitrides during growth. Carbon, as a group-IV atom, is an amphoteric impurity in both GaN and AlN.  $C_{\text{N}}$  is a shallow acceptor; it introduces several impurity levels, the lowest one (corresponding to the neutral charge state) is located about 0.1 eV above the VBM in GaN, and a little higher, about 0.3 eV, in AlN. When atoms around the impurity are allowed to relax, a small inward shift is found in the case of GaN (4 % of the bond length). There is no relaxation in the case of AlN. These results differ somewhat from those obtained by pseudopotential method [9], where small inward relaxation is found for GaN (2 % of the bond length), and small outward relaxation for AlN (also 2 %).

$C_{\text{Ga}}$  introduces a resonant state above the CBM in GaN, and  $C_{\text{Al}}$  creates in AlN an effective-mass donor level nearly degenerate with the conduction band. The relaxation around the carbon atom at the cation site is large, and it reduces the nearest neighbor bond length by  $\approx 18$  % in GaN and  $\approx 17$  % in AlN.

Substitutional Zn and Mg atoms on a cation site form shallow acceptor states. They are the most commonly used acceptors in the III-nitrides. Our calculated (LMTO GF) level position for the  $Zn_{\text{Ga}}$  impurity in GaN is 0.1 eV above the VBM for the neutral state, and  $Zn_{\text{Al}}$  produces in AlN a level 0.2 eV above the VBM. Magnesium creates even shallower acceptor states. As results from our GF calculations the  $Mg_{\text{Ga}}$  in GaN is close to the VBM for the neutral charge state. The  $Mg_{\text{Al}}$  lies in AlN  $\approx 0.1$  eV above the VBM. For Mg as well as Zn impurities we find outward relaxations around the defects. The shift is small in GaN, 2 % and 4 % of the bond length for Mg and Zn, respectively, but larger in AlN, 7 % and 10 %.

### 4. Pressure effects

Below we report the pressure dependence of some defect levels as calculated by means of the LMTO GF method. The level shifts are therefore derived without taking relaxations into account. This approximation may lead to somewhat inaccurate pressure coefficients in cases where large atomic displacements are found near the defects. Such cases are currently being examined in detail by means of supercell calculations of volume dependent relaxations. [10]

We consider the pressure behavior of the defect levels for the following types of states: 1) The  $V_N$  being, in GaN, resonant with the conduction band, 2) the N antisite being a deep donor state, and 3) the shallow acceptors: Zn, and Mg. For each of these cases we have calculated the energy positions of the defect levels at five different volumes. Conversion of deformation potentials into pressure coefficients was made using the theoretical [11] bulk moduli for cubic GaN, 184 GPa, and AlN, 215 GPa.

The calculated pressure coefficient of the main energy gap of GaN is +38 meV/GPa. In the case of  $V_N$ , the resonance state is shifted at the rate -24meV/GPa with respect to the CBM (i. e., +14meV/GPa with respect to the VBM). At pressures above 4 GPa the  $t_2$  state appears as a true bound state in the band gap.

The deep donor level generated by  $N_{Ga}$  (doubly occupied  $a_1$  state) is shifted up with respect to the valence band edge with the pressure coefficient +9 meV/GPa.

In the case of the shallow acceptors in GaN we found that the defect states do not shift with pressure with respect to the valence band ( $Mg_{Ga}$ ), or are only shifted slightly ( $Zn_{Ga}$  with about +1 meV/GPa). The pressure coefficient of  $Zn_{Ga}$ , being practically the same as that of the valence band edge, confirms a recent experimental finding. [12]

The calculated pressure coefficient of the main energy gap of AlN is +42 meV/GPa . As in GaN, in AlN, the levels lying higher in the band gap also have larger pressure coefficients. Going from the lower to higher positions of the states we have got the following pressure coefficients (with respect to the valence edge):  $Mg_{Al}$ : +1.5 meV/GPa,  $Zn_{Al}$ : +7 meV/GPa,  $V_N$ : +15 meV/GPa,  $N_{Al}$ : +26 meV/GPa.

The results above show that the pressure coefficient of a given defect level depends on its energetic position. The pressure behavior of the shallow acceptor states is similar to that of the valence band maximum, while the pressure coefficients are larger for states lying higher in the band gap.

## 5. Summary

In conclusion, we have calculated the energy positions of vacancies and antisites together with some common dopants in GaN and AlN, including lattice relaxation effects.

Detailed calculations of relaxations are still in progress, but the supercell calculations presented so far show that we find pronounced outward lattice relaxation around cation antisites. In the more complex case of the nitrogen antisite, which seems to be similar to the EL2 in GaAs, large inward relaxation is found. The distance from the N impurity atom to the nearest neighbor is reduced by  $\approx 30\%$  and becomes comparable to the  $N_2$  dimer bond length.

Pronounced inward relaxation (about 18 % of the bond length) is also found around the C impurity on the cation site. In the remaining cases studied relaxations are rather small or negligible, except for  $V_{Al}$  and  $Zn_{Al}$  where the outward displacements amount to  $\approx 10\%$  of the bond length. We notice, that outward relaxations in general are larger in AlN than in GaN, maybe because the Ga-3d electrons prevent the Ga-N bond length from becoming too short. [8]

Where comparisons can be made, our results are similar to those obtained by means of first-principles pseudopotential calculations. [5] [6] [7] [9]

We have shown that, both in GaN and in AlN, the pressure coefficients of the defect states depend on the position of the state in the gap, and they do not depend on the type of state, i. e., whether they are donors or acceptors.

The energy levels as quoted in this paper are the eigenvalues of the self-consistent Kohn-Sham equations. A comparison to experiments should instead be made by using calculated transition-state energies. Often a good approximation to this is obtained by averaging eigenvalues for "neighbouring" charge states.

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