

## Native defects and carbon impurity in cubic BN

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Using the Green's function technique based on the linear muffin-tin orbital method in the atomic-spheres approximation we study the electronic structure of native defects and substitutional carbon impurities in cubic BN. To include the lattice relaxation effects a supercell approach in connection with the full-potential linear muffin-tin-orbital method is applied.

### 1 Introduction

In a previous paper [1] we reported the results of electronic structure calculations of native defects and impurities in GaN and AlN. Here we add information about the nature of the III-nitrides by means of ab-initio calculations of electronic properties of defects in BN. BN appears in two allotropic forms: hexagonal and cubic. We focus here on the cubic structure, and study native defects such as vacancies and antisites, as well as substitutional carbon impurities on boron and nitrogen sites. Two calculational methods are used. The first one is the Green's function (GF) technique [2] in the frame of the linear muffin-tin orbital method (LMTO) [3] in the atomic-spheres approximation (ASA). The GF LMTO method allows us to calculate the energy levels of different charge states, but only *ideal* (unrelaxed) substitutional defects can be treated by this method. In order to include the structural effects we resort to the second method, which is the supercell approach combined with the full-potential version [4] of the LMTO scheme. In contrast to the GF LMTO 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 can estimate the impurity levels in the band gap as the centre-of-gravity of the impurity band. In our calculations we have used cells containing 32 atoms. Additional 'empty' spheres are introduced at the tetrahedral interstitial sites. We chose all (non-overlapping) muffin-tin spheres to have the same size. The  $\mathbf{k}$ -space integrations used 216  $\mathbf{k}$ -points in the Brillouin zone, and convergence tests were made with 512  $\mathbf{k}$ -points.

The local-density approximation (LDA) [5] is used, by which exchange and correlation effects are accounted for by a simple local potential. The fundamental gaps derived from the LDA band structures are generally 50-100% too small. To overcome this problem in the GF LMTO method we have chosen to rigidly shift the conduction bands upwards to match the experimental minimum gap (the 'scissors operator').

In the next sections we present the results of GF calculations comparing them with the supercell results.

### 2 Calculations: Defect levels and relaxation effects

In Figure 1 the charge occupations and the energy level positions as calculated by the GF method are shown for all the defects considered. The level positions for the neutral states as calculated by the supercell approach are also indicated (dashed lines). Comparing the results of the two types of calculations one should remember that the GF calculations are performed without lattice relaxations whereas they are included in the supercell calculations.

#### 2.1 Vacancies

The boron vacancy,  $V_B$ , in the neutral state is a triple acceptor with a level close to the valence band maximum (VBM). By filling in up to three more electrons charged states appear above the VBM. According to the GF method  $V_B$  gives rise to several acceptor states in the range 0.6 eV to 2.4 eV above the VBM. Total energy minimization in the supercell geometry predicts an outward, symmetrical relaxation around the boron vacancy. The nearest neighbors are shifted away by 11% of the bond length. The neutral state, as calculated by the supercell method with the lattice relaxation

included is lying slightly higher (0.9 eV) than the level position obtained without relaxations included by the GF method (0.6 eV), or by the supercell approach (0.7 eV).

The nitrogen vacancy,  $V_N$ , behaves differently, acting as a shallow donor. Both kinds of calculations yield an  $a_1$  (s-like) state of  $V_N$  close to the valence band edge (0.2 eV - GF and supercell calculations without relaxations, 0.6 eV - supercell approach with lattice relaxations included), whereas the  $t_2$  (p-like) state appears close to the conduction band edge (5.1 eV, 4.8 eV and 5.3 eV, respectively for GF and supercell calculations without and with relaxations). In a previous calculations of the  $V_N$  in the wurtzite phase [6] the position of the p-like level was found  $\approx 1$  eV below the conduction band minimum (CBM). Since the band gap of cubic BN is 6.2 eV this value compares favorably with the value of  $\approx 5$  eV above the VBM obtained for the position of the p-like state in the present work. Lattice relaxations are small near the nitrogen vacancy. We find that the nearest neighbor boron atoms relax outwards by 5 % of the bond length.

The above small relaxations lead to small upward shifts of the defect levels.

## 2.2 Antisites

Antisite defects introduce deep levels in BN. The cation antisite defect,  $B_N$ , is in the neutral state a double acceptor (occupied with four electrons). According to the GF calculations the  $B_N$  neutral state level is about 0.8 eV above the VBM. Negative charge states,  $B_N^-$  and  $B_N^{--}$ , are lying at 1.3 eV and 2.1 eV. With the supercell approach we find an outward relaxation around the cation antisite. The distance to the nearest neighbors is increased by 6 % of the ideal bond length. The corresponding neutral state level lies significantly higher (about 1.7 eV above the VBM) than obtained by the supercell method without relaxations included (1.2 eV) and by the GF method (0.8 eV). Thus, the relaxation causes an upward shift of the defect level of the order of 0.5 eV.

The neutral nitrogen antisite defect,  $N_B$ , introduces a doubly occupied  $a_1$  state in the middle of the band gap and an empty triplet close to the CBM. The GF calculation for  $N_B$  yields an s-like state 4.5 eV above the VBM and an empty p-type state at 5.0 eV. The supercell calculations *without* relaxations give the values 4.2 eV and 5.1 eV, respectively. The outward symmetrical relaxation is found to be about 9% of the bond length. The supercell calculations *with* relaxations give the values about 1 eV lower; 2.7 eV and 4.3 eV, respectively.

## 2.3 Carbon impurity

The importance of the C impurity follows from the fact that carbon atoms may be unintentionally incorporated into the nitrides during growth. Carbon, as a group-IV atom, is an amphoteric impurity, so we consider the substitutional carbon on both the boron and the nitrogen site.

The GF calculations show that  $C_B$  introduces a state degenerate with the CBM, whereas the supercell calculations give the level position  $\approx 1$  eV below the CBM (5.3 eV above the VBM). The relaxation around the carbon atom is small reducing the nearest neighbor bond length by  $\approx 3$  %, and it changes slightly the position of the impurity level (from 5.2 eV to 5.5 eV above the VBM).

$C_N$  is a shallow acceptor. It introduces impurity levels close to the VBM. The neutral state is located about 0.1 eV above the VBM, according to the GF calculation, and a little higher,  $\approx 0.5$  eV, as found by the supercell approach. The lattice relaxation is vanishingly small in this case (below 1%).

## 3 Summary

In conclusion, we have calculated the energy positions of vacancies and antisites together with carbon dopants in cubic BN, including lattice relaxation effects. In the case of native defects we find outward, symmetrical relaxation around the defect, between 5 and 11 % of the ideal bond length. Comparing the supercell results without and with lattice relaxations included it seems that in the case of vacancies relaxations cause rather small upward shifts of the energy levels, whereas for antisites the effect is much larger. The relaxations around the substitutional C impurity are very small.

Comparing the results of the two kinds of calculations it should be recalled that the supercell calculations lead to impurity bands with finite widths and we can only estimate the impurity level position as the centre-of-gravity of the impurity band. This was determined by means of the density-of-states functions.

The energy levels as quoted in this paper are the eigenvalues of the self-consistent Kohn-Sham equations. A comparison to experiments should in fact rather be made by using calculated transition-state energies. (i. e., using half-integer occupation numbers). Often a good approximation to this is obtained by averaging eigenvalues for "neighboring" charge state.

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## FIGURES

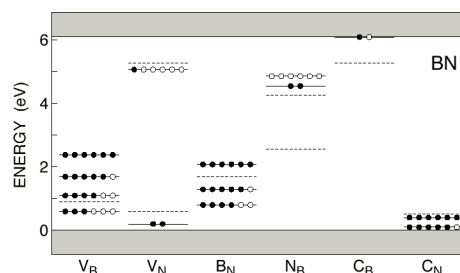


Figure 1. The defect level positions for the native defects and carbon impurity in BN. The energy levels for the neutral charge states, as calculated by the supercell approach, are indicated by dashed lines without occupation symbols.