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# Mg–H and Be–H complexes in cubic boron nitride

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## Abstract

*Ab initio* calculations on hydrogen complexes with Mg and Be impurities in c-BN are reported. We find that both impurities are acceptors and both bind H to form passive defects. However, their structures are different. For Be–H, the H atom lies at a puckered bond-centre configuration similar to that of C–H in GaAs, while in Mg–H, the H atom lies at a site anti-bonding to a N neighbour of the impurity. The hydrogen-related vibrational modes of the two complexes are also reported.

## 1. Introduction

Boron nitride is a semiconductor with a large band gap of 6.4 eV which has many properties in common with GaN. It has extreme hardness, high melting point, high thermal conductivity, low dielectric constant and is chemically inert. The zinc-blende phase is stable under high temperature and high pressure and is easily doped with Be and Mg [1, 2]. p–n junction diodes have also been fabricated using beryllium and silicon as p and n dopants. The ionization energies of Be and Si have been given as 0.23 and 0.24 eV [2]. However, the Be $(-/0)$ level varies with temperature, pressure and concentration. Values of 0.24, 0.31 and 0.35 eV at 7.7 GPa and 2100 °C for Be concentrations of 2900, 4500 and 1700 ppp, respectively, have been reported [3].

Hydrogen is present in almost all crystal growth conditions, and therefore may be present in as-grown material. Although successful p doping of GaN has been achieved with Mg, it is necessary to anneal the material grown by VPE in order to eliminate hydrogen which forms passive complexes with Mg. Thus hydrogen may passivate dopants in BN as it does in many semiconductors [4, 5]. In Si and GaAs, hydrogen lies at a bond centre near the acceptor [6]. However, in GaN, hydrogen lies at a site anti-bonding to a nitrogen neighbour to Be and this raises a question about the preferred site for H in BN.

Park and Chadi [7], using a first-principles LDA method in a 32-atom supercell, demonstrated that Be lies at a B site in c-BN and is an acceptor. A full-potential linear

augmented-plane-wave study [8] showed an outward displacement of 3% for the nitrogen neighbours and the $(-/0)$ level lay at $E_v + 0.4$ eV.

Nevertheless, theoretical studies on the properties of hydrogen in BN are scarce. An *ab initio* Hartree–Fock study found that neutral hydrogen prefers a bond-centred position in c-BN [9], while a local density tight-binding method [10] indicated $H^0$ to be located on the centre of a rhombus formed by two neighbouring B–N bonds.

In view of these contradictory results, we have investigated the location of H in c-BN doped with Be and Mg.

## 2. Method

The calculations were carried out with the AIMPRO supercell method employing a basis s, p, d Gaussian set [11]. See table 1. Details of the method have been given previously [12]. Supercells possessing 64 atoms were used together with the $2^3$ Monkhorst–Pack scheme [13]. The charge density was Fourier expanded with energy cut-offs up to 200 au. Local vibrational modes (LVM) of defects were evaluated from the energy second derivatives between the neighbouring atoms of the defect. A Musgrave–Pople interatomic potential describing the bulk was first derived by fitting to a set of energy double derivatives for c-BN. These potentials could then be used to evaluate the entries to the dynamical matrix for host atoms surrounding a defect.

**Table 1.** AIMPRO calculation results. The types of orbital ranging from the lowest exponential coefficient to the largest are given in parenthesis. See equation (24) of reference [11].

| Boron | (ddpp) | Optimized in BN and $\alpha$-boron |
|---|---|---|
| Nitrogen | (dddd) | Optimized in BN, GaN and $N_2$ |
| Beryllium | (dddd) | Optimized in BeO |
| Hydrogen | (pppp) | Optimized in $H_2O$ and $H_2$ |
| Magnesium | (dddddd) | Optimized in MgO |

## 3. Results

Table 2 gives the calculated lattice parameter, bulk modulus and its pressure derivative for c-BN. These were found by using a fit to the Birch–Murnaghan equation of state [14]. The error in the calculated lattice parameter is about 1%.

**Table 2.** Lattice constant, $a_0$, bulk modulus, $B$, and its first pressure derivative, $B'$.

|  | $a_0$ (Å) | $B$ (GPa) | $B'$ |
|---|---|---|---|
| Calculated | 3.584 | 396 | 3.84 |
| Experimental [15] | 3.616 | 369–400 | 4.0 |

The second derivatives of the energy with respect to atomic positions were used to find a Musgrave–Pople interatomic potential between B and N [16]. This potential gave an optical phonon frequency at $\Gamma$ of 1350 cm$^{-1}$, close to the experimental value of 1305 cm$^{-1}$ [17]. However, the short-range potential does not lead to a splitting of the LO and TO modes. Experimentally, the LO mode is at 1066 cm$^{-1}$.

The second derivatives of the energy between these inner eight atoms were evaluated and fitted to the derivatives of a Musgrave–Pople potential where the potential for atom $i$ is

$$V_i = (1/4) \sum_j k_r^{(i)} (\Delta r_{ij})^2 + (r_0^2/2) \sum_{j>k} k_\theta^{(i)} (\Delta \theta_{jik})^2 + r_0 \sum_{k>j} k_{r\theta}^{(i)} (\Delta r_{ij} + \Delta r_{ik}) \Delta \theta_{jik}$$

$$+ \sum_{k>j} k_{rr}^{(i)} \Delta r_{ij} \Delta r_{ik} + r_0^2 \sum_{l>k>j} k_{\theta\theta}^{(i)} \Delta \theta_{jik} \Delta \theta_{kil}.$$

Here $\Delta r_{ij}$ and $\Delta \theta_{jik}$ are the changes in the length of the $i$–$j$ bond and the angle between the $i$–$j$ and $i$–$k$ bonds, respectively. The sum is over the nearest-neighbour atoms only. Table 3 gives the coefficients $k_r^{(i)}$, $k_\theta^{(i)}$, $k_{r\theta}^{(i)}$, $k_{rr}^{(i)}$ and $k_{\theta\theta}^{(i)}$.

**Table 3.** The Musgrave–Pople potential for BN, in eV Å$^{-2}$; $r_0 = 1.5503$ Å.

| Atom | $k_r$ | $k_\theta$ | $k_{r\theta}$ | $k_{rr}$ | $k_{\theta\theta}$ |
|------|-------|-----------|--------------|----------|-------------------|
| B | 16.161572 | −0.315638 | −0.319521 | 4.708087 | −3.244078 |
| N | 16.161572 | 0.833029 | −1.131736 | 6.081233 | −3.776663 |

The introduction of either Be or Mg at the boron site leads to a breathing displacement of 4.7% and 14.1% respectively in the N nearest neighbours. These values become 4.9% and 14.9% for the negatively charged complexes. We then investigated the structure and vibrational modes of the Be–H and Mg–H complexes.

Seven possible sites (figure 1) for H were investigated to ascertain the most stable defect. These include the bond centre (C), a site anti-bonding to the impurity or host atom (A, F), puckered bond-centre sites (B, D), a site between two N neighbours (E) and a remote bond-centre site (G). The relative energies for the Be–H and Mg–H defects are listed in table 4.
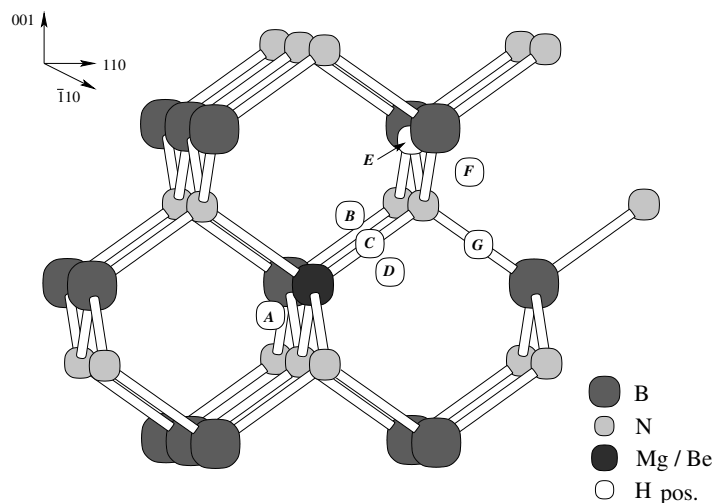


**Figure 1.** Configurations investigated for a hydrogen atom passivating Be and Mg in c-BN.

For Be–H, the lowest-energy configuration corresponds to the puckered bond-centre B shown in figure 1 and is similar to a configuration found previously for hydrogen [10]. H is bonded to Be and a N neighbour of Be, with a Be–N–H angle of 44°. The N–H, Be–H bond lengths are 1.07 and 1.45 Å respectively. The Be–N bond is increased by 17% relative to that in the Be acceptor. The binding energy for H with Be was estimated to be 1.45 eV from the difference in energies of the dissociated and bound centres evaluated in the same supercell.

**Table 4.** Relative energies (eV) for the seven hydrogen sites investigated and shown in figure 1.

| H sites | Mg–H | Be–H |
|---------|------|------|
| A | 2.008 | 1.326 |
| B | 0.230 | 0 |
| C | 0.368 | 0.167 |
| D | $\Longrightarrow$C | 0.154 |
| E | $\Longrightarrow$F | $\Longrightarrow$B |
| F | 0 | 0.512 |
| G | $\Longrightarrow$D $\Longrightarrow$C | $\Longrightarrow$D |

The energies for the Mg–H complexes are also listed in table 4. The stable configuration corresponds to a N anti-bonding site labelled F in figures 1 and 2 similar to the complex in GaN. The N–H and Mg–N bond lengths are respectively 1.01 Å and 1.79 Å. The binding energy of 1.48 eV for H with Mg was found as described above for Be.
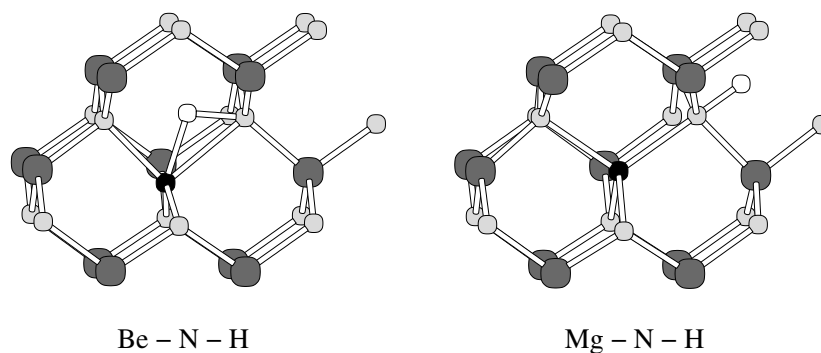


Be − N − H          Mg − N − H

**Figure 2.** Lowest-energy structures for the Be–N–H and Mg–N–H complexes. The notation is the same as for figure 1.

Figure 3 shows the Kohn–Sham energy levels for BN, $Be_B^-$, $Mg_B^-$, Be–H and the Mg–H defects in the 64-atom cell corresponding to $k = (0.25, 0.25, 0.25)$. It is clear that Be and Mg are acceptors and that the hydrogenated centres are passive.

The calculated H-related vibrational modes are given in table 5. The stretch mode lies at 3315 cm$^{-1}$ and is similar to those of the corresponding Mg–H defects in c- and w-GaN [18–20]. We also find a resonant E wag mode near the top of the one-phonon maxima but the method is less accurate in this region. This mode is IR active and in principle might be observed.

**Table 5.** H-related vibrational modes, in cm$^{-1}$, for Mg–H and Be–H defects.

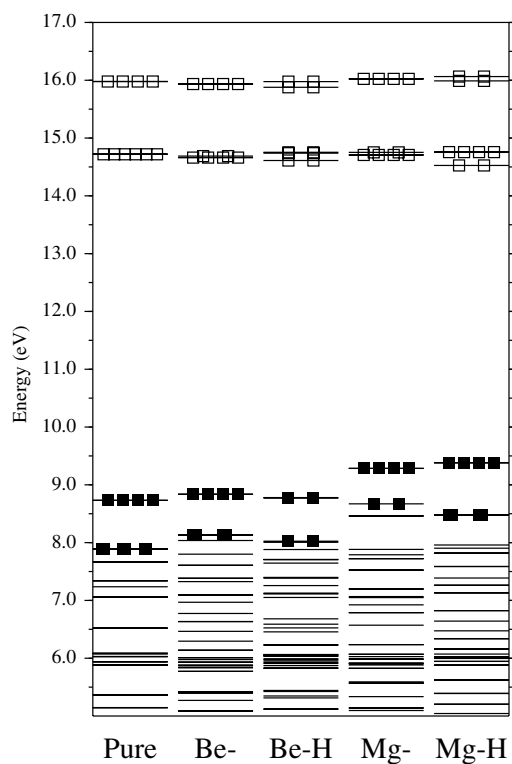| | | $^{14}$N | | | | $^{15}$N | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mode | $^{10}$B–H | $^{11}$B–H | $^{10}$B–D | $^{11}$B–D | $^{10}$B–H | $^{11}$B–H | $^{10}$B–D | $^{11}$B–D |
| Mg–N–H | $A_1$ | 3316 | 3316 | 2418 | 2417 | 3309 | 3309 | 2408 | 2408 |
| | E | 1219 | 1195 | 1076 | 1040 | 1218 | 1193 | 1073 | 1038 |
| | $A'$ | 2537 | 2537 | 1873 | 1873 | 2537 | 2537 | 1873 | 1873 |
| Be–N–H | $A'$ | 1958 | 1957 | 1466 | 1465 | 1958 | 1957 | 1465 | 1464 |
| | $A''$ | 1223 | 1218 | 1196 | 1195 | 1214 | 1207 | 1181 | 1180 |

**Figure 3.** Kohn–Sham levels for BN, Be$^-$, Mg$^-$, Be–H, Mg–H defects.

## 4. Conclusions

The calculations show that substitutional Be and Mg are acceptors in cubic BN and are passivated by hydrogen. The position of H is different in the two defects. In BeH, the H atom lies at a puckered bond centre while it lies at the site anti-bonding to a N neighbour in the case of MgH. This difference is undoubtedly due to the different sizes of the impurities. This configuration and its stretch local mode are similar to those of the corresponding complex in GaN. The configuration in BeH is similar to that of CH in GaAs although the H atom lies on the bond in that case.

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