Thermodynamic Stability of Boron: The Role of Defects and Zero Point Motion

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Abstract: Its low weight, high melting point, and large degree of hardness make elemental boron a technologically interesting material. The large number of allotropes, mostly containing over a hundred atoms in the unit cell, and their difficult characterization challenge both experimentalists and theoreticians. Even the ground state of this element is still under discussion. For over 30 years, scientists have attempted to determine the relative stability of α- and β-rhombohedral boron. We use density functional calculations in the generalized gradient approximation to study a broad range of possible β-rhombohedral structures containing interstitial atoms and partially occupied sites within a 105 atoms framework. The two most stable structures are practically degenerate in energy and semiconducting. One contains the experimental 320 atoms in the hexagonal unit cell, and the other contains 106 atoms in the triclinic unit cell. When populated with the experimental 320 electrons, the 106 atom structure exhibits a band gap of 1.4 eV and an in-gap hole trap at 0.35 eV above the valence band, consistent with known experiments. The total energy of these two structures is 23 meV/B lower than the original 105 atom framework, but it is still 1 meV/B above the α phase. Adding zero point energies finally makes the β phase the ground state of elemental boron by 3 meV/B. At finite temperatures, the difference becomes even larger.

1. Introduction

The element boron has exceptional properties such as a low volatility and a high melting point (2450 °C); it is stronger than steel, harder than corundum, and lighter than aluminum. Moreover, boron has a small reactivity at room temperature. It is under investigation as a constituent in hydrogen storage materials (e.g., LiBH₄), and it is used in high power electronics (LaB₆), in superconductors (MgB₂, Tc = 39 K), in heat-resistant alloys, as wall coatings in nuclear reactors, and as dopant in or alternatives to carbon systems (nanotubes, polymers, diamond, graphite).

Even though there is a wide interest in boron, the element is far from completely understood. As many as 16 boron allotropes are known. The cubic form is only known to encompass 1708 atoms in the unit cell, and the 192 atom tetragonal and the 12 atom α-rhombohedral (AR) crystal structures are the only ones that are well characterized.

However, the most stable polymorph, at least at high temperatures, is the β-rhombohedral (BR) structure. In 1970, a framework consisting of 105 atoms was proposed. Later, in 1988, it was shown experimentally that the unit cell contains 320 valence electrons, where the electron count was corrected by interstitial atoms and partial occupations. At the same time, BR boron was found to be a semiconductor with a band gap of 1.6 eV.

Various theoretical papers were dedicated to finding the BR structure. The first calculations on the BR 105 atom framework were performed by Bullett in 1982. He discusses the electronic structure of AR and BR boron in terms of icosahedra, the building blocks of both structures. Both structures are an attempt of nature to reconcile the 5-fold symmetry of the perfect icosahedra with a space filling crystal structure. In 2001, Jemmis et al. analyzed the bonding in the 105 atom framework by a cluster fragment approach. They divided the structure into B₂₇ and B₁₃ units and used their recent nmo rule to show that the former have electron excess, whereas the latter are electron-deficient. The net count provides a rationalization of the electron...
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2. Computational Methods

First-principles calculations were performed within DFT, using the Perdew–Wang 91 general gradient approximation (GGA) functional.16 In our opinion, a GGA is preferable over standard LDA, as GGAs correct for many of the deficiencies of LDA, such as the well-known over-binding. The projector augmented wave (PAW) method17,18 was used as implemented in the total energy and molecular dynamics Vienna Ab initio Simulation Package (VASP).19–22 Nonlinear core corrections were applied.23

The Kohn–Sham orbitals were expanded in plane waves with kinetic energy cutoffs of 400 eV (the total energy differences listed in Table 3 were calculated with this cutoff). We checked basis set completeness by calculating the total energy difference between AR and BR boron both with 400 and 700 eV cutoff. Changing the cutoff affected the total energy difference by merely 0.03 meV/atom (the total energies finally compared were recalculated using the 700 eV kinetic energy cutoff).

The Brillouin zones were sampled with 10 × 10 × 10 (12 AR), 4 × 4 × 4 (105 and 111 BR), 3 × 3 × 3 (106 BR), and 3 × 3 × 1 (320 BR) Monkhorst-Pack k-point grids,24 resulting in 110, 13, 14, and 5 k-points, respectively, in the irreducible parts. The Brillouin zone integration was performed with a modified tetrahedron method.25

The calculated total energy differences between the boron phases and the β-rhombohedral structures are on the order of several millielectronvolts per atom. Such energy differences may seem small, and one might wonder whether they can be calculated reliably (with a method such as the PAW method). However, they are calculated as energy differences between cells that contain many atoms and are structurally similar. For example, we obtain energy differences of several millielectronvolts/atom when moving one boron atom from one site to another site within an otherwise unaffected cell (save for relaxation in response to the moving atom) of approximately a hundred atoms (see Table 3). The actual energy change for the displacement of this single atom is 2 orders of magnitude larger. Following similar reasoning, the small energy differences between the α- and β-rhombohedral structures can also be reliably calculated, as both phases have many structural similarities, both being based on theicosahedron as a basic building block. Very high accuracies have even been obtained with (more-approximate) pseudopotential methods, such as in the free energy difference between α- and β-Sn.26

### Table 1. Optimized Crystal Structure of α-Boron, Space Group R3m (No. 166), Compared to the Experimental Structure

<table>
<thead>
<tr>
<th>site</th>
<th>Wyckoff position</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tr>
<td>B13</td>
<td>18h</td>
<td>14.0</td>
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<td>13.1</td>
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<tr>
<td>B16</td>
<td>18h</td>
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<td>4.9</td>
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</tr>
<tr>
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<td>18h</td>
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<td>1.5</td>
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<tr>
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<td>18h</td>
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<td>1.3</td>
</tr>
<tr>
<td>B19</td>
<td>18h</td>
<td>1.3</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>B20</td>
<td>36h</td>
<td>0.0</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>22.1</td>
<td>23.5</td>
<td>23.4</td>
</tr>
</tbody>
</table>

### Table 2. Partial Occupation (Number of Atoms) of Sites of BR Boron according to Slack et al.7 for the Three Samples Reported (A, B, and C)

<table>
<thead>
<tr>
<th>site</th>
<th>Wyckoff position</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tr>
<td>B18</td>
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<td>1.3</td>
</tr>
<tr>
<td>B19</td>
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<tr>
<td>B20</td>
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<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>22.1</td>
<td>23.5</td>
<td>23.4</td>
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</tbody>
</table>

### Table 3. Total Energies (meV/B Relative to the BR 105 Structure) and Description of All Calculated Structures of BR Boron, Indicating the Vacant B13 and the Filled B16–20B Sites (The Nomenclature Introduced in the Text is Used to Describe the Unit Cell)

<table>
<thead>
<tr>
<th>system</th>
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<th>B13</th>
<th>B14</th>
<th>B16</th>
<th>B17</th>
<th>B18</th>
<th>B19</th>
<th>B20</th>
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<tr>
<td></td>
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<td>-B13</td>
<td>+B16</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
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<td>-</td>
<td>100</td>
</tr>
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<td>16</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>16</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>-</td>
<td>-</td>
<td>-18</td>
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<td>a</td>
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<td>b</td>
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<td>-</td>
<td>-</td>
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<td>a</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>a</td>
<td>-</td>
<td>-</td>
<td>12a</td>
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<tr>
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<td>c</td>
<td>c</td>
<td>b</td>
<td>-</td>
<td>-</td>
<td>23</td>
</tr>
</tbody>
</table>

Phonon frequencies were calculated using a finite difference method.\(^\text{(27)}\) Displacements of 2 mA and supercells of \(2 \times 2 \times 2\) primitive cells for AR boron and the primitive cell for BR boron were found to give frequencies numerically converged to within 1 cm\(^{-1}\). From the phonon modes, we calculated the ZPEs and temperature-dependent crystal free energies in the full Brillouin zone. The ZPEs are estimated to be converged to within 0.1 meV/B.

### 3. \(\alpha\)-Rhombohedral Boron

The crystal structure, bonding, and lattice dynamics of AR boron are well understood and described extensively in the literature, (e.g., Bullet\(^\text{9}\) or Vast et al.\(^\text{28,29}\) and references therein). However, we need a very accurate total energy for AR boron to determine whether AR or BR boron is most stable. We therefore performed a relaxation of all atomic and cell parameters and calculated the total energy and electronic DOS. Table 1 shows that both the lattice parameters and atomic positions of the fully relaxed cell agree with the experimental values to a degree that is usual for DFT calculations.

The total energy of the experimental cell with relaxed atomic positions is \(-6.6879\) eV per boron atom (eV/B). Relaxing the cell parameters as well lowers the total energy by only 0.2 meV/B to \(-6.6881\) eV/B. The energies are relative to those of non-spin-polarized atoms. The calculated packing fraction in this cell is 41% (the packing fractions are calculated using a radius of 0.89 Å for the boron atoms). The calculated bulk modulus is 208 GPa, where the experimental values range from 213 to 224 GPa.\(^\text{31}\) Previously calculated bulk moduli range from a value of 205 GPa,\(^\text{17}\) to 211 GPa.\(^\text{23}\)

In Figure 1, the calculated electronic DOS of AR boron is shown. AR boron has an indirect band gap of 1.54 eV and a direct band gap of 1.94 eV. Dipole-allowed optical transitions have an onset at 2.59 eV. Previous calculations produced indirect band gaps of 1.4–1.7 eV,\(^{33,35,36}\) and direct gaps from 1.8 to 2.3 eV.\(^{9,33,36}\) On the basis of optical experiments, Horn suggests a (direct) gap of approximately 2.0 eV.\(^\text{37}\) Terauchi et al.\(^\text{38}\) derived a (direct) optical gap of 2.4 eV from their electron energy loss experiment. In general, the calculated results are in reasonable agreement with experiments.

### 4. \(\beta\)-Rhombohedral Boron

1. **105 Atom Framework and B16 Interstitial Position.**

The 105 atom framework for BR boron that was proposed by Hoard\(^\text{6}\) is very open and consists of 15 nonequivalent boron positions (B1 up to B15). It is well described in the literature (e.g., Jemmis et al.\(^\text{10}\)) and shown in Figure 2. We only mention here that the single B15 atom, at the center, connects two B\(_{28}\) fragments by bonding to the six atoms at B13 sites. This framework is the starting point for further study. The BR structure has space group \(R3m\) (No. 166) with lattice constants \(a = 10.139\) Å and \(\alpha = 65.2^\circ\).\(^\text{6}\) These values were used for all BR structure calculations up to the point where the AR and BR structures are finally compared. Of course in all those calculations the atomic positions were optimized.

The calculated electronic DOS of this structure is plotted in Figure 3. There is an energy gap of 1.13 eV at an electron count of 320, whereas the structure itself holds 315 electrons. The

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**Figure 1.** Electronic DOS (states/eV/B), energy relative to \(E_F\), of AR boron. Integrated DOS (IDOS) (number of electrons/36) is also plotted.

**Figure 2.** Side view of the unit cell of 105 atom BR boron. Most atoms are part of icosahedra. The central atom (purple) is in the B15 position and connects the two groups of three interpenetrating icosahedra via atoms at B13 sites (red).

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DOS compares well with the calculated band structure by Prasad et al., which has a gap of 1.03 eV. In their calculation, however, the 105 atom BR structure is 280 meV/B less stable than the AR structure while we only find a difference of 26 meV/B. We do not understand this large discrepancy.

Häussermann et al. found an energy difference of 20 meV/B, which agrees well with our value. Nevertheless, BR boron is known to be a semiconductor. This indicates that additional atoms are required.

The BR structure was experimentally refined by Callmer et al. They found one additional boron position (B16) that was fully occupied and so obtained a unit cell of 111 atoms. After structural relaxation, we find that this structure is 100 meV/B less stable than the 105 atom framework. The DOS of the refined structure is also shown in Figure 3. The energy gap is now 0.84 eV and is positioned below \( E_F \).

### 4.2. Partial Occupations

Further experimental refinement of the BR boron structure by Slack showed that the (hexagonal) unit cell contains 320 atoms with lattice constants \( a = 10.93 \, \text{Å} \) and \( c = 2.178 \, \text{Å} \). This results in a density of 2.333 g/cm\(^3\) and a packing fraction of only 38%, which is lower than the value for AR boron. The atoms are distributed over four additional sites (B17 up to B20), and the previously mentioned B13 and B16 positions are also partially occupied. The atomic occupation numbers of the B13 and B16–B20 sites for the three samples reported are given in Table 2.

Jemmis et al. analyzed the bonding in the 105 atom framework by means of electronic structure calculations in the molecular fragments approach. They find that three B13 sites must be vacant and eight boron atoms should be distributed over B16, B19, and B20 sites to saturate all bonds in the hexagonal unit cell. The B16, B19, and B20 sites are placed around the so-called “A” hole in the framework and form tetrahedra. These tetrahedra are connected in triples by means of the atoms at the B16 sites.

The B13, B16, and B19 positions are depicted in Figure 4. The left panel shows that the partially occupied sites are located in three equivalent slabs in the hexagonal unit cell. Each B17 site (not shown for clarity) is located very close to two B13 sites and is somewhat displaced toward the middle of the slab.

In the following, we will consider several structures in unit cells containing up to 320 atoms that are approximations to the experimental ground state structures. The (free) energies of those structures provide an upper bound to those of the experimental structures.
However, these structures are still electron-deficient. Imai et al. of 320, has decreased quite somewhat to 0.65 eV (Figure 6).

The first step to the ground state structure is to consider single atom substitutions in the 105 atom framework. Theory\textsuperscript{10} and experiments (see Table 2) agree that at least one B13 site is vacant and one atom should be added at a B16 site. This is precisely what was done by Imai et al.,\textsuperscript{12} but it was not mentioned at which B16 site the boron was added. Furthermore, no structural relaxation was included. The energy decreased by no less than 20 meV/B, but they indicate that their kinetic energy cutoff was not large enough to have reached convergence. The DOS from these calculations has a large band gap of 1.3 eV above $E_F$. This gap is reproduced (1.4 eV) in our DOS, as shown in Figure 6. In our structure (labeled 105B16, see Table 3), the atom at the $\alpha$B13 site is moved to the (nearest) $\alpha$B16 site. This decreases the energy by 10 meV/B. Recently, Masago et al.\textsuperscript{14} also calculated the effect of B13$\rightarrow$B16 swaps, considering all B16 sites possible within the 105 atom unit cell. They find that the energy decreases by 4 meV/B. We attribute this difference to the different exchange-correlation functionals used; Masago et al. used plain LDA, whereas we employ the Perdew–Wang '91 GGA.\textsuperscript{16}

Motivated by symmetry considerations, we subsequently added an atom at the $\alpha$B16 site (106B16a). The energy lowers by another 8 meV/B. The gap in the DOS, at an electron count of 320, has decreased quite somewhat to 0.65 eV (Figure 6). However, these structures are still electron-deficient. Imai et al.\textsuperscript{12} also considered a 106 atom structure, where they occupied a B17 site. It resulted in a raising of the total energy per atom compared to the 105 atom framework, which is presumably due to not having carried out a structural relaxation.

Next, total energy calculations were done in the (three times as large) hexagonal 320 atom unit cell. We considered three vacant B13 sites and various distributions of the eight interstitial atoms. We conclude the following from these calculations: (1) A B17 site can only be occupied when two neighboring B13 sites are vacant. (2) Simultaneously, the neighboring B18 sites must be filled. (3) A B16 and B19 boron should not neighbor an occupied B17 site. (4) It is, in fact, favorable to leave the B17 and B18 positions vacant altogether. (5) At each side of a slab, at least one B16, B19, or B20 site should be occupied. (6) No neighboring B16, B19, and B20 sites should be filled simultaneously. (7) The opposite interstitial sites (e.g., $a$ and $\bar{a}$) in one slab should not be occupied simultaneously. (8) A filled B19 site is slightly more stable than a B20 site. (9) The filled B16 sites are more stable than the B19 interstitial sites. (10) When a B19 site is occupied, it should neighbor a vacant B13 site.

The picture that emerges from these considerations is that in addition to the three vacant B13 sites the eight interstitial boron atoms should be distributed over six B16 and two B19 interstitial sites as homogeneously as possible in accordance with previous work by Jemmis et al.\textsuperscript{10} Both occupied B19 sites should lie along the same vector as a vacant B13 site (e.g., a $2\alpha$ and $3\alpha$B19 where the $2\alpha$ and $3\alpha$B13s are vacant).

In the discussion of their X-ray data, Slack et al.\textsuperscript{7} note that B17 is probably only occupied whenever the neighboring B13E and B13D (in the notation of Slack) are vacant. Indeed, we also observe that a B17 atom can only occur if two neighboring B13 sites are vacant. Moreover, we find that the neighboring B18 site has to be filled simultaneously. This gives support to the suggestion by Slack et al. that B17 and B18 atoms occur in pairs. However (item 4 above), we also see that it is energetically not favorable to occupy any B17 and B18 positions. Slack et al. also postulate that B19 and B20 occur in pairs. However, such pairs only occur when a neighboring B16 is present. Our findings suggest such triples are not energetically favorable.

Slack’s samples were grown from the melt. Defects (complexes) that are unlikely from total energy considerations may be stabilized by entropic effects at elevated temperatures and could be “frozen” into the samples upon cooling. We believe this may explain the partial agreement between our total energy studies and the experimental results.

We now use conclusions listed above to further improve the 106 atom structure. When an atom is moved from the $\alpha$B16 to a $\bar{b}$ site (106B16b), the energy decreases by 5 meV/B, resulting 23 meV/B below the 105 structure. The gap in the DOS splits into two gaps, one of 0.35 eV at $E_F$ and one of 1.0 eV at an electron count of 320 (Figure 7). The peak above the Fermi level is analyzed to belong to atoms between the (vacant) $\alpha$B13 and the (occupied) $\alpha$B16 sites. We move the atom at the $\alpha$B16 site to the $\alpha$B19 site (106B19) since the B19 site is closer to the B13 site than the B16 site. (Two B19 atoms are needed anyway in the 320 atom unit cell, and this is a good check on

![Figure 6. Electronic DOS (states/eV/B), energy relative to $E_F$, of 105B16 (blue, lower graph) and 106B16a (red, upper graph) atom BR boron. The $\alpha$B13 atom is removed, and the $\alpha$B16 and the $\pm\alpha$B16 atoms are added, respectively. The Fermi levels are indicated with vertical lines, and the IDOS (number of electrons/320) is also plotted.](image1)

![Figure 7. Electronic DOS (states/eV/B), energy relative to $E_F$, of 106 atom BR boron. Integrated DOS (number of electrons/320) is also plotted. The $\alpha$B13 atom is replaced by the $\bar{b}$B16 boron and, respectively, the $\alpha$B16 (106B16b) (red, upper graph) and the 106B19 (blue, lower graph) boron.](image2)
has an observed (optical) gap of 1.6 eV. The gap of 320B19 is
and therefore cannot represent the experimental structure which
and a fairly large gap (0.6 eV) just above. It is no semiconductor
of 320EXP has a small gap (0.2 eV) just below the Fermi level
DOSs of 320B19 and 320EXP are displayed in Figure 8. That
energies of the 320 atom structures are not improved over that
concerning the total energy and the gap in the DOS. The total
interstitial sites in the calculations are brought together in
Figure 7, there is also a localized state above the valence band. It only has contributions from a handful of
neighbors, and transitions from the valence band to
state are dipole forbidden (both have only $p$ character). The
optical gap that results is at least 1.4 eV, in good agreement
with experimental findings. If two additional electrons (from,
e.g., carbon impurities) fill the localized state, it would act as
a hole trap instead of an electron trap, as found in experiment.
Moreover, the two impurity electrons would also bring the total
number of electrons in the unit cell to 320, which would make
the agreement with experiment nearly perfect.

We like to stress that although the 106B16b structure is still
electron-deficient it exhibits an electronic structure very similar
to that of experiment for a specific configuration of a B13
vacancy and two occupied interstitials. This, and it having
the lowest energy calculated, strongly suggests that such combina-
tions of defect sites are an essential building block of BR boron.
In terms of partial occupancies, this structure has B13 (83%),
B16 (33%), B17, and higher (0%). The average occupancy of
the samples studied by Slack give B13 (75%), B16 (27%), B17
(7%), B18 (7%), B19 (7%), and B20 (2%). Given that the
106B16b only has three defects (one vacancy and two intersti-
tials), the compositions agree well; indeed, with only three
defects, one can hardly approach the experimental compositions
better. So there seems ample room within the experimental
constraints for 106B16b defect complexes to occur in large
quantities. Moreover, Slack’s experimental samples may contain
“frozen-in” defect structures that are not stable at low temper-
atures, as noted above. Therefore, perfect agreement with
experiment is not to be expected. Of course, many other defect
configurations than 106B16b can also occur. Interestingly, Slack
et al. do not point out correlations between the occupation of
B16 sites, where we do find that a specific configuration of
B16 occupations gives a considerable lowering of the total
energy. We speculate that such correlations might have been
overlooked, as the B16 atoms involved are at a considerable
distance apart. It might be an interesting topic for further
experimental investigation.

Finally, we also relaxed the lattice parameters (including the
cell volume) of the 106B16b structure. This led to a decrease
of 0.4% in the volume and marginal changes in the lattice
parameters. (Because of the interstitials, the rhombohedral
symmetry is broken. As mentioned, changes are very small. The
positions and cell parameters are included in the Supporting
Information.) We found a bulk modulus of 199 GPa which
agrees excellently with the experimental values of 185–210
GPa. With the same high kinetic energy cutoffs as that used
for the AR structure, the total energy of this structure becomes
$-6.87 eV/B$. We conclude that on the basis of total energies
the AR boron is 1 meV/B more stable than the most stable
BR structure found.

5. Zero Point Energy and Temperature Dependence

Comparing total energies from static electronic structure
calculations alone neglects the ZPE of a system. Whereas for
heavier elements neglecting the ZPE is reasonable, for the lighter
elements, including boron, it is not. Therefore, in the optimized

6813.
1–4.
(45) Beckel, C. L.; Yousaf, M.; Fuka, M. Z.; Raja, S. Y.; Lu, N. Phys. Rev. B
cells, we calculated the phonon frequencies. The number of atoms in the unit cell differs greatly between AR and BR boron. This causes the band dispersion of the phonon modes to have a large (relative) effect: For AR boron, the difference in ZPE with (using full Brillouin zone integration) and without (using only the Γ-point phonons) band dispersion is 3 meV/B, whereas for BR, it is only 0.2 meV/B. This is mainly caused by the acoustic modes that do not contribute when using only Γ-point phonons. In AR boron, the acoustic modes account for 1/12 of the total number modes, whereas in BR, they account for only 1/106. All phonon contributions reported here are, therefore, integrated over the entire Brillouin zone.

In Table 4, the calculated Γ-point frequencies for AR boron are compared to experimental values. They agree extremely well. By integrating phonon frequencies over the Brillouin zone, we obtain a ZPE of 130 meV/B. This brings the total energy, including ZPE, of AR boron to −6.558 eV/B.

The same procedure was carried out for the most stable 106 structure (106B16b). This gave a ZPE of 126 meV/B, bringing the total energy, including ZPE, of 106B16b BR boron to −6.561 eV/B. For the first time, this gives a BR energy lower than that of AR boron.

The above-reported total energies are, in fact, the Helmholtz free energies at 0 K. At higher temperature, the phonon modes are occupied according to Bose–Einstein statistics. In the harmonic approximation, the Helmholtz free energy is determined by the harmonic lattice vibrations, that is, the phonons, at a volume V,\(^{46}\)

\[
F(V,T) = U_0(V,T) + \frac{1}{\Omega_{BZ}} \times \sum_i \int_{BZ} \left( \frac{\hbar \omega_i}{2} + \ln(1 - e^{-\hbar \omega_i / k_B T}) \right) dq
\]

The first term, \(U_0\), is the total energy of the crystal. The integration is over the entire Brillouin zone of which \(\Omega_{BZ}\) denotes the volume. A modified tetrahedron integration method was used.\(^{25}\) The first term in the integral is the zero point energy, where \(\omega_i\) are the phonon angular frequencies at wave vector \(q\). The second term in the integral refers to the thermally induced occupation of the various phonon modes.

We fix the volume to the equilibrium value at 0 K and neglect thermal expansion. The bulk moduli of the AR and BR structure are rather similar, so we expect the differences in thermal expansion to be small as well. Since we are only interested in the differences between AR and BR boron, we assume this to be a good approximation.

At finite temperature, there is also a contribution to the free energy from the configurational entropy (CE):

\[
\Delta F^{\text{CE}} = -k_B T \ln \left( \sum_i g_i e^{-E_i / k_B T} \right)
\]

where \(g_i\) and \(E_i\) are the multiplicities and energies of the various (defect) structures. For BR boron, many defect structures are possible. At a certain temperature and in thermodynamic equilibrium, only those structures significantly contribute whose energies are within \(k_B T\) of the ground state structure. If we only consider the multiplicities of the lowest energy structures (106B16b and 320B19), the \(\Delta F^{\text{CE}}\) is −0.6 meV/B at 300 K. At higher temperatures, the configurational entropy will push down the BR free energy even more. Moreover, well above room temperature, other structures become thermodynamically favorable, and we expect that BR boron is further stabilized. AR boron, on the other hand, has no intrinsic defects at low temperatures and hence no CE contribution. Since the CE effects are small below 300 K, they will not be considered further.

The free energies as a function of temperature are depicted in Figure 9. The difference between AR and BR boron at higher temperatures is marginally larger than that at 0 K. This means that BR boron is the thermodynamically stable allotrope, in correspondence with experimental findings. At temperatures well beyond room temperature, the entropy of the defects will become considerable and thus will stabilize the BR structure even more.

6. Conclusions

To summarize, we used first-principles (DFT, GGA) calculations on BR and AR boron to determine the boron ground state
structure. The calculated properties of AR boron, including Γ-point phonon modes, electronic band gap, and bulk modulus, compare very well to experimental values.

The BR 105 atom framework is 26 meV/B higher in energy than AR boron but is stabilized by partial occupations and interstitial atoms. The most stable structure is a 106 atom structure with one B13 site vacant and two atoms added at specific B16 sites. On the basis of this structure, we also constructed a 320 atom unit cell that is nearly as stable. Both are semiconductors with a gap of 0.35 eV. The (optical) gap of the 106 atom structure is (at least) 1.4 eV, which compares favorably with the experimental gap of 1.6 eV.

Relative to AR boron, these structures are still 1 meV/B higher in energy. However, taking the ZPE into account, the BR 106 atom unit cell boron wins at 4 meV with respect to AR boron and becomes the most stable one. Including temperature effects does not change this picture.

Finally, the experimentally determined atomic occupations of BR boron were modeled in a unit cell of 320 atoms. This structure, however, is 6 meV/B higher in energy than the most stable one, and it is no semiconductor.

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Supporting Information Available: Unit cell and positions of the 106B16b structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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