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# Boron hydrogen in crystalline form

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## Abstract

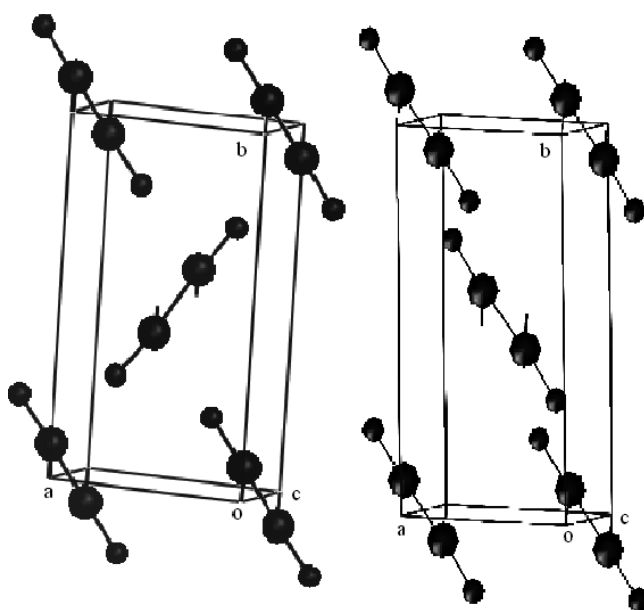
In a three-dimensional crystal two different orientations of boron hydrogen chains have been considered. The geometrical orientations of the chains are based on the space groups  $P2_1/a$  and  $P2_1/n$  depending on whether the single bond–double bond pattern on the two chains in the unit cell is in phase or antiphase, respectively. Using the full potential linearized augmented plane waves (FP-LAPW) density functional theory within the generalized gradient approximation, the optimal volumes, the ground state energies, band structures and the density of states of levels have been reported. Our results show that the in-phase pattern behaves as a poor conductor while the antiphase has a gap of 0.5 eV.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Boron compounds have many important industrial applications in high-temperature semiconductors [1], high density fuels [2] and the aerospace industry [3, 4]. Therefore, boron compounds in one, two and three dimensions in general have been a subject of interest for many authors over the last decade.

The ground and excited states of an icosahedral  $B_{12}H_{12}$  cluster simulating the  $B_{12}$  cluster in  $\beta$  rhombohedral boron have been calculated by Fujimori and Kimura [5] using the *ab initio* self-consistent field–molecular orbital (SCF–MO) method. They found the excited state positioned at roughly 1.5–2.0 eV. Systematic investigations on two- and three-dimensional bare boron clusters of up to 46 atoms predicted the existence of nanotubular, convex and spherical clusters as well as of quasiplanar surfaces as a series of parallel layers analogous to graphite [5–9]. A one-dimensional linear chain of boron was studied at the linear muffin-tin orbital (LMTO) level [6]. *Ab initio* quantum chemical methods were used to study the ground state energies and geometrical configurations of boron and boron hydrogen  $(BH)_n$  chains [10]. We found that  $(BH)_n$  possesses a band gap of 0.6 eV and a zig-zag structure. Such properties could lead to a new class of semiconductors and therefore to new applications.



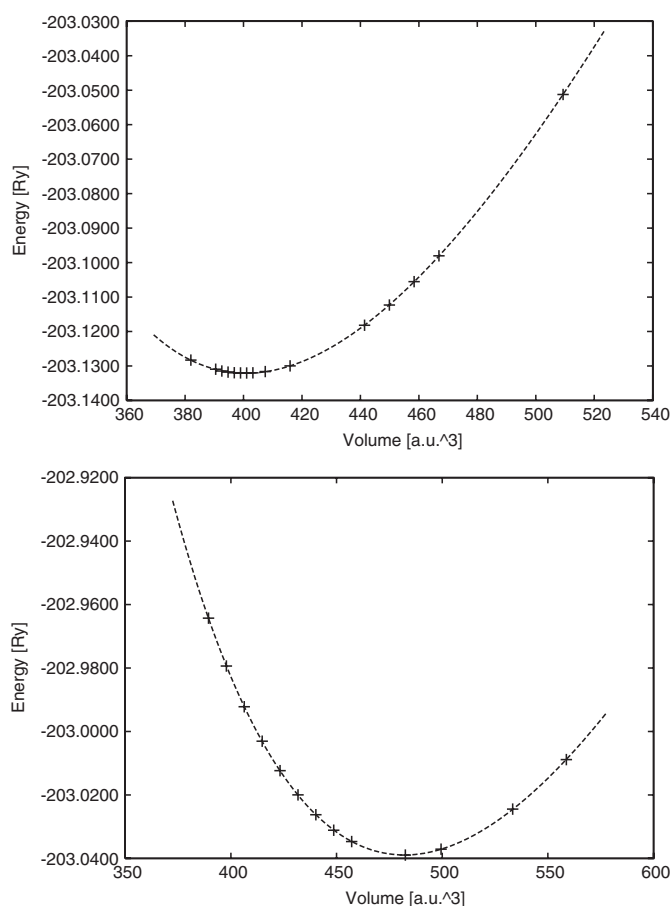
**Figure 1.** The unit cell of the  $P2_1/n$  antiphase (left) and the  $P2_1/a$  in-phase (right) configurations of the  $(BH)_n$  chain.

Isolated  $(BH)_n$  chains are not expected for real systems, but they may be ordered in 2D forming a sheet or in 3D forming a crystalline structure. The pyrolysis of diborane produces a variety of borane products as  $B_{10}H_{14}$  [11]. This work does not set out to span all possible structures, but to focus on calculations of the monoclinic structure.

## 2. Characterization of the three-dimensional structure of trans- $(BH)_n$

*Ab initio* quantum chemical methods in the frame of the Hartree–Fock self-consistent-field approximation (HF-SCF), and the Møller–Plesset second-order perturbation theory (MP2), that is implemented in the GAMESS-UK code [12], were employed to determine the ground state energies and the geometrical structures of  $(BH)_n$  chains [10]. For the purpose of the optimization we have chosen four degrees of freedom  $r_1$ ,  $r_2$  and  $\theta$  to allow bond alternation between successive boron atoms and the B–H bond. The resulting equilibrium bond lengths are  $r_1 = 1.67 \text{ \AA}$  and  $r_2 = 1.59 \text{ \AA}$ , respectively. They correspond to single and double bonds. The BH bond length is  $1.17 \text{ \AA}$  and the equilibrium  $\theta$  angle is  $78.72^\circ$ . Starting from these values we build the proposed monoclinic unit cell.

The unit cell contains two transplanar  $B_2H_2$  chain units. Two possible orderings of the adjacent chains in the unit cell are proposed. These configurations are consistent with the space groups  $P2_1/a$  (in-phase) and  $P2_1/n$  (antiphase) as shown in figure 1. In order to characterize these two structures, the following lattice constants should be known:  $a$ ,  $b$ ,  $c$  and the monoclinic angle  $\beta$ . We estimate the lattice constants to be  $a = 4.1865$ ,  $b = 7.3514$ ,  $c = 2.0532 \text{ \AA}$  and  $\beta = 90.5^\circ$ , bearing in mind that the optimization parameters of a single chain should be retained in the 3D structure and the geometry of the unit cell. The positions of the atoms in the unit cell can be obtained trigonometrically. The bond lengths are within  $\mp 0.02 \text{ \AA}$  and the angle  $\theta$  is within  $\mp 0.02^\circ$  of the isolated chain values.



**Figure 2.** Total energies of the antiphase (top) and in-phase (bottom) configurations of the  $(BH)_n$  chain in terms of the volume of the unit cell.

### 3. Results

#### 3.1. Structural optimization

The full potential linearized augmented plane waves (FP-LAPW) density functional theory within the generalized gradient approximation [13] that is implemented in the WIEN2k code [14] has been used to investigate the above two structures. Before proceeding with the calculations, two parameters have to be optimized for both structures,  $k$ -mesh and  $K_{\max}$ . Starting from the above initial geometry we found that 1400 points in the Brillouin  $k$ -mesh and  $K_{\max} = 4.0$  were enough to give a total energy that is accurate up to 1 mRyd, and the field gradient accurate to a few per cent. The second step in the calculations is to optimize the volume and consequently to find the precise positions of the atoms in the unit cell, for the found  $k$ -mesh and  $K_{\max}$ . Figure 2 shows the total energies of the in-phase and antiphase configurations in terms of the volume of the unit cell. Where the minimum energy of the  $P2_1/a$  in-phase structure reaches  $-203.03891$  Ryd at volume  $71.778 \text{ \AA}^3$ , it is  $-203.13208$  Ryd at  $59.679 \text{ \AA}^3$  for  $P2_1/n$  antiphase. In practice the ground state configuration will be in favour of the  $P2_1/n$  antiphase.

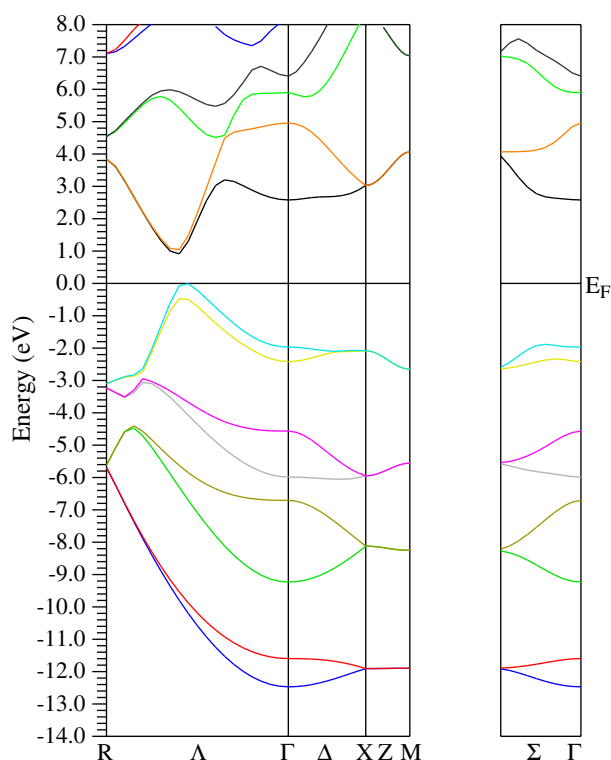


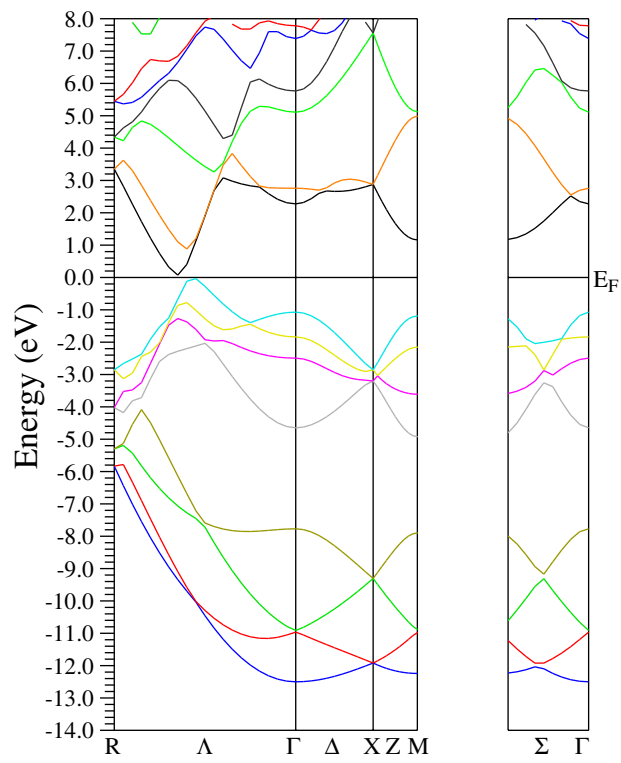
Figure 3. Band structure of the antiphase configuration of  $(\text{BH})_n$ .

### 3.2. Band structure and density of states

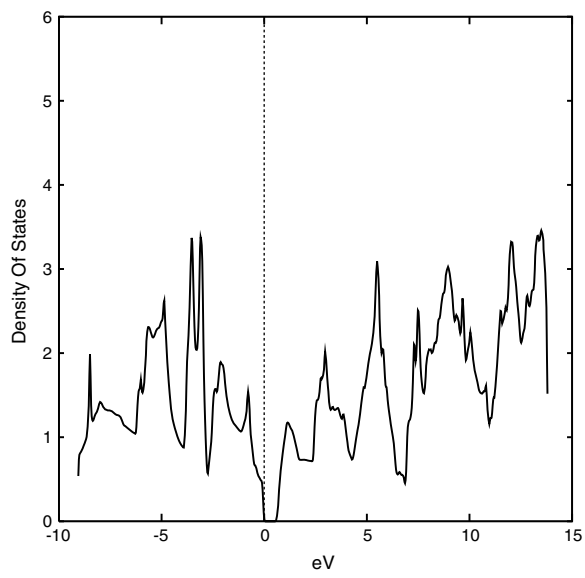
The boron atoms hybridize in the  $sp^2$  form in the isolated chain due to bond conjugation and produce four energy bands in total in one dimension. In the 3D crystalline structure, as shown in figures 3 and 4, these bands split, leading to eight bands for both configurations. The amount of splitting is proportional to the dimerization and the overlapping between adjacent chains. Figure 3 represents the antiphase  $P2_1/n$  ordering band structure, where a gap opens at the Fermi level at the top of the valence band as shown in the DOS plot (figure 5).

This band gap equals 0.5 eV which is less than the isolated chain value [10] due to the weak interchain interaction in 3D. The nearest distance between the hydrogen atoms  $d_H - d_H$  in adjacent chains is about 2.3 Å, while it is 1.25 Å for the in-phase configuration, which allows charge leakage between the adjacent chains leading to stronger overlapping in comparison with the antiphase case and consequently a smaller band gap. Figure 6 represents the DOS of the  $P2_1/a$  configuration and an indirect gap of = 0.1 eV opens at the Fermi level. Such a stronger overlap increases the splitting of the bands, as is clear from the band plot. To confirm this argument, we have enlarged the unit cell along the  $b$  axes until we obtained  $d_H - d_H = 1.85$  Å and then recalculated the band structure for the in-phase case only. The resultant band and the density of states plots, figures 7 and 8, respectively, show a gap similar to the antiphase value and the amount of splitting of the bands decreases.

Characteristic analysis of the band structure of the in-phase and antiphase band structure plots do not indicate any band crossing, i.e. the wavefunctions have similar symmetry. Further



**Figure 4.** Band structure of the in-phase configuration of  $(BH)_n$ .



**Figure 5.** Density of states of the antiphase configuration of  $(BH)_n$ .

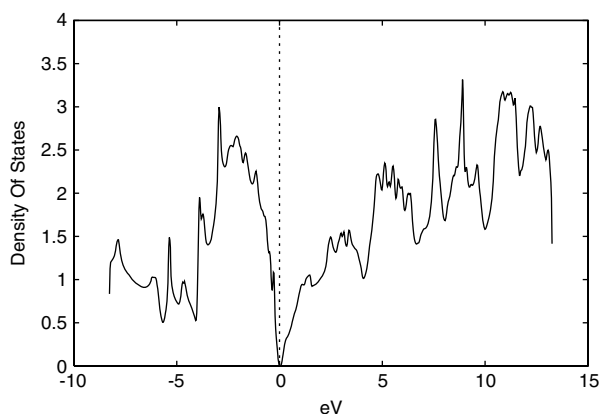


Figure 6. Density of states of the in-phase configuration of  $(\text{BH})_n$ .

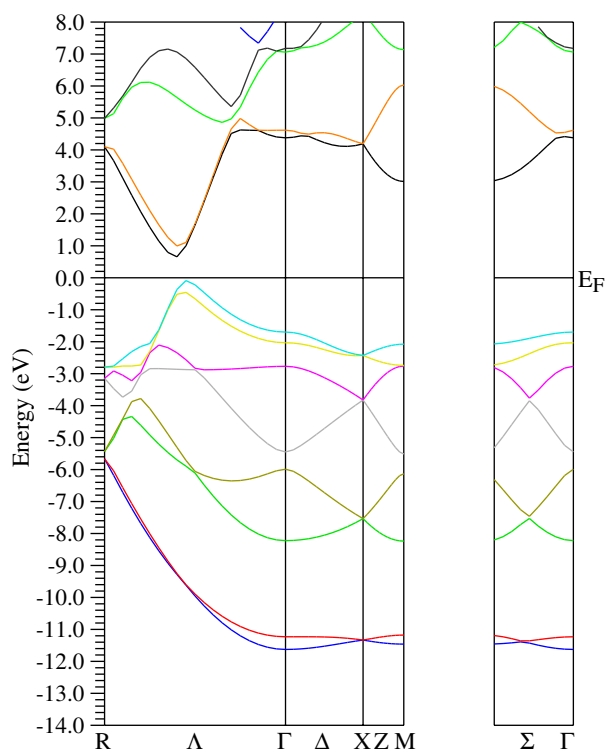
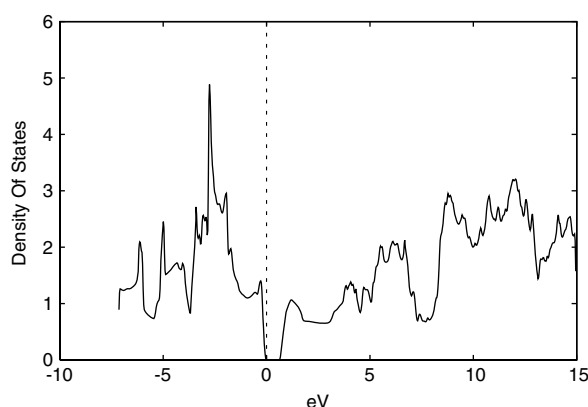


Figure 7. Band structure of the in-phase configuration of  $(\text{BH})_n$  when  $d_{\text{H}} - d_{\text{H}} = 1.85 \text{ \AA}$ .

analysis of the contributions to each band revealed some differences between the in-phase and antiphase structures.

For the in-phase case: the contributions to the upper band of the valence come from  $sp^2$  hybridization between the  $s$  and  $p$  orbitals of the boron atoms. The lowest conduction band comes mainly from the overlap between the hydrogen atoms. The lowest valence band is an  $sp^2$  hybridization of the boron atoms. The second, third, fifth and sixth bands from bottom in



**Figure 8.** Density of states of the in-phase configuration of  $(\text{BH})_n$  when  $d_{\text{H}} - d_{\text{H}} = 1.85 \text{ \AA}$ .

the valence band are formed from the  $sp$  hybridization of the hydrogen atoms. The remaining two in the valence band are due to boron atoms. In the case of the antiphase configuration: the lowest two and the highest two bands in the valence band come from the boron atoms, while intermediate bands are formed by hybridization between hydrogen and boron orbitals. The lowest band in the conduction band is due to boron atoms only.

#### 4. Conclusion

Two different orientations of boron hydrogen chains based on the space groups  $P2_1/a$  and  $P2_1/n$  have been considered. The FP-LAPW density functional theory within the generalized gradient approximation was employed to calculate the optimal volumes, the ground state energies, the band structures and the density states. The volume optimizations show that the  $P2_1/n$  antiphase configuration is lower in energy and therefore expected to exist in real systems. The band structure and the density of states plots predict different electronic properties according to the space groups. While the in-phase structure is a poor conductor due the hydrogen–hydrogen interaction, the antiphase one is a semiconductor with a gap of 0.5 eV which is about half the value found for silicon. In addition, the gap of the in-phase configuration can be scaled as the  $b$  axis of the crystal. Such properties will open up a new era of semiconducting materials and consequently exciting new applications.

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