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Tight-Binding study of Boron structures

Joseph W. McGrady [a], Dimitrios A. Papaconstantopoulos [a,*], Michael J. Mehl [b]

[a] SPACS, George Mason University, Fairfax, VA, USA
[b] Naval Research Laboratory, Washington, DC, USA

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ABSTRACT

We have performed Linearized Augmented Plane Wave (LAPW) calculations for five crystal structures (alpha, dhcp, sc, fcc, bcc) of Boron which we then fitted to a non-orthogonal tight-binding model following the Naval Research Laboratory Tight-Binding (NRL-TB) method. The predictions of the NRL-TB approach for complicated Boron structures such as R105 (or β-rhombohedral) and T190 are in agreement with recent first-principles calculations. Fully utilizing the computational speed of the NRL-TB method we calculated the energy differences of various structures, including those containing vacancies using supercells with up to 5000 atoms.

1. Introduction

Boron is of interest in materials science because it has at least 16 allotropes, making it one of the most structurally complex elements known [1]. Determining the ground state structure of Boron has been difficult, providing another source of motivation for pursuing research of this element. However, it appears that in recent years the uncertainty about the ground structure of Boron may have begun shrinking.

In 2008, Widom and Mihalkovič determined that the slightly disordered β-rhombohedral (R105) structure is actually Boron's true ground state, as opposed to the α-rhombohedral (R12) structure [2]. They performed an optimization of the occupancy configurations of the R105 structure; however all possible configurations were not included. VASP was used with the Local Density Approximation (LDA), as well as the Generalized Gradient Approximation (GGA)-based Ultrasoft Pseudopotential (USPP), and HARD potentials. R105 was found to be lower in energy than R12 using USPP and HARD, but not LDA. Zero-point energy was not included in the calculations, although they state that zero-point energy would make R105 even more stable. Setten et al. found that R105 Boron is above R12 in energy unless zero-point energy is included [3]. There are crystallographic refinements of R105 Boron without any vacancies [4], but they do not reach the true ground state.

In a 2009 paper, Ogitsu et al. also found that R105 Boron is lower than the R12 structure after performing a full optimization of its occupancy configurations using a 1280 atom supercell [5]. Due to the very large number of possible occupancy configurations of the structure, only a small number of first principles calculations using the LDA were performed for a set of representative occupancy configurations. These R105 total energies were then used to create a set of fitting coefficients based on the Ising model which allowed the total energy to be predicted based on the occupancy configuration. Further, they used the symmetry and physical irrelevance of many of the configurations to reduce the number of calculations needed in the optimization. Monte Carlo annealing simulations were performed in order to determine the stable configurations. The most stable structures were then further optimized with respect to the other lattice parameters. Zero-point energy was also included in their total energy results through ab-initio calculation of the phonon density of states of R12 and R105 Boron.

Oganov et al. summarize these recent findings by stating that the controversy over the ground state of Boron has been resolved, with R105 emerging as the true ground state [6]. Our results using an accurate and computationally efficient tight-binding approach reach the same conclusion.

2. Tight-binding method

We have used the NRL-TB method [7–9] in our exploration of the structure of Boron. NRL-TB is advantageous because of its fast performance when compared with first-principle methods such as the LAPW method [10]. In general, the NRL-TB method diagonalizes a $9N \times 9N$ matrix for the s, p, and d orbitals, where N is the

* Corresponding author.
E-mail address: dpapacon@gmu.edu (D.A. Papaconstantopoulos).

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number of atoms in the unit cell. For Boron we have omitted the d orbitals, so we diagonalize only a $4N \times 4N$ matrix. NRL-TB′s fast performance (it is about 1000 times faster than LAPW) makes the TB approach far more practical when dealing with structures with many atoms in the unit cell, as in the present work.

The NRL-TB method is based on a non-orthogonal version of the Slater–Koster two-center formalism [11] and uses a set of parameters fitted to first-principles total energy and energy band results in order to predict the total energies of structures which were not fitted. These parameters can be broken into the on-site parameters, the Hamiltonian parameters, and the overlap parameters. The parameter set is created by performing a non-linear least-square fit to the first-principles data and determining a set of coefficients of two polynomials, listed below.

The on-site parameters depend on the orbital angular momentum and density of neighboring atoms, parametrized by the formula

$$h_{i\alpha} = a_{i\alpha} + b_{i\alpha}\rho_i^{2/3} + c_{i\alpha}\rho_i^{4/3} + d_{i\alpha}\rho_i^2 \tag{1}$$

where ρ_i is the atom density seen from atom i, and is given by the equation

$$\rho_i = \sum_{j \neq i} \exp\left[-\lambda^2 R_{ij}\right] F_c(R_{ij}) \tag{2}$$

where $F_c(R_{ij})$ is a smooth cutoff function, and R_{ij} is the distance between atoms i and j.

The Slater–Koster matrix elements of the Hamiltonian and overlap parameters are found from the equation

$$P_\gamma(R) = (e_\gamma + f_\gamma R + \bar{f}_\gamma R^2) \exp\left(-g_\gamma^2 R\right) F_c(R) \tag{3}$$

where γ is the type of interaction (the interactions are ssσ, spσ, ppσ, and ppπ in the case of Boron), R is the distance between atoms, and $F_c(R)$ is the same cutoff function as the one in Eq. (2). The coefficients $e_\gamma, f_\gamma, \bar{f}_\gamma$, and g_γ are different for the Hamiltonian and overlap matrices, but both have the functional form given in (3).

A shift in the first-principle (in our case LAPW) eigenvalues is performed that simplifies the total energy formula from Density Functional Theory (DFT) by making the sum of the eigenvalues equal to the total LAPW energy. The DFT total energy expression is

$$E[n(\boldsymbol{r})] = \sum_i \epsilon_i + G[n(\boldsymbol{r})] \tag{4}$$

in which $\sum_i \epsilon_i$ is the sum of the eigenvalues over all k-points in the Brillouin zone and $G[n(\boldsymbol{r})]$ comprises the other terms for the DFT total energy. New eigenvalues are created using the equation

$$\epsilon_i' = \epsilon_i + V_0 \tag{5}$$

in which the shift V_0 is given by the formula

$$V_0 = G[n(\boldsymbol{r})]/N_e \tag{6}$$

where N_e is the total number of valence electrons and $n(\boldsymbol{r})$ is the electronic density. After performing the shift, the total LAPW energy is equal to the sum of the eigenvalues:

$$E[n(\boldsymbol{r})] = \sum_i \epsilon_i' \tag{7}$$

The parameters are determined by a non-linear least-square fit using a Levenberg–Marquardt algorithm [12,13] which minimizes the mean-square error:

$$M = \sum_i^j w_E(i)\left|E_{LAPW}(i) - E_{TB}(i)\right|^2 + \sum_{i,k,n} w_B(i,k,n)\left|\varepsilon_{LAPW}(i,k,n) - \varepsilon_{TB}(i,k,n)\right|^2 \tag{8}$$

where $E_{LAPW}(i)$ and $E_{TB}(i)$ are the total energies of the LAPW and Tight-Binding calculations for the ith structure, and $\varepsilon_{LAPW}(i,k,n)$ and $\varepsilon_{TB}(i,k,n)$ are the LAPW and TB eigenvalues, respectively, of the nth band of the kth k-point of the ith structure. The weights $w_E(i)$ and $w_B(i,k,n)$ are chosen so that we can emphasize the relevant parts of the calculation. Typically w_B is of order unity for bands near the Fermi energy, and w_E is between 500 and 1000. The sums are over all structures i, over all k-points k for each structure, and over all valence/conduction bands n that are occupied or within about 1 Ry of the Fermi energy. The RMS error of the total energy fit of Eq. (8) used to construct the parameter set given in Table A2.1 in Appendix 2 is 2 mRy.

3. Total energy results

LAPW calculations for the sc, bcc, fcc, dhcp, and α-rhombohedral (R12) Boron structures were performed and used in a non-orthogonal NRL-TB method fitting to generate a set of 41 Tight-Binding coefficients. The coefficients were calculated only for the s and p orbitals. The d-states were omitted since Boron has only three s and p valence electrons.

The set of parameters listed in Table A2.1 was used to predict the total energies of 15 additional structures which were not fitted, many of which would be difficult to calculate with a first-principle method considering their size and complexity. A k-point mesh was generated for these Tight-Binding calculations, which was on an $8 \times 8 \times 8$ grid.

The method of determining the total energy of a structure was to perform full optimizations for the structures. For structures with only one independently varying lattice parameter, this only required performing a volume optimization by calculating the total energy of the structure for a set of different volumes and obtaining the minimum energy. For structures with more than one independently varying lattice parameter, the entire process of volume optimization was repeated for multiple values of each additional independent parameter, and the minimum from all the configurations was taken as the true minimum total energy for the

Table 1
The per-atom volumes and total energies found for the structures explored are listed in columns 3 and 4, respectively. The table is ordered from lowest to highest total energy. In the first column, additional unit cell information such as angle and c/a is provided. The structures to which the parameters were fitted are marked as fitted in the first column.

Structure	Space group	Volume (Bohr^3/atom)	Total energy (mRy/atom)
R105hex vacancy (c/a=2.18)	$P\bar{3}m1$-D_{3d}^3	51.392	−104.72
R105 (angle=64.74°)	$R\bar{3}m$-D_{3d}^5	51.078	−104.63
T190 (site configuration 588, c/a=1.4)	$P4_2/nnm$-D_{4h}^{12}	49.699	−100.93
γ-28 (b/a=1.11, c/a=1.39)	$Pnnm$-D_{2h}^{12}	46.955	−100.61
R12 (angle=58.5°) **(fitted)**	$P\bar{3}m$-D_{3d}^5	48.507	−100.21
T50 (c/a=0.57)	$P4_2/nnm$-D_{4h}^{12}	51.14	−87.07
aGa (c/a=1.1, angle=120.32°)	$Cmca$-D_{2h}^{18}	44	−75.09
betaSn (c/a=2.31)	$I4_1/amd$-D_{4h}^{19}	44.5	−59.73
c19 (angle=55.6°)	$R\bar{3}m$-D_{3d}^5	43	−55.44
DHCP (c/a=1.21) **(fitted)**	$P6_3/mmc$-D_{6h}^4	42.25	−46.84
A9 (c/a=1.31)	$P6_3/mmc$-D_{6h}^4	47.25	−25.78
C32 (c/a=1.02)	$P6/mmm$-D_{6h}^1	42.67	−17.87
shex (c/a=1.03)	$P6/mmm$-D_{6h}^1	42	−15.19
sc **(fitted)**	$Pm\bar{3}m$-O_h^1	44.739	−11.51
diam.	$Fd\bar{3}m$-O_h^7	57.07	0.97
aHg (angle=53.9°)	$R\bar{3}m$-D_{3d}^5	39	2.69
A6 (c/a=1.29)	$I4/mmm$-D_{4h}^{17}	42	2.98
fcc **(fitted)**	$Fm\bar{3}m$-O_h^5	39.366	4.06
hcp (c/a=2.03)	$P6_3/mmc$-D_{6h}^4	39.5	8.02
bMn	$P(4_1)32$-O^7	39.573	11.64
bcc **(fitted)**	$Im\bar{3}m$-O_h^9	41.156	31.28