

Electronic Energy and Density of states of α - and β - Rhombohedral Boron and Their Related Structures Calculated by a First-Principle Pseudopotential Method Using Plane-Wave Basis.

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Electronic energy and density of states (DOS) of α - and β - rhombohedral boron and the following α -boron related structures have been calculated by a first-principle pseudopotential method using plane-wave basis, CASTEP; (1)face-centered cubic arrangement of boron atoms, (2) face-centered cubic arrangement of regular-icosahedra of B₁₂, and (3) a slightly deformed cubic close packing of the same regular-icosahedra. The calculations gave the results that the slightly deformed cubic close packing of the regular icosahedra, where the rhombohedral angle is *ca.* 58°, is the lowest in electronic energy among the α -boron-related structures considered. The comparison with the case of aluminum has also been conducted. As for DOS of β - boron, partial occupancy of interstitial positions such as B(16) sites would play a key-roll in generation of localized energy levels between energy gap.

Key words: α - boron, β - boron, density of state, electronic energy

1. INTRODUCTION

Although detailed studies on the analysis of crystallographic and electronic structure for polymorphs of elementary boron(B) have been done, the nature of the bonds is still disputable. As they are formed of icosahedral subunits, which contain twelve boron atoms, their properties have usually been understood on the basis of the molecular orbital theory of B₁₂ icosahedron. However, even for the α - rhombohedral boron (α -B), the simplest structure among polymorphs, there is a problem such that which is stronger, intra- or intercluster bonds. The fact that atomic distance of the intercluster bond is shorter than the intracluster in α -B implies that the analysis only on the basis of cluster model might be insufficient^{1*}. In addition, the electronic structure of β -rhombohedral boron (β -B), estimated by Franz and Weber[2], has not been fully understood from the quantum mechanical calculation in spite of earlier Bullet's work[3].

In the present study, a band calculation of α - and β -B and their related structures has been done using a CAMbride Serial Total Energy Package(CASTEP)[4], which is the total energy pseudopotential method based on the density-

functional theory (DFT) using plane-wave basis.

II. METHODS

The atomic arrangements of α -B are described as composed of units of nearly regular icosahedra in a slightly deformed face-centered-cubic (fcc) close packing[5]. Therefore, we considered the followings as α -B related structures.

- 1) fcc arrangement of B atoms, which is observed in the metallic element in the same group, aluminum(Al)
- 2)fcc packing (the rhombohedral angle, χ , =60°) of clusters of regular icosahedron, B₁₂
- 3)nearly fcc packing (χ <60° or χ >60°) of clusters of regular icosahedron, B₁₂

All the calculations have been done for 36 atoms.

As for β -B, atomic structure was first published by Hoard *et al.*[6] and further refinements were done by Geist *et al.*[7], Callmer [8]and Slack *et al.*[9]

The latter two clarified that (1) one symmetry-equivalent atomic sites in the unit cell, B(13), is partially vacant, and (2) one or five different symmetry-equivalent interstitial atomic sites, B(16) to B(20), are partially occupied. DOS calculations based on these data have been done in the present study under rather arbitrary assumption that certain sites of these are 100% occupied and different certain sites are 100% vacant, though not-genuine superstructure of B vacancies and interstitial B atoms are inevitably introduced.

^{1*} Recently, Fujimori *et al.* [1] clarified that the inter-cluster bond, shorter than intracluster bond, does not mean stronger bond from electron density distribution measurements in α -B.

Calculation conditions are as follows. The pseudopotential to describe the electron-core interaction is a norm-conserving nonlocal potential generated using the optimization scheme of Lin *et al.*[10] and bundled in Ceriu2^{2*} graphical user interface. This potential is relatively "soft". That is, a relatively small basis set can be used even in the case of 2p elements. Fixed kinetic cutoff energy for plane-wave expansion of wavefunctions of 400eV^{3*} was used for α -B and its related structures. As for β -B, a cutoff energy as small as 250 eV could be used because of limited computational resources. As this value seems to be insufficient for quantitative discussion, only shape of DOS and the relative position of Fermi-level(E_F) will be discussed^{4*}. K -points sampled from the reciprocal space are generated by Monkhorst-Pack scheme[11], assuming the spacing in the reciprocal space was 0.45 nm⁻¹. Number of sampled k -points from the irreducible part of the Brillouin zone, were 25 for α -B related structures and 14 for β -B.

As for the method of approximation to the exchange-correlation term of DFT, local density approximation (LDA) was used.

III. RESULTS AND DISCUSSION

3.1 Comparison of electronic energy of α -boron with related structures

At first, total energies versus the volume of the unit cell for α -B and fcc-B have been calculated. Here, fractional coordinates of B atoms are fixed and only the lattice constant was varied. The results are given in Fig.1. The energy of α -B has its minimum when the cell volume is about 7 Å³/B-atom, which is about 4% smaller than the equilibrium volume (=7.29 Å³/B-atom), shown by an arrow in the figure. The

energies of the hypothetical fcc-B, shown in the figure, are much higher than those of α -B. Thus, α -B is calculated correctly to be lower in energy. The same calculation has been done on the same IIIa element, Al. The results are shown in Fig.2. In this case, fcc Al has much lower energy than hypothetical α -B like structure. The energy of fcc-Al has its minimum when the cell volume is about 16.2 Å³/Al-atom, which is about 2.6% smaller than the equilibrium volume (=16.6 Å³/Al-atom), shown by an arrow in the figure.

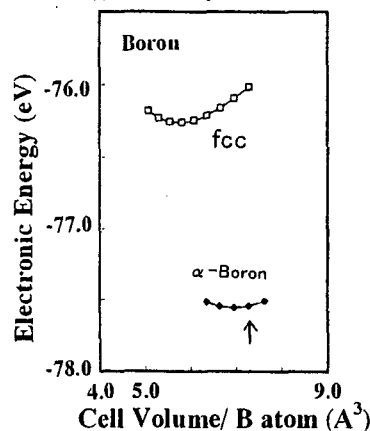


Fig.1 Variation of electronic energy of α -boron and hypothetical fcc structure with the cell volume.

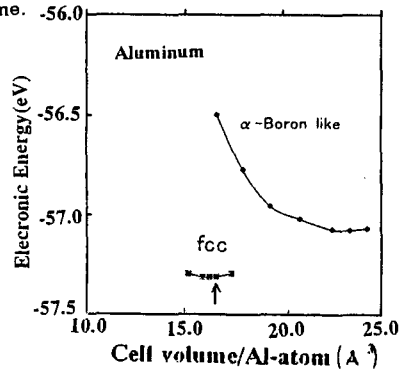


Fig.2 Variation of electronic energy of aluminum (fcc structure) and hypothetical α -boron like structure with the cell volume.

Encouraged by the fact that the order of the energy of assumed crystal structures of B and Al are rightly predicted, we carried out the energy comparison among the analogous structures to α -B, stated in the Method section. They are 1) fcc packing ($\chi = 60^\circ$) of clusters of regular icosahedron, B_{12} , and 2) nearly fcc packing ($\chi < 60^\circ$ or $\chi > 60^\circ$) of clusters of the same icosahedron. In the former calculations, a_h was assumed to be 4.908 Å and c_h , 12.021 Å, corresponding to the energy-minimum volume of 7 Å³/B-atom in the calculation of α -B, as stated above, and we assumed the varied length of regular icosahedra. In the latter, the same volume of 7 Å³/B-atom was assumed and effect of varied rhombohedral angle, χ , was examined

^{2*} Ceriu2 is a trademark of Molecular Simulations Inc.

^{3*} A series of calculations using different cutoff energies of 250, 320, 400, 800, and 1200eV have been preliminarily conducted for α -B with the equilibrium lattice constant. DOS curve agrees quite well with each other and total energies calculated are -77.01, -77.39, -77.53, -77.60, and -77.62 eV, respectively. Thus, convergence of total energy with respect to cutoff energy can be expected. The calculation using cutoff energy of 400eV may be used for the discussions of relative stability of different structures if energy difference is more than ca 0.1eV. Also, we thought that relative stability dependence on lattice parameters can be discussed using this fixed cutoff energy.

^{4*} We confirmed that shape of DOS are not varied by increasing cutoff energy in case of Hoard et al's structural data where memory of the computer required for calculation is much smaller than the calculation for β -boron of Callmer's and Stack *et al.*'s data because of symmetry of the structure.

That is, a_h/c_h ratio was changed from 0.378 to 0.408, which corresponds to $56.6^\circ \leq \chi \leq 60^\circ$

Figure 3 shows the calculated electronic energies versus the lengths of the side of regular icosahedra. Numerical values in the figure represent distances between adjacent icosahedra. It should be noted that atomic distance of the intercluster bond is shorter than the intracuster in the structure which has the lowest energy among the structures considered here. This corresponds to the case of actual α -B where the length of the intracuster bond of equilibrium α -B is 1.77~1.89 Å and that of intercluster bond is 1.62 Å.

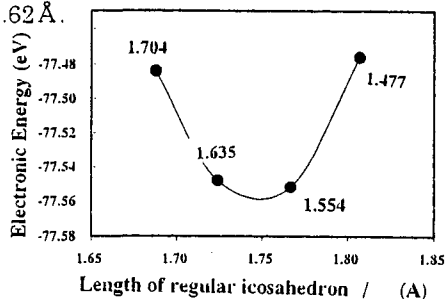
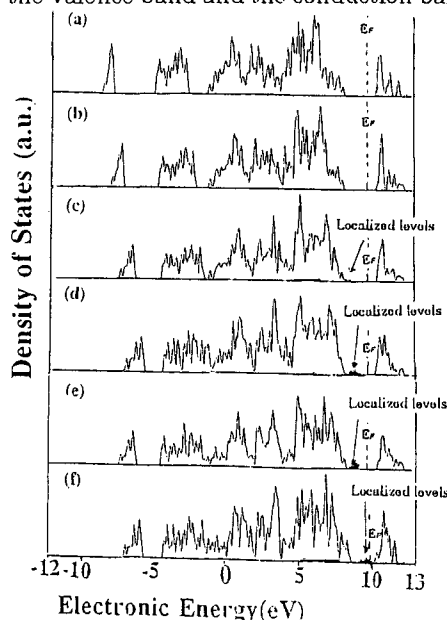


Fig.3 Variation of electronic energy of the cluster composed of B12-regular icosahedra with the length of the side. Hexagonal lattice parameter was assumed to be $a_h=4.908$ Å and $c_h=12.021$ Å. Those mean cubic closed packing of the cluster and the cell volume of $7 \text{ Å}^3/\text{B-atom}$

Figures 4(a) to (d) represent the density of states (DOS) of above structures. As are shown, energy band gap of ca 2 eV can be seen between the valence band and the conduction band.



Figs.4 (a) to (d), Density of states (DOS) of the cluster composed of B12-regular icosahedra. Hexagonal lattice parameter was assumed to be $a_h=4.908$ Å and $c_h=12.021$ Å. Assumed length of the side of icosahedra are 1.638 Å, (a), 1.724 Å, (b), 1.767 Å, (c), and 1.808 Å, (d). (e), DOS of the cluster composed of B12-regular icosahedra with the side length of 1.767 Å and the hexagonal lattice parameter of $a_h=4.836$ Å and $c_h=12.38$ Å. (f), DOS of α -boron.

As for the structures composed of relatively small regular icosahedron, (a) and (b), no localized energy level can be seen between the gap, whereas localized energy levels are generated between gap just above the valence band in the case of the structures composed of relatively large regular icosahedron, (c) and (d).

Figure 5 represents the energy dependence on the rhombohedral angle, χ , of packing of clusters of regular icosahedron, B_{12} , where the length of the side is fixed at 1.767 Å. The electronic energy has the lowest value when packing of clusters of icosahedron, B_{12} is slightly different from fcc packing ($\chi=60^\circ$). DOS of this structure is shown in Fig.4(e), which is not so different from Fig.4(d), the case where $\chi=60^\circ$

Thus, the energy lowering of the α -B by slight deformation of the cubic close packing of regular icosahedra could be reproduced by the present calculation. However, energy lowering by deformation of B_{12} cluster from regular icosahedron could not. Among the structures with α -B type, the lowest energy is about -77.55eV, as show in Fig.1, whereas the value as low as -77.58eV can be attained if the clusters of regular icosahedron, the length of the side of which is 1.767 Å, are packed with the χ of 58° , as shown in Fig.5.

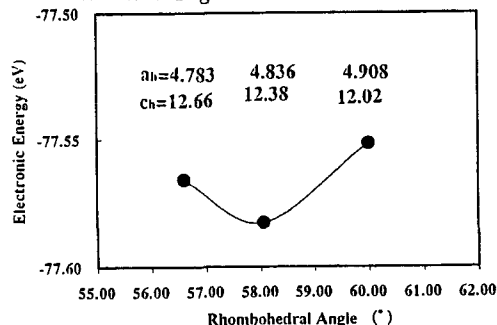


Fig.5 Variation of electronic energy of the cluster composed of B12-regular icosahedra with the rhombohedral angle, χ , assuming that cell volume of $7 \text{ Å}^3/\text{B-atom}$ and the side length of 1.767 Å

Numerical error should be taken into account, for adequate convergence of total energy with respect to cutoff energy to discuss such small energy differences among different structures has not been fully attained in the calculation. Geometrical optimization of α -B has not been carried out, either. However, LDA approximation used here may have some problems. Generally, LDA approximation underestimate the distribution of Fermi hole near core and overestimate that in the region far from the core, resulting in overestimation of the cohesive energy, underestimation of the lattice parameters and narrower energy level from the vacuum level. These are also observed in the present study, as smaller lattice constants predicted by the calculation compared to the equilibrium values.

It should also be noted that the position of E_F of α -B in the energy band-gap is erroneously

predicted, as given in by Fig.4(f). E_F should be located at slightly above the top of valence band so as to explain p-type semiconducting behavior of α -B. However, present calculation shows that it is located slightly below the bottom of the conduction band, and this may result in higher electronic energy of α -B compared to the hypothetical structure of packing of regular icosahedra. This discrepancy was not found when the method of augmented-spherical-wave (ASW) calculations are used, as will be stated elsewhere.

3.2 Density-of-states of β -boron

As stated in the Introduction section, Bullet first calculated DOS of the "idealized" structure of β -B, based on the Hoard data, and could show a substantial gap of *ca* 1.5eV in DOS. However, the calculation showed that Fermi level exist near the top of the valence band and the band scheme proposed by Franz and Werheit from the photo-absorption and photo-conductivity experiments could not be explained. To clarify the effect of partial occupancy of sites, calculation on the structures proposed by Callmer and Slack have been done.

Though both of them described the probability of partial occupancy, rather arbitrary assumption that certain fixed sites are fully occupied and other sites are fully vacant. That is, for Callmer structure, one of six equivalent B(13) sites assumed to be fully vacant and one of six B(16) sites fully occupied. For Slack structure, one of six B(17) sites is also assumed to be occupied in addition to Callmer structure and other candidates of interstitial sites of B(18)-B(20) sites are assumed to be fully vacant. The selection of occupied (and vacant) sites gave small difference in calculated results.

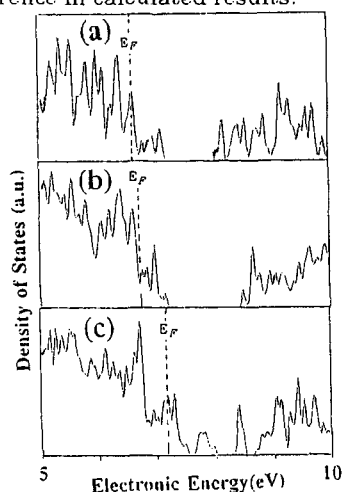


Fig. 6 Density of states of β -boron using Hoard et al's [6], (a), Callmer's [8], (b), and Slack et al's [9], (c), structural data.

Figure 6 shows the comparison of DOSs thus calculated. Calculated DOS of β -B using Hoard's data, shown by Fig.6(a), has a good resemblance to the previous results by Bullet,

though the calculation method is different. It should be noted that E_F is located just at the peak of DOS near the top of the valence band, indicating that this form might be unstable. On the contrary, when Callmer's data are used, DOS has a dent near the top of the valence band and E_F is located just at that dent, as shown in Fig.6(b), suggesting that the Peierls instability is dissolved by moving one B atom from a B(13) site to a B(16) site. Both have no localized level between energy gap of 1.4 eV except for the ones near the top of the valence band. In case the structural data by Slack is used, localized energy levels are predicted between the gap, as shown by Fig.6(c), and this is quite like to Franz and Weber's estimation, though E_F is not located in an isolated energy level from the valence band.

IV. CONCLUSION

Electronic energy and density of states of α - and β -rhombohedral boron have been calculated using a total energy pseudopotential method with a plane-wave basis. The fact that intercluster bond is shorter than the intracluster bond and the energy lowering of the α -boron by slight deformation of the cubic close packing of regular icosahedra could be reproduced by calculations. Partial occupancy of interstitial sites would play a key-roll in electronic structure of β -rhombohedral boron such as a generation of localized energy levels between energy band-gap.

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