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To cite this article: Haruhiko Dekura et al 2009 J. Phys.: Conf. Ser. 176 012004

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Possibility of imperfections in $\alpha$-boron

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Abstract. Recently, we have shown by density functional theory calculations that $\alpha$-boron is the most stable phase at low temperature among icosahedron-based boron crystals. This is consistent with low-temperature crystal growth of $\alpha$-boron. A problem of the calculation is, however, that the conclusion would be changed if defect states for $\beta$-boron, which are observed in experiment, were taken into account. This urges us to suspect the perfectness of $\alpha$-boron crystal. In this paper, we investigate possibility of imperfections of $\alpha$-boron from the standpoint of crystal stability. Intrinsic defects of vacancy and self-interstitial have been examined. Based on the total energy calculations, we conclude that intrinsic defects are not present at a level above 0.1 at%.

1. Introduction

The problem of stability of polymorphic modifications has long been an important issue of boron physics and chemistry. There are many polymorphic modifications for boron. Here, we are more specifically concerned with the stability between $\alpha$- and $\beta$-rhombohedral boron, because these two are most often obtained polymorphs showing strong contrast in many respects. Since $\alpha$-boron (hereafter term rhombohedral will be omitted for brevity) was for the first time isolated from decomposition of boron hydrides [1], it has been recognized that the preparation temperature is relatively low compared with the temperature of $\beta$-boron synthesis. McCarty et al reported that $\alpha$-boron was obtained from pyrolytic decomposition of $\text{Bi}_3$ on a surface heated to a temperature in the range 800 to 1100°C [1]. At higher temperatures, $\beta$ phase becomes stable. Later, Horn succeeded to obtain $\alpha$ phase from a molten metal (B-Pt) at the eutectic temperature 830 °C [2] (however 750°C in Ref. [3] ). On the other hand, there is no report on crystal growth of $\beta$-boron at low temperatures comparable to these data.

In spite of these facts, many researchers believed that $\beta$ phase is stable over the whole temperature range. Probably, this believe comes from an authoritative reference of Hoard and Hughes [4]. Although they notice the fact of low-temperature synthesis of $\alpha$-boron, it seems reasonable for them to consider that $\alpha$ phase is obtained only in some specific circumstance, for example, using specific starting materials. However, Kimura’s group showed that by starting from amorphous boron, $\alpha$ phase is obtained in a very narrow temperature range around 1200°C with the width ~20 deg [5]. Below this temperature, no crystallization occurred. From this observation, it seems that $\alpha$ phase is the stable phase at low temperatures. Indeed, it is otherwise difficult to understand low-temperature synthesis of $\alpha$-boron in molten metals (Pt-B) [2] or Pd-B [6] [7].
The stability problem becomes more important in connection with advent of superconductivity of \( \beta \)-boron at high pressure [8]. The stability of \( \beta \)-boron at high pressure was examined by various experimentalists [9, 10]. On theoretical side, relatively simple structural models were examined [11], and \( \alpha \)-Ga type had been proposed [12, 13]. However, there was no systematic study on the stability of \( \beta \)-boron before five years ago. In this situation, the authors have studied the stability of \( \alpha \) and \( \beta \)-boron by \textit{ab initio} calculations [14]. Our conclusion is that \( \alpha \) phase is the stable phase at low temperature, whereas \( \beta \) phase is stable at high temperature. The transition temperature between \( \alpha \) and \( \beta \) is about 700\(^\circ\)C. This value is obtained by taking the phonon contribution within the harmonic approximation. Later, by taking anharmonic effects into account within quasiharmonic approximation, we have obtained phase diagram of boron [15]. Considering the anharmonic effect in this way does not significantly change the transition temperature.

Although the calculated phase diagram seems to give reasonable account to experimental facts, there is a problem of defect states affecting the thermodynamic stability. In obtaining the phase diagram mentioned above, we ignored defect states of \( \beta \)-boron. If the defect states in \( \beta \)-boron are taken into account, the transition temperature becomes too low (-100\(^\circ\)C). Our calculation shows that even though the energy reduction by defects is only minor, \( i.e. \), \( \Delta E_t \sim 4 \text{ meV} \), its thermodynamic consequence becomes appreciable, because the entropy effect is sensitive to the energy difference [14]. Recent study of \( \beta \)-boron by Widom and Mihalkovic extends calculation to include further defect states [16]. It found that \( \beta \)-boron is more stable even at zero temperature that contradicts to the above experimental facts. Further studies were published in this regard [17, 18].

By observing this unfavorable effect of the defects in \( \beta \)-boron, the present authors supposed that even \( \alpha \)-boron must have intrinsic defects similar to \( \beta \)-boron [14]. Any calculation ignoring defects in \( \alpha \)-boron would lead to a conclusion of relative stability of \( \beta \)-boron at finite temperatures. However, there has been thus far no information about the defect states in \( \alpha \)-boron. This is why the problem of defects for \( \alpha \)-boron was not pursued in our study [14].

Defects do exist in \( \alpha \)-boron, if we are not concerned with the concentration. Since McCarty’s first isolation of \( \alpha \)-boron, it has been recognized that crystals can be of black or red color [19, 20, 4]. The color can originate from defects and impurities. However, the impurities responsible for the red color of \( \alpha \)-boron are not well characterized. These impurities may not be important for the stability problem of \( \alpha \) and \( \beta \)-boron, unless the concentration is too high. In this paper, we are mainly interested in intrinsic defects, \( i.e. \), interstitial or vacancy, as in \( \beta \)-boron. Since Decker and Kasper made a precise determination of the crystal structure of \( \alpha \)-boron [19], such intrinsic defects have not been considered, because the atomic occupancies of all the lattice sites are 100 %. This clearly contrasts with the situation of \( \beta \)-boron, for which several cites of partial occupancy were found [21, 22, 23, 24]. Among various polymorphs, \( \alpha \)-boron is regarded as the most perfect [25]. Of course, X-ray determination of 100 % occupancy does not guarantee perfect crystal with no trace-level defects. Presence of intrinsic defects with a marginal concentration could have a role in the crystal stability.

This is the first study addressing the perfection of \( \alpha \)-boron from standpoint of crystal stability. The types of intrinsic defects studied in this paper are simple point defects, \( i.e. \), vacancy and interstitial. Complex types are excluded here. Before performing first principles calculations, we give an estimate of the concentration of defects which is relevant to the present issue. Then, the formation energies of defects are calculated by first-principles pseudopotential method.

2. Preliminary
Let us first examine the accuracy of the experimental atomic density of \( \alpha \)-boron. For \( \alpha \)-boron, the formal value of atoms per cell \( N_{_a} \) is 12. Decker and Kasper determined this \( N_{_a} \) from the measurement of the lattice parameters and the mass density [19]. They obtained
\( a_0 = 5.057 \pm 0.003 \text{ Å (0.06 \% error)} \) and \( \alpha = 58.06 \pm 0.05 \text{ deg (0.09 \%)} \), from which the cell volume has been calculated as \( V = 87.3 \pm 0.16 \text{ Å}^3 \) (0.2 \%). The mass density \( \rho \) was obtained as \( \rho = 2.46 \text{ g/cm}^3 \). Using the nominal value for the mass of boron, \( M = 10.811 \text{ amu} \), we obtain

\[
N_{\text{at}} = \rho V / M = 11.96 \text{ atom/cell}, \tag{1}
\]

with the relative error of 0.3 \%. Therefore, concentrations of intrinsic defects below 0.3 \% are permissible without causing any contradiction with the existing experimental data. This concentration roughly amounts to one defect in 30 primitive unit cells, with a total number of atoms 360. Although a 400-atom supercell is currently manageable in our code, for calculating the formation energy, usually we do not need such a large supercell. In this study, we examined three primitive unit cells as the supercell. This is conveniently carried out using a hexagonal unit cell.

Concerning the formation energy of defects \( \Delta E_d \), let us estimate the magnitude of \( \Delta E_d \) which could have discernible effect on the present problem. In case of \( \beta \)-boron [14], the effect of defects on the free energy \( \Delta F_c \) has been estimated through the configurational entropy,

\[
\Delta F_d = kT \ln \left( \sum_i w_i e^{\Delta E_i / kT} \right), \tag{2}
\]

where \( w_i \) is the multiplicity of a specific type of defect \( i \). In order for this contribution to yield a sizable effect, temperature \( T \) should be higher than the lowest \( \Delta E_i \) among various defects. The transition temperature between \( \alpha \)- and \( \beta \)-boron is around 1000 K, so that in order for the defects of \( \alpha \)-boron to affect the thermodynamics through Eq. (2), the \( \Delta E_d \) should be of the order 1000 K, i.e., 0.1 eV. This means that any defect with \( \Delta E_d > 1 \text{ eV} \) may be irrelevant with the thermodynamic stability of \( \alpha \)- and \( \beta \)-boron.

3. Method

In this study, first-principles pseudopotential method with local density approximation (LDA) is used for the total-energy calculation. The used code is ‘Osaka2002’ [26]. Troullier-Martins’ pseudopotentials [27] are used, with aid of a full separable Kleinman-Bylander form [28].

The cutoff energy for the plane-wave basis is 55 Ry. A Monkhorst-Pack mesh of \( (2 \times 2 \times 2) \) is used for \( k \)-point sampling [29]. With these conditions, convergence of the total energy was below 2 meV/atom, and that of formation energy below 0.5 meV/atom. Structural optimization was performed for atomic positions only.

Structural models of defects in \( \alpha \)-boron are constructed on 12-atom primitive unit cell and 36-atom supercell. The 36-atom supercell is constructed as a hexagonal cell as shown in figure 1. For vacancy, there are only two sites: polar (\( p \)) site and equatorial (\( e \)) site of the icosahedron. In contrast, for interstitial site, there are many possibilities. However, by our experience of impurity study in \( \alpha \)-boron [30, 31] and by analogy to other boron-rich solids such as \( \text{B}_{12}\text{P}_2 \), the center of the main diagonal (\( O \)) site is almost always the most stable site. Hence, here only \( O \) site is considered.

The formation energy \( \Delta E_f \) is obtained by difference of the total energies before and after the reaction. For example, the formation energy \( \Delta E_f \) of vacancy in the primitive unit cell is obtained

\[
\Delta E_f = E(\text{B}_{11}\Box) - \frac{11}{12} E(\alpha - \text{B}). \tag{3}
\]

Here, vacancy is denoted by \( \Box \) and interstitial boron is denoted by \( \text{B}_i \). The B atom which was missed after creation of a vacancy is supposed to move outside the specimen, but still in the crystal state of \( \alpha \)-boron. In this way, \( \Delta E_f \) can vary by changing the reference state, in other
words, it is controllable by changing the starting conditions, such as the initial phase (liquid, amorphous, alloy, etc). The sign convention of definition (3) is usual one in impurity physics of semiconductors. Positive $\Delta E_f$ means that creation of a defect is difficult.

4. Results and discussion
The calculated $\Delta E_f$ of various defects are listed in table 1. The formation energies are all positive, and the values are from 4 to 6 eV. These values are typical for usual semiconductors [32, 33, 34]. For vacancy, there is virtually no difference between the polar and equatorial sites. The formation energy $\Delta E_f$ decreases with decreasing concentration of defect, however the decrease is minor. To see this dependence more clearly, we plot $\Delta E_f$ as a function of the concentration $n$ in figure 2. As shown in figure 2, the $\Delta E_f$ at low-concentration limit is 4.7 eV for vacancy and 6.3 eV for interstitial. Therefore, judging from the aforementioned criteria on the formation energy, it is concluded that vacancy or interstitial defects are not responsible for the crystal stability of $\alpha$-boron. The crystal of $\alpha$-boron must be perfect within about 0.1 at.%. There are several issues to be considered before establishing this conclusion. One deficiency of our calculations is that the cell parameters were not optimized. Instead, we monitored the residual stress $\Delta \sigma$, which was caused by fixing the lattice parameters. The bulk modulus of

Figure 1. Sites of intrinsic defects in $\alpha$-boron $B_{12}$; $B_1$ is self-interstitial, while $\Box_p$ and $\Box_e$ are vacancy of polar site and equatorial site, respectively. The rhombohedral crystal is described in a hexagonal system. Hence, three icosahedra $B_{12}$ are seen.
Table 1. Formation energy $\Delta E_f$ of defects in $\alpha$-boron as a function of the defect concentration $n$. The residual force $\Delta f$ and residual stress $\Delta \sigma$ are also listed in order to check the accuracy. $a_B$ is the Bohr radius.

| Defect      | $\Delta E_f$ (eV/atom) | $n$ (at.%) | $\Delta f$ ($\times 10^{-2}$ Ry/$a_B$) | $\Delta \sigma$ (GPa) |
|-------------|------------------------|------------|----------------------------------------|-----------------------|
| use of a primitive cell $B_{12}$ |                        |            |                                        |                       |
| $B_{11}\square_p$         | +4.86                  | 8.3        | 1.5                                    | 29.4                  |
| $B_{11}\square_e$         | +4.86                  | 8.3        | 3.1                                    | 14.7                  |
| $B_{12}B_i$                | +6.90                  | 7.7        | 3.0                                    | 19.1                  |
| use a conventional cell, $3\times B_{12}$ |                        |            |                                        |                       |
| $B_{35}\square_p$         | +4.77                  | 2.8        | 0.6                                    | 12.2                  |
| $B_{35}\square_e$         | +4.77                  | 2.8        | 0.53                                   | 6.0                   |
| $B_{36}B_i$                | +6.54                  | 2.7        | 1.45                                   | 5.3                   |

Figure 2. Concentration dependence of $\Delta E_f$. The obtained $\Delta E_f$ of interstitial and vacancy at low concentration limit are 6.3 and 4.7 eV/atom, respectively.

boron $B$ is about 200 GPa [14], so that the listed value of the residual stress in table 1, for example $\Delta \sigma = 10$ GPa, amounts to a volume change $\Delta V/V = \Delta \sigma/B = 5\%$. Then, the error due to the cell relaxation is estimated by $\Delta E = (1/2)B V (\Delta V/V)^2$, giving a value of 0.13 eV. This order of magnitude is not significant for the present problem.

Another problem of the calculations is the supercell size. The concentration dependence shown in figure 2 confirms that use of larger supercells makes no significant difference. The effect of zero-point energy is not significant. Use of generalized gradient approximation (GGA) changes the energy difference of perfect and defective $\alpha$-boron only slightly. Therefore, it is unlikely that further examination of calculation parameters changes the above conclusion.

It is concluded, within the accuracy of density-functional-theory (DFT) calculation, that
simple interstitial or vacancy does not occur at a level above 0.1 at.% in α-boron. If we want to ascribe the relative stability of α-boron over β-boron to the presence of defects in α-boron, we have to seek the origin of the discrepancy in the model structure for the defects. Aside from simple interstitial or vacancy, there might be complex forms of native defects, which are not considered here. Experimentally, it is a common recognition that crystal growth of α-boron is possible only when contaminations are carefully removed [1, 19, 20, 4, 6].

5. Conclusion
When defect states of β-boron are taken into account, the existing calculations show that β-boron must be the stable phase even at low temperature, which contradicts to the experiment. One solution of this difficulty is to allow presence of defects in α-boron; then this would cancel out the effect of defects in β-boron. With this motivation, we have studied intrinsic defects of α-boron. Simple model of vacancy and interstitial at O site as a point defect has been examined. The ∆Ef at low-concentration limit is large - 4.7 eV for vacancy and 6.3 eV for interstitial. These values are too large to influence the crystal stability of α-boron compared with defective β-boron. Therefore, it is concluded within the present modes of structure that intrinsic defects do not exist in α-boron at a level at which thermodynamic stability of α- and β-boron is altered.

Acknowledgments
This work was partly supported by a Grant-in-Aid for Scientific Research in Priority Areas "Areas of New Materials Science Using Regulated Nano Spaces" (No. 20045009) of MEXT, Japan. The computations were performed on the supercomputer facilities of the Cybermedia Center, Osaka University.

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