Phase stability in α- and β-rhombohedral boron

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Phase stability in α- and β-B has been investigated by using first-principles quasiharmonic phonon calculations. It is found that the defect-free α-B is more stable than the defect-free β-B at lower temperatures up to the predicted 1388 K. It is revealed that the defect-free β-B is mechanically unstable at high temperatures (above 1840 K), indicated by the appearance of imaginary phonon modes, which can be suppressed by introducing defects, e.g., the extra B atoms. This discovery is consistent with the experimental observations that defects occur commonly in β-B.

Boron (B) has attracted great interest due to the discovery of superconductivity at high pressure[1] as well as the vast variety of polymorphs.[2–4] Additionally, the B-rich compounds possess fascinating properties such as superconductivity in MgB_2 (Ref. 5) and ferromagnetism in La-dropped CaB_6.[6] However, B remains the least studied element among the elemental semiconductors due to the complex structure. All the known B polymorphs have the same B_{12} icosahedral units linked by three-center covalent bonds within the icosahedron and connected by two-center covalent bonds between the different icosahedra.[3,7,8] Knowledge of phase stability between the various polymorphs is scarce. Even its equilibrium state in the ambient condition is still under debate, especially the phase stability between α- and β-rhombohedral B.[2–4] α-B (hR12) is the simplest one, consisting of a distorted B_{12} icosahedron per unit cell forming a fcc-like structure. β-B (hR105 for the defect-free structure) is the most commonly found modification and can be considered as a fcc-like structure consisting of the B_{84} quasispheres together with the B_{10}-B-B_{10} chains located in the octahedral interstices formed by the B_{84} spheres.[2] Experimentally, β-B is found to have several partially occupied Wyckoff sites usually described by the structure framework of hR111 or hR141;[9–12] in the latter case, 1.7 extra atoms per unit cell are included. These measurements[9–11] indicate two main defect sites in β-B. One is the partially occupied B(13) site (here the numbering scheme[9] of Hoard *et al.* is adopted) with the occupancy factor of ~0.75, neighboring to the central atom in the B(15) site. The other one is the extra B(16) site (occupancy factor of ~0.25) within the B_{84} sphere, neighboring to the B(1) site. However, so far it is unclear why these defects do occur in β-B. Thermodynamically, it seems that β-B is more stable under the ambient condition and therefore recommended by the Scientific Group Thermodata Europe (SGTE).[13] On the other hand, through the fact that α-B is commonly prepared at lower temperatures [<1400 K (Ref. 14)] while β-B at high temperatures,[2] it seems possible that α-B is thermodynamically stable below 1400 K. Theoretically, first-principles calculations conclude that α-B is more stable than β-B (hR105) at 0 K.[15–17] Even taking into account various defects, the mentioned first-principles phase stability still holds.[15,17]

The present work aims to explore two pending problems of boron starting from first-principles phonon calculations.

One is the origin of defects in β-B at high temperatures, i.e., the occurrence of extra B atoms; the other one is the phase stability between the defect-free α- and β-B. Herein the first-principles calculations are performed by VASP;[18] the phonon calculations are carried out using the supercell approach[22] as implemented in ATAT.[23]

Figure 1 illustrates the predicted force constants for the defect-free α-B (hR12) at the equilibrium volume and the corresponding phonon-dispersion relations, which are in good agreement with the measured Raman modes at the Γ point.[26] The force constants and phonon-dispersion relations of the defect-free β-B (hR105) are shown in Fig. 2 for the equilibrium $(V/V_0=1)$ and the larger $(V/V_0=1.125)$ volumes. In comparison with Fig. 1, the basic features of force constants between the defect-free α- and β-B are similar. However, the force constants of β-B are more complex, with the occurrences of more negative values together with some unusual changes at the larger volume as shown in Fig. 2. Here the most unusual decrease of force constant with increasing volume is one of the stretching terms marked by "s" in Fig. 2, which is caused by the unusual increase of the nearest bond length (at equilibrium volume) between atoms in the B(1) site (e.g., the *a-b* atoms shown in Fig. 2), indi-
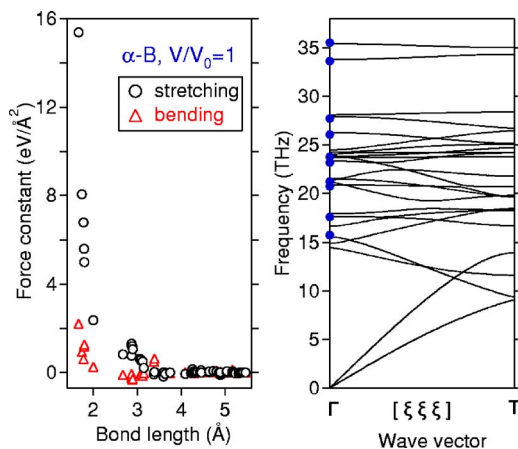

FIG. 1. (Color online) Calculated force constants for α-B (hR12) at the equilibrium volume and the corresponding phonon-dispersion relations. The symbols at Γ point show the measured Raman modes (Ref. 26).
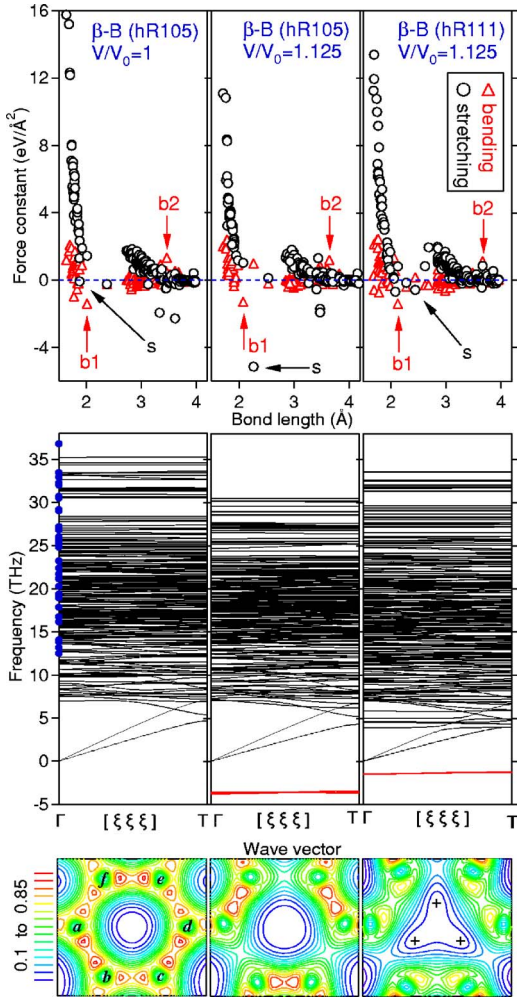
FIG. 2. (Color online) Calculated force constants (up panels), phonon-dispersion relations (middle), and charge-density contours (down) for β-B (hR105 and hR111) at the equilibrium ($V/V_0=1$) and larger ($V/V_0=1.125$) volumes. The symbols at Γ point ($V/V_0=1$) show the measured infrared modes (Ref. 28). The hexagonal ring (a-b-c-d-e-f) consists of atoms in the B(1) site. a-b, c-d, and e-f are the nearest neighbors ($V/V_0=1$) to link the B_{12} icosahedra, and the correspondingly unusual stretching force constant is marked by "s". The "b1" and "b2" indicate the unusual bending force constants within the B(13) site. The "+" symbols indicate the projected positions of atoms in the B(16) site.

cating the most possible place of covalent bond cleavage in the defect-free β-B (hR105). The appearance of imaginary phonon modes indicates the mechanical instability of β-B (hR105) at larger volumes. Phonon calculations at several volumes indicate that the imaginary phonon modes in the defect-free β-B occur with V/V_0 larger than 1.067 (pertaining to the temperatures above 1840 K).[27] It is expected that the appearance of imaginary phonon modes can be suppressed by introducing defects; this has been confirmed in Fig. 2. The phonon calculations for β-B [hR111, $V/V_0=1.125$, where the extra B(16) site is fully occupied] in comparison with those of β-B (hR105, $V/V_0=1.125$) indicate that (i) the largest negative stretching force constant increases and is close to zero, and (ii) the values of imaginary phonon modes increase obviously. Therefore, the presence of

TABLE I. Calculated relative energies (meV/atom) of α- and β-B at 0 K with respect to the defect-free β-B (hR105, the reference state). Based on hR105, the β (hR111) indicates that the extra B(16) site is fully occupied; β-106, one atom added in the B(16) site; β-104, one atom removed from the B(13) site; β-105, a combination of β-106 and β-104, i.e., adding one atom in the B(16) site and removing one from the B(13) site. The average value of β-105 is shown for the available six configurations (Ref. 15).

α (hR12)	β (hR111)	β-106	β-105	β-104
−24.9	112.0	−12.8	−11.4	1.8

extra B atoms in the B(16) site hinders the bond cleavage between atoms in the B(1) site. The unusual decrease of force constant with increasing volume and the effect of atoms in the extra B(16) site are distinctly shown in Fig. 2 in terms of the charge-density distributions of a hexagonal ring (a-b-c-d-e-f) consisting of atoms in the B(1) site: (i) with increasing volume (for hR105) the charge densities between atoms a-b decrease quickly, resulting in a large increase of the bond length; (ii) with the presence of atoms in the B(16) site, the maximum charge densities shift to the inner part of the hexagonal ring, implying the glue of the extra B atoms. We believe that the unusual increases of bond length between atoms in the B(1) site are mainly responsible for the instability of the defect-free β-B (hR105) at larger volumes.

The unusual bending force constants, marked by "b1" and "b2" in Fig. 2, are caused by atoms in the B(13) site with the first and third nearest bond lengths, respectively. It can be understood that the most asymmetric charge densities (not shown) around atoms in the B(13) site account for the larger (both negative and positive) bending force constants. It is expected that the asymmetric surroundings, i.e., the unusual bending force constants, can be reduced by introducing defects in the B(13) site, i.e., the partial occupation. Instead of probing the influences of partially occupied B(13) site on the lattice dynamics of β-B (due to huge calculations), the indirect proofs are presented, i.e., the predicted B(13) and B(1) sites for the defect-free β-B (hR105) have the largest and the second largest standard derivations (0.005 and 0.003, respectively) with respect to the measured ones,[9–11] where the calculated average standard deviation is 0.0013. These discoveries are consistent with the experimental observations[9–11] that (i) the B(13) site is partially occupied ($\sim$0.75), although it is not an inherent property at 0 K, see the following part; and (ii) mainly the extra atoms in the B(16) site (occupancy of $\sim$0.25, an inherent property as shown in the following part) are the nearest neighbors to atoms in the B(1) site.

Table I shows the relative energies at 0 K for the defect-containing β-B (hR111, β-106, β-105, and β-104; see the definitions in Table I) with respect to the reference energy of the defect-free β-B. The lower relative energies of β-105 and -106, and the quite higher relative energy of β-B (hR111), indicate that the presence of partially occupied (instead of fully) extra atoms in the B(16) is an inherent property of β-B, while the slightly higher relative energy of β-104 (also the relative energies: β-105 $>$ β-106) indicates that
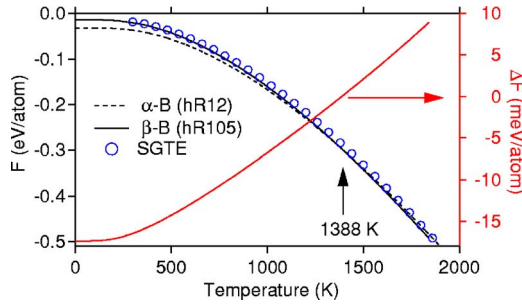
FIG. 3. (Color online) Calculated free energies (F) of the defect-free α- and β-B, together with the free-energy difference (ΔF) between them, as a function of temperature. The cycles are the SGTE data of β-B (Ref. 13), where the reference state is the enthalpy of β-B at 298 K and 1 bar.

that it is not a thermodynamically favored way to remove B atoms from the B(13) site at 0 K.

The predicted phonon-dispersion relations of β-B (hR105) at the equilibrium volume are compared with the measured infrared phonon frequencies[28] as shown in Fig. 2. Obviously the measured maximum optical mode is larger than the prediction; however, this discrepancy can be understood due to the extra B atoms and other impurities present in the experimental β-B samples, which [such as extra atoms in the B(17) site[11]] make the shortest bond length less than that in the defect-free β-B and, in turn, increases the maximum phonon frequency. Figure 2 also shows the increase of phonon-dispersion relations of β-B (hR111) due to the presence of extra B atoms. Comparing the equilibrium phonon-dispersion relations between the defect-free α- (hR12) and β-B (hR105), the distributions of frequency in the lower frequency region (e.g., around 10 Thz) of β-B are obviously higher than those of α-B. The higher phonon density of state (DOS) in the lower frequency region results in a lower average phonon frequency. This lower average frequency is linked to a "softer" structure of β-B, which in turn results from an enlargement in the bond lengths. This has also been confirmed by the calculations that β-B has lower density, lower bulk modulus, and lower Debye temperature, but has larger thermal-expansion coefficient than α-B,[29] implying the weakening of covalent bonds in β-B. Consequently, the free energy of β-B will decrease more quickly than that of α-B at high temperatures due to the phonon contributions. Figure 3 shows the free energies of the defect-free α- and β-B as a function of temperature predicted by the quasiharmonic approximation (QHA). The predicted free energies of β-B (hR105) are in excellent agreement with the SGTE data of β-B;[13] only a slight discrepancy appears at higher temperatures (>1000 K), which may be due to the neglect of defects and anharmonic effects. Figure 3 shows that α-B is more stable than β-B by 17.4 meV/atom at 0 K *with* the phonon contribution (24.9 *without* the phonon contribution, see Table I), which is consistent with other first-principles calculations.[15–17] The thermodynamic phase transition between α-B and β-B is predicted to be at 1388 K as indicated in Fig. 3, which is in perfect agreement with the observation at around 1400 K.[14] The present result is much better than

the recently predicted 970 K by phonon calculation,[15] wherein the harmonic approximation (HA) and only the phonon modes at the Γ point were used, and the imaginary modes were ignored. Note that the present predicted phase-transition temperature is 1274 K by using the HA and the phonon modes in the whole Brillouin zone.

It should be pointed out that the influences of defects (partially occupied Wyckoff sites, i.e., the disorder and the extra atoms) and anharmonicities on the free-energy difference (ΔF) between α- and β-B can be cancelled to some content. The defects are present in both α- and β-B,[15] therefore their effects on free energies of α- and β-B may be similar. Note that the details of defects are not available for α-B experimentally, which hinder the accurate estimations of their influences; on the other hand, the effect of defects on free energy may be cancelled because (i) the presence of defects (e.g., extra B atoms) will result in larger force constants, the phonon DOS therefore shifts to the high frequency region, and in turn the free energy *increases* at high temperatures; and (ii) the presence of defects will cause the *decrease* of free energy at high temperatures due to the contribution of configurational entropy. On the other hand, the influences of anharmonicities on the predicted free energies are negligible at the lower temperatures of interest [the Debye temperatures of α- and β-B are around 1300 K,[15,29] close to the phase-transition temperature and much lower than the melting point of 2348 K (Ref. 13)]. The effect of anharmonicities on the ΔF may be cancelled due to the similar properties between α- and β-B including the crystal structure, Debye temperature, bulk modulus, and the pressure derivative of bulk modulus.[29] We believe that α-B is a stable modification at lower temperatures, while β-B modification is a commonly found one at lower temperatures perhaps due to the kinetic factors which prevent the phase transition from β to α-B.

In summary, we found that the defect-free α-B is more stable than the defect-free β-B at temperatures up to 1388 K. The thermodynamic stability of β-B at high temperatures is ascribed to the higher phonon DOS at the lower frequency region due to the weakening of covalent bonds in β-B. The obtained thermodynamic data (especially the ΔF between α- and β-B) can be used to improve the widely used SGTE database with β-B being the stable element reference. It is revealed that the defect-free β-B is thermodynamically stable but mechanically unstable above 1840 K (but $<$melting point) or at larger volumes ($V/V_0 > 1.067$) indicated by the appearance of imaginary phonon modes, which can be suppressed by introducing defects. This discovery is consistent with the experimental observation that defects, i.e., several partially occupied Wyckoff sites, occur commonly in β-B.

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