New Ground-State Crystal Structure of Elemental Boron

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(Received 8 March 2016; revised manuscript received 27 May 2016; published 15 August 2016)

Elemental boron exhibits many polymorphs in nature based mostly on an icosahedral shell motif, involving stabilization of 13 strong multicenter intraicosahedral bonds. It is commonly accepted that the most thermodynamic stable structure of elemental boron at atmospheric pressure is the β rhombohedral boron (β-B). Surprisingly, using high-resolution transmission electron microscopy, we found that pure boron powder contains grains of two different types, the previously identified β-B containing a number of randomly spaced twins and what appears to be a fully transformed twinlike structure. This fully transformed structure, denoted here as τ-B, is based on the Cmcm orthorhombic space group. Quantum mechanics predicts that the newly identified τ-B structure is 13.8 meV/atom more stable than β-B. The τ-B structure allows 6% more charge transfer from B17 units to nearby B12 units, making the net charge 6% closer to the ideal expected from Wade’s rules. Thus, we predict the τ-B structure to be the ground state structure for elemental boron at atmospheric pressure.

DOI: 10.1103/PhysRevLett.117.085501

Boron and related materials exhibit such extreme properties as low density, high hardness, high melting temperature, superconductivity, and ferromagnetism [1–14], making them candidates for such applications as high power electronics, superconductors, heat resistant alloys, coatings in nuclear reactors, body armor vests, abrasives, and cutting tool materials [15–17]. However, boron leads to quite complex structures arising from its unique bonding character that prefers formation of icosahedral shell complexes that stabilize 13 strong multicenter intraicosahedral bonds (requiring 26 electrons, Wade’s rule). These complex structures make it difficult to interpret and understand the relationships between structure and properties. Indeed, even the ground state structure of boron has been controversial for over 30 years [6,15–17].

A number of crystalline structural forms for elemental boron have been discovered over the last two centuries [18–20]. However, only three phases correspond to pure boron: α-B12 [18], β-B105 [19], and γ-B25 [20], with most of the others probably stabilized by impurities [21–23]. It has been long suspected that the β rhombohedral boron (β-B105) structure is the most thermodynamic stable allotrope at low pressures [6,15–17]. However, the quantum mechanics studies [15,16] predict that the α-B12 structure is more stable than β-B105 by 25.3 meV/atom, leading to a long debate of which phase is the ground state structure for elemental boron [6,15–17,24]. Recent quantum mechanics studies have suggested that particular choices for the partial occupation sites in β-B105 and including zero point motion might lead to an energy for β-B105 that is more stable than α-B12 structure at ambient conditions [16,25].

Twinned structures have been observed in β-B105 [26,27] and boron related materials such as B3C [28]. Although the growth conditions to form these twinned structures are not clear [27,29], the twinned structure might dramatically change material properties such as charge capacitance [30]. In this light, understanding the twinned structure in β-B105 and the other icosahedral based materials provides essential information for understanding material behaviors at realistic conditions.

Herein, we report high-resolution transmission electron microscopy (HRTEM) on high purity boron that shows two phases:

1. About two thirds of the representative grains correspond to the well-known β rhombohedral boron (β-B) structure [see Fig. S1 of Supplemental Materials (SM) [31]]. These grains all contained a significant number of well-separated and randomly spaced twins.

2. The other one third of the grains displays a perfectly ordered zigzag “twinlike” atomic structure that extends across the entire grain.

In order to understand the nature of fully transformed grains, we constructed a model for the zigzag structure and used quantum mechanics to optimize it, leading to a Cmcm structure, denoted as τ-B with ordered twins that exactly match the HRTEM. Most interesting is that the quantum mechanics finds this τ-B structure to be more stable than β-B by 13.8 meV/atom and more stable than α-B12 by 9.5 meV/atom. Moreover, x-ray diffraction (XRD) analysis of boron powders containing the fully transformed grains agrees with the predicted τ-B structure. Combining these experimental and quantum mechanics results, we conclude that the τ-B structure is the true ground state structure for elemental boron.

The original β-B (denoted β-B105) structure proposed by Hoard in 1970 [40] consists 105 atoms with 15 nonequivalent boron positions (B1 to B15) in the unit cell, which is well described in previous literature [43]. The unit cell of

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\(\beta\)-B\(_{105}\) consists of 8 icosahedral clusters at the vertex sites and 12 icosahedral clusters at the edge centers in the rhombohedral unit cell, as shown in Fig. 1(a). In addition, the single B15 atom is located in the cell center connecting to two B\(_{28}\) units (each of which consists of three partial icosahedral clusters) through B13 sites along the [111] direction as shown in Fig. 1(b). The \(\beta\)-B\(_{105}\) structure has space group \(R\bar{3}m\). Later, the \(\beta\)-B\(_{105}\) structure was refined experimentally [44] and determined to contain 320 atoms in the hexagonal unit cell with five additional partially occupied sites (POS). The most occupied of these POS, are B13 (74.5% occupied) and B16 (27.2% occupied), as shown in Fig. 1(a) (the other POS sites have partial occupancies <10% [44]). Since the hexagonal unit cell corresponding to the rhombohedral unit cell contains 320 = 3 x 106.67 atoms, the refined \(\beta\)-B\(_{105}\) structure was denoted as \(\beta\)-B\(_{106}\) in the recent literature [16,25,43].

In our quantum mechanics simulations, we consider two \(\beta\)-B structures, (i) \(\beta\)-B\(_{105}\) which corresponds to the original structure without POS; the quantum mechanics predicted structure leads to lattice parameters of \(a = 10.11\) Å and \(\alpha = 65.4^\circ\), which agree very well with experimental values [40] of \(a = 10.14\) Å and \(\alpha = 65.2^\circ\). (ii) \(\beta\)-B\(_{106}\) containing one B13 vacancy site and two B16 occupied sites (this leads to exactly 106 atoms/cell). This particular \(\beta\)-B\(_{106}\) structure is selected because previous quantum mechanics calculation [16] showed it to be the lowest energy structure among the structures consistent with the POS. The quantum mechanics predicted \(\beta\)-B\(_{106}\) structure leads to lattice parameters of \(a = 10.09\) Å, \(b = 10.16\) Å, \(c = 10.16\) Å, \(\alpha = 65.1^\circ\), \(\beta = 65.0^\circ\), and \(\gamma = 65.1^\circ\), which also agrees very well with experimental values.

The \(\beta\)-B\(_{106}\) structure is more stable than \(\beta\)-B\(_{105}\) structure by 24.2 meV/atom, which is consistent with previous quantum mechanics simulations [16]. Thus, we conclude that the B\(_{106}\) description is a better assignment than \(\beta\)-B\(_{105}\) for the \(\beta\)-B structure, and we will mainly discuss this phase from this point on. Our quantum mechanics calculations for the fully minimized structures find \(\beta\)-B\(_{106}\) to be less stable than \(\alpha\)-B\(_{12}\) phase by 1.1 meV/atom without considering zero point energy (ZPE) corrections [16]. We calculated the ZPEs using a finite difference method [16]. The ZPEs for \(\alpha\)-B\(_{12}\) and \(\beta\)-B\(_{106}\) phases are 130.0 and 126.6 meV/B, respectively, which agrees very well with the values of 130 and 126 meV/B in the previous study [16]. Using ZPE corrections for these two phases, we find that \(\beta\)-B\(_{106}\) is more stable than \(\alpha\)-B\(_{12}\) by 2.3 meV/B, which agrees very well with the value of 2.9 meV/B from a previous study [16]. Previous studies [16] did not consider London dispersion when comparing the stability of the \(\alpha\)-B\(_{12}\) and \(\beta\)-B\(_{106}\) phases. Here, we include the London dispersion as incorporated in the Grimme D3 correction [45]. Including the ZPE and dispersion corrections, we predicted that \(\beta\)-B\(_{106}\) is less stable than \(\alpha\)-B\(_{12}\) phase by 4.3 meV/B and less stable than \(\tau\)-B\(_{106}\) by 13.8 meV/B.

The commercial \(\beta\)-boron powder used in this study was procured from H. C. Starck [H. C. Starck GmbH, Germany, purity level >99.2% with MgO (<0.8%) as the main impurity]. To determine the crystal structure of these powders, we performed XRD analyses to obtain the pattern shown in Fig. 2 where the simulated XRD pattern computed based on the quantum mechanics derived \(\beta\)-B\(_{106}\) structure is compared with experiment. Our experimental pattern contains additional peaks shown by red arrows in Fig. 2. The additional peaks could not be attributed to impurities, and their presence suggested that the boron powder contained a new structure in addition to \(\beta\)-B.
To investigate the powder samples further, we performed HRTEM experiments on individual grains, as shown in Fig. 3(a). The chemical composition of individual particles was measured using electron energy loss spectroscopy (EELS) and confirmed to be pure boron (Fig. S2 of SM [31]). The HRTEM images obtained from more than 20 individual grains find that 65% have the β-B crystal structure (Fig. S1 of SM [31]), while 35% were observed to have a perfectly ordered zigzag pattern with the icosahedra alignment alternating every other plane. Here, we denote the new zigzag structure as τ-B. We note here that our XRD peak intensities do not reproduce the ratio of β-B and τ-B grains that we characterized by TEM, and we attribute this to variations in grain morphology and the fact that we only observed 20 grains.

This zigzag structure has a mirror symmetry across the (001) plane and appears to be a uniformly twinned version of β-B [Fig. 3(b) provides a view along the [010] direction]. Where observed, this new zigzag structure extends across the entire grain as can be seen from multiple zone axes (Fig S3 and Fig. S4 of SM [31]). The observed HRTEM images (Figs. S3, S3, and S4) from multiple zone axes suggest that this new structure has a structure similar to β-B but with a plane of mirror symmetry at the {001}, edge of every unit cell. Such extensive ordering is most unusual; usually twinned structures exhibit multiple and highly variable crystalline layers between the twin boundaries. This suggested that the observed structure might be a new crystal structure.

To examine the nature of this unique “twinlike” structure using quantum mechanics, we constructed and optimized with quantum mechanics two unique “twinlike” structures (τ-B\textsubscript{105} and τ-B\textsubscript{106}) based on the β-B\textsubscript{105} and β-B\textsubscript{106} structures, respectively. (i) The optimized τ-B\textsubscript{105} belongs to the Cmmm orthorhombic space group, with primitive cell parameters of $a = 10.10$ Å, $b = 10.10$ Å, $c = 17.56$ Å, and $γ = 65.4°$. The primitive unit cell [shown in Fig. 1(c)] contains 210 atoms, exactly twice that of β-B\textsubscript{105}. (ii) The new τ-B\textsubscript{106} structure belongs to the P1 space group with cell parameters of $a = 10.08$ Å, $b = 10.17$, $c = 17.57$, $α = β = 90°$, and $γ = 65.2°$, while its unit cell contains 212 atoms, exactly twice that of β-B\textsubscript{106}. We calculate that the energy of τ-B\textsubscript{106} is 12.4 meV lower than τ-B\textsubscript{105}, so we conclude that τ-B\textsubscript{106} is the more stable structure for the τ-B phase, and we will focus on the τ-B\textsubscript{106} model further and discuss the τ-B\textsubscript{105} model only in the charge calculation.

We calculate that the energy of the τ-B\textsubscript{106} structure is 13.8 meV/B lower than β-B\textsubscript{106}, and 12.7 meV/B lower than the $α$-B\textsubscript{12} phase. The absolute quantum mechanics energies and the cohesive energies are listed in Table S1 of SM [31]. Since the τ-B is the unique twinlike structure of β-B, we assume that the ZPE correction to τ-B phase is the same as β-B. Thus, including ZPE and dispersion correction, we expect that τ-B\textsubscript{106} more stable than β-B\textsubscript{106} by
13.8 meV and more stable than $\alpha$-B$_{12}$ by 9.5 meV. Thus, $\tau$-B$_{106}$ is the ground state of elemental boron.

To compare directly the experimentally discovered fully transformed and fully twinned grains with the new theoretically calculated $\tau$-B structure, we simulated the x-ray and electron diffraction patterns and HRTEM images using the quantum mechanics derived atomic positions of the $\tau$-B structure. The comparison of experimental and simulated XRD is shown in Fig. 2. This new $\tau$-B$_{106}$ structure accounts for the missing peaks in the experimental XRD, as indicated by the red dashed lines in Fig. 2. The other peaks in the experimental XRD come from the $\beta$-B, as indicated by the dashed blue lines in Fig. 2. Thus, comparing the simulated and experimental XRD patterns indicates that the powder samples contain a mixture of $\beta$-B and $\tau$-B structures.

Experimental and simulated selected area electron diffraction (SAED) patterns are compared in Fig. 3. The experimental TEM SAED [Fig. 3(d)] was obtained from the grain that is shown in Fig. 3(b), and the simulated SAED [Fig. 3(e)] is based on the quantum mechanics derived $\tau$-B structure, except that we have averaged over the POS since these would be randomly occupied in various regions to yield the full space group symmetry, $Cmcm$, of the $\tau$-B$_{106}$ structure. Viewed along the [010] zone axis, the $\tau$-B structure looks like rhombohedral boron with twins present at every second lattice plane. The $\tau$-B structure can also be represented with the unit cell shown in Fig. 3(f). The lattice spacings of the (100) and (001) planes are labeled as $d_1$ and $d_2$, and their corresponding distances in reciprocal space are noted in the SAED patterns in Figs. 3(d) and 3(e). These experimental and simulated diffraction patterns index identically. Moreover, the experimentally measured ratio ($d_2/d_1 = 1.90$) agrees well with the geometry of the quantum mechanics simulated $\tau$-B$_{106}$ structure, where $c/(a \times \sin(\gamma)) = 1.92$. The experiments found very lower intensity reflections marked by arrowheads which were found to be equally spaced along the (001) planes [Figs. 3(d) and 3(e)]. We also note that the relative intensity of spots in SAED is highly dependent on foil thickness, precise orientation, etc. and precession electron diffraction might be required to obtain a better match.

Moreover, the close match between the experimental [Fig. 3(c)] and simulated [Fig. 3(f)] HRTEM images further confirms the presence of the $\tau$-B$_{106}$ structure in the B powders. In addition, experimental HRTEM images and Fourier transforms patterns (Figs. S3 and S4 of SM [31]) obtained using grains that were oriented along different zone axes, i.e., (010) and (110) support this observation and agree with our hypothesis that the experimentally observed new phase is the $\tau$-B$_{106}$ structure.

The calculated stability of the new $\tau$-B structure relative to other boron polymorphs, ($\beta$-B$_{106}$, $\alpha$-B$_{12}$, and $\gamma$-B$_{28}$) is displayed in Table I. We see that $\tau$-B$_{106}$ is more stable than $\alpha$-B$_{12}$ by 12.7 meV/atom, while other phases $\beta$-B$_{106}$, $\gamma$-B$_{28}$ are higher in energy than $\alpha$-B$_{12}$ by 1.1, and 27.3 meV/atom, respectively, which is consistent with previous quantum mechanics simulations [15,16].

TABLE I. Energy of various boron phases relative to the $\alpha$-B$_{12}$ phase.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\alpha$-B$_{12}$</th>
<th>$\beta$-B$_{106}$</th>
<th>$\tau$-B$_{106}$</th>
<th>$\gamma$-B$_{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy without ZPE correction (meV/atom)</td>
<td>0</td>
<td>1.1</td>
<td>−12.7</td>
<td>27.3</td>
</tr>
<tr>
<td>Energy with ZPE correction (meV/atom)</td>
<td>0</td>
<td>−2.3</td>
<td>−16.1</td>
<td>...</td>
</tr>
<tr>
<td>Energy with ZPE and dispersion correction (meV/atom)</td>
<td>0</td>
<td>4.3</td>
<td>−9.5</td>
<td>...</td>
</tr>
</tbody>
</table>

In summary, we discovered a new $\tau$-B phase for elemental boron by combining XRD and HRTEM experiments with quantum mechanics simulations. This new phase can be thought of as a perfectly ordered twinline version of the original $\beta$-B structure, with a doubled unit cell. The quantum mechanics studies indicate that this new

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phase is substantially more stable that either α-B_{12} or β-B, making it the true ground state structure of boron.

QA and WAG were supported by the Defense Advanced Research Projects Agency (Grant No. W31P4Q-13-1-0010, program managers, John Paschkewitz), by the Army Research Laboratory under Cooperative Agreement No. W911NF-12-2-0022, and by the National Science Foundation (Grant No. DMR-1436985, program manager, John Schlueuter). KMR, KYX and KH were supported by the Defense Advanced Research Projects Agency (Grant No. W31P4Q-13-1-0001). We gratefully acknowledge Professor Richard Haber and Dr. Chawon Hwang at Rutgers University, for coordinating our access to the commercial boron powders. We thank ARL for permission to use their HRTEM simulation facility.

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[31] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.117.085501, which includes Refs. [32–42], Figs. S1–S6, Tables S1. The Supporting Materials include: (i) experimental and simulation details; (ii) TEM characterization of β-B; (iii) electron energy loss spectroscopy (EELS) analysis indicating that the grains studied were pure boron; (iv) TEM characterization of the newly observed r-B phase along a (010) zone axis; (v) TEM characterization of newly observed r-B phase along a (110) zone axis; (vi) charge distributions (NBO analysis) of B_{12} and B_{37} units in β-B10S and r-B10S structures; and (vii) the predicted structural parameters in Crystallographic Information File base format.


