

New Ground-State Crystal Structure of Elemental Boron

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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/B *more stable* than β -B. The τ -B structure allows 6% more charge transfer from B_{57} units to nearby B_{12} 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.

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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 applications [7–17]. 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 - B_{12} [18], β - B_{105} [19], and γ - B_{28} [20], with most of the others probably stabilized by impurities [21–23]. It has been long suspected that the β rhombohedral boron (β - B_{105}) structure is the most thermodynamic stable allotrope at low pressures [6,15–17]. However, the quantum mechanics studies [15,16] predict that the α - B_{12} structure is more stable than β - B_{105} 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 - B_{105} and including zero point motion might lead to an energy for β - B_{105} that is more stable than α - B_{12} structure at ambient conditions [16,25].

Twinned structures have been observed in β - B_{105} [26,27] and boron related materials such as B_4C [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 - B_{105} 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/B and more stable than α - B_{12} by 9.5 meV/B. 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 - B_{105}) 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

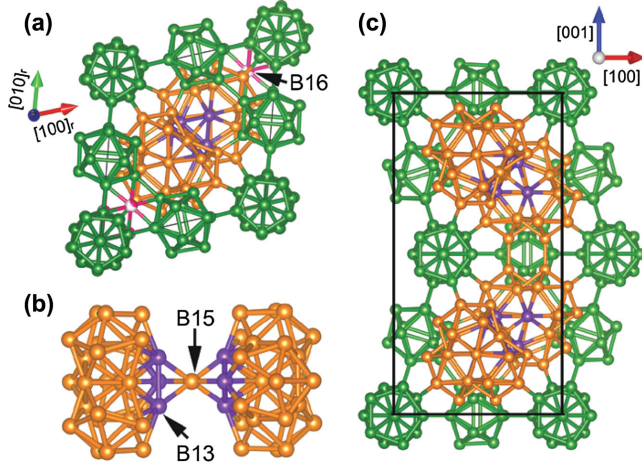


FIG. 1. (a) Structure of β -B₁₀₅ with the partial occupation site B16 shown with half red half white ball, viewed along $[001]_r$ direction. (b) The B₂₈-B-B₂₈ unit in the β -B crystal structure. The B₂₈ units are represented by orange balls. The B13 site is represented by the purple balls. Figure (b) is part of (a) rotated to (011) plane. (c) Structure of the new τ -B₁₀₅ phase, view along $[010]$ direction.

β -B₁₀₅ 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 B₂₈ units (each of which consists of three partial icosahedral clusters) through B13 sites along the $[111]_r$ direction as shown in Fig. 1(b). The β -B₁₀₅ structure has space group $R\bar{3}m$. Later, the β -B₁₀₅ 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 $320 = 3 \times 106.67$ atoms, the refined β -B₁₀₅ structure was denoted as β -B₁₀₆ in the recent literature [16,25,43].

In our quantum mechanics simulations, we consider two β -B structures. (i) β -B₁₀₅ 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) β -B₁₀₆ containing one B13 vacancy site and two B16 occupied sites (this leads to exactly 106 atoms/cell). This particular β -B₁₀₆ 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 β -B₁₀₆ 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 β -B₁₀₆ structure is more stable than β -B₁₀₅ structure by 24.2 meV/atom, which is consistent with previous

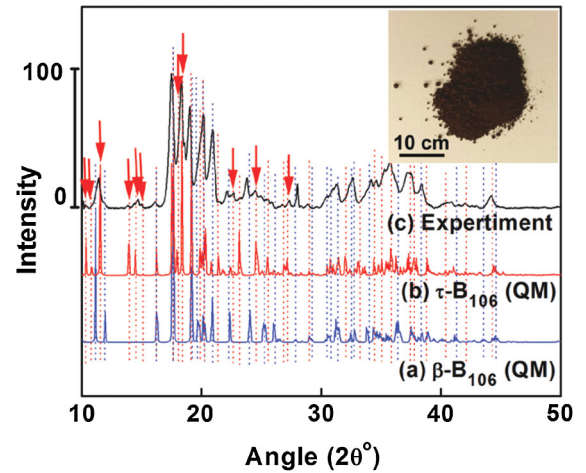


FIG. 2. Experimental x-ray diffraction scan compared with simulated patterns based on quantum mechanics calculations. The phases identified from the powders were found to be a combination of rhombohedral β -B (blue) and τ -B (red) phases indicating with the dotted lines. The inset shows the boron powder.

quantum mechanics simulations [16]. Thus, we conclude that the B₁₀₆ description is a better assignment than β -B₁₀₅ for the β -B structure, and we will mainly discuss this phase from this point on. Our quantum mechanics calculations for the fully minimized structures find β -B₁₀₆ to be less stable than α -B₁₂ 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 α -B₁₂ and β -B₁₀₆ 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 β -B₁₀₆ is more stable than α -B₁₂ 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 α -B₁₂ and β -B₁₀₆ phases. Here, we include the London dispersion as incorporated in the Grimme D3 correction [45]. Including the ZPE and dispersion corrections, we predicted that β -B₁₀₆ is less stable than α -B₁₂ phase by 4.3 meV/B and less stable than τ -B₁₀₆ by 13.8 meV/B.

The commercial β -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 β -B₁₀₆ 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 β -B.

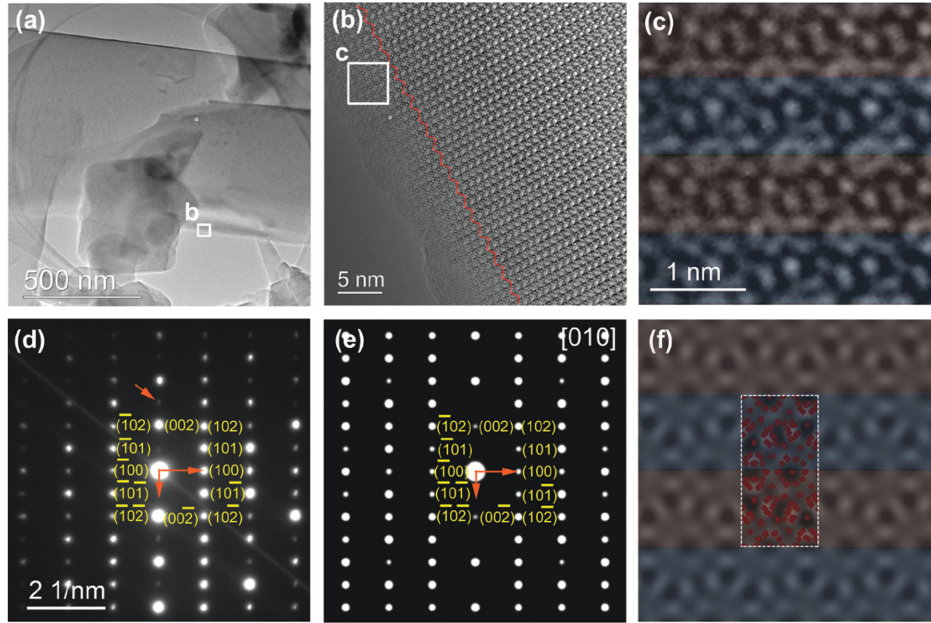


FIG. 3. TEM characterization of τ -B₁₀₆. (a) A typical low magnification TEM image showing the powder morphology. (b) Higher magnification TEM images of the boron structure viewed along the [010] zone axis. (c) Experimental high resolution TEM image. The mirror symmetry or twinning was observed to repeat perfectly for every other layer of the β -B unit cell in the real space image. (d) A SAED pattern recorded for the region imaged in **b** and indexed to be the τ -B₁₀₆ structure. (e) The calculated SAED of the quantum mechanics predicted τ -B₁₀₆ structure, projected along the [010] orientation. The relative intensity of spots in SAED is highly dependent on foil thickness, precise orientation, *etc.* (f) The simulated HRTEM image calculated using the quantum mechanics predicted τ -B₁₀₆ structure. This matches the experimental image and demonstrates the mirror symmetry for the alternating unit cell of τ -B₁₀₆. The reflections associated with the matrix and the twin are highlighted and indexed in (d). The unit cell for τ -B consists of 212 atoms and the atom positions (red) are overlaid on the simulated image in (f).

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. 3, 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 $\{001\}_r$ 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 -B₁₀₅ and τ -B₁₀₆) based on the β -B₁₀₅ and β -B₁₀₆ structures, respectively. (i) The optimized τ -B₁₀₅ belongs to the *Cmcm* orthorhombic space group, with primitive cell parameters of $a = 10.10$ Å, $b = 10.10$ Å, $c = 17.56$ Å, and $\gamma = 65.4^\circ$. The primitive unit cell [shown in Fig. 1(c)] contains 210 atoms, exactly twice that of β -B₁₀₅. (ii) The new τ -B₁₀₆ structure belongs to the *P1* space group with cell parameters of $a = 10.08$ Å, $b = 10.17$, $c = 17.57$, $\alpha = \beta = 90^\circ$, and $\gamma = 65.2^\circ$, while its unit cell contains 212 atoms, exactly twice that of β -B₁₀₆. We calculate that the energy of τ -B₁₀₆ is 12.4 meV lower than τ -B₁₀₅, so we conclude that τ -B₁₀₆ is the more stable structure for the τ -B phase, and we will focus on the τ -B₁₀₆ model further and discuss the τ -B₁₀₅ model only in the charge calculation.

We calculate that the energy of the τ -B₁₀₆ structure is 13.8 meV/B lower than β -B₁₀₆ and 12.7 meV/B lower than the α -B₁₂ 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 -B₁₀₆ more stable than β -B₁₀₆ by

13.8 meV and more stable than α -B₁₂ by 9.5 meV. Thus, τ -B₁₀₆ is the ground state of elemental boron.

To compare directly the experimentally discovered fully transformed and fully twinned grains with the new theoretically calculated τ -B structure, we simulated the x-ray and electron diffraction patterns and HRTEM images using the quantum mechanics derived atomic positions of the τ -B structure. The comparison of experimental and simulated XRD is shown in Fig. 2. This new τ -B₁₀₆ 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 β -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 β -B and τ -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 τ -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 τ -B₁₀₅ structure. Viewed along the [010] zone axis, the τ -B structure looks like rhombohedral boron with twins present at every second lattice plane. The τ -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 τ -B₁₀₆ 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 τ -B₁₀₆ 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., $\langle 010 \rangle$ and $\langle 110 \rangle$ support this observation and agree with our hypothesis that the experimentally observed new phase is the τ -B₁₀₆ structure.

The calculated stability of the new τ -B structure relative to other boron polymorphs, (β -B₁₀₆, α -B₁₂, and γ -B₂₈) is displayed in Table I. We see that τ -B₁₀₆ is more stable than α -B₁₂ by 12.7 meV/atom, while other phases β -B₁₀₆, γ -B₂₈ are higher in energy than α -B₁₂ by 1.1, and 27.3 meV/atom, respectively, which is consistent with

TABLE I. Energy of various boron phases relative to the α -B₁₂ phase.

Structure	α -B ₁₂	β -B ₁₀₆	τ -B ₁₀₆	γ -B ₂₈
Energy without ZPE correction (meV/atom)	0	1.1	-12.7	27.3
Energy with ZPE correction (meV/atom)	0	-2.3	-16.1	...
Energy with ZPE and dispersion correction (meV/atom)	0	4.3	-9.5	...

previous quantum mechanics simulations [15,16]. Considering ZPE and dispersion corrections, τ -B₁₀₆ is more stable than α -B₁₂ by 9.5 meV/atom and more stable than β -B₁₀₆ by 13.8 meV/atom.

The predicted density of τ -B₁₀₆ is 2.326 g/cm³, which is similar to predicted densities of 2.328 g/cm³ for β -B₁₀₆, 2.476 g/cm³ for α -B₁₂, and 2.566 g/cm³ for γ -B₂₈. The bonding in β -B is complex making it difficult to understand why τ -B₁₀₆ is more stable than β -B₁₀₆ but the electron counting rules proved valuable in understanding other phases of boron [43,46] should apply equally to τ -B. To gain insight into why τ -B phase is more stable, we calculated the charge distributions of the B₁₂ and B₅₇ (B₂₈-B-B₂₈) units in the β -B₁₀₅ and τ -B₁₀₅ structures, as shown in Fig. S5 of SM [31]. The electron counting rules in β -B₁₀₅ imply that two electrons must be added to each B₁₂ unit to satisfy Wade's rule while the B₅₇ units should donate three electrons to satisfy the mno rule [43]. The charge distributions in β -B₁₀₅ show that the three B₁₂ units in the edge center of rhombohedral unit cell have -0.464 charge and one B₁₂ unit in the corner has -0.085 charge for a net transfer of 1.477 while the B₅₇ units has a balancing charge of +1.477 charge. [The B₅₇ units transfer more electrons to three edge center B₁₂ units because the B₂₈ unit in B₅₇ is closer to these three B₁₂ units (~6.1 Å) than the one B₁₂ in the corner (9.1 Å)] These changes are consistent with the electron counting rules but with smaller amounts than the idealized rules. In contrast, the B₅₇ units in the τ -B₁₀₅ structure transfers 1.566 electrons to the nearby B₁₂ units, leading to -0.511, -0.511, -0.519 charges for three edge center B₁₂ units and -0.025 for one corner B₁₂ unit (a total of 1.566). Thus, τ -B₁₀₅ leads to a 6% increase in the charge transferred to the τ -B₁₀₅ units, making them closer to the electron counting rule [43], which may be why τ -B₁₀₅ is more stable.

In summary, we discovered a new τ -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 twinlike version of the original β -B structure, with a doubled unit cell. The quantum mechanics studies indicate that this new

phase is substantially more stable than either α -B₁₂ or β -B, making it the true ground state structure of boron.

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Q. A. and K. M. R. contributed equally to this work.

Q. A., K. M. R., K. H., and W. A. G. wrote the Letter. K. M. R. performed the experimental measurements and image simulations including TEM and XRD, K. Y. X. contributed to the TEM, and Q. A. performed the quantum mechanics simulations. Q. A., K. M. R., K. Y. X., K. H., and W. A. G. analyzed the data and discussed the results. K. M. R. first observed the new structure before Q. A. performed the quantum mechanics simulations.

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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 τ -B phase along a $\langle 010 \rangle$ zone axis; (v) TEM characterization of newly observed τ -B phase along a $\langle 110 \rangle$ zone axis; (vi) charge distributions (NBO analysis) of B₁₂ and B₅₇ units in β -B105 and τ -B105 structures; and (vii) the predicted structural parameters in Crystallographic Information File base format.
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