Structures, stability, mechanical and electronic properties of α-boron and its twined brother α*-boron

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The structures, stability, mechanical and electronic properties of α-boron and its twined brother α*-boron have been studied by first-principles calculations. Both α-boron and α*-boron consist of equivalent icosahedral B\textsubscript{12} clusters in different connecting configurations of "3S-6D-3S" and "2S-6D-4S", respectively. The total energy calculations show that α*-boron is less stable than α-boron but more favorable than β-boron and γ-boron at zero pressure. Both α-boron and α*-boron are confirmed dynamically and mechanically stable. The mechanical and electronic properties of α-boron and α*-boron indicate that they are potential superhard semiconducting phases of element boron.

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Boron is considered as the most mystic element due to its fascinating chemical complexity that leads to vast variety of polymorphs\textsuperscript{\textsubscript{14,22}}. Among these polymorphs, rhombohedral α-boron and β-boron (with 12 and 106 atoms in unit cells, respectively) are well-known and almost degenerate in energy at ambient condition. α-boron is more favorable than β-boron at high pressure and β-boron is more stable in high temperature condition. In 2008, Oganov et al.\textsuperscript{\textsubscript{5,10}} discovered an ionic phase of elemental boron (orthorhombic γ-boron with 28 atoms in its unit cell), which consists of icosahedral B\textsubscript{12} clusters and interstitial B\textsubscript{2} pairs acting as anions and cations, respectively, in a NaCl-type arrangement. This new phase of boron is stable between 19 and 89 GPa but quenchable at ambient conditions, which confirms the previous discovery of a new crystal of boron\textsuperscript{2} and thus provides us the missing piece of a puzzle of the phase diagram of boron\textsuperscript{3}.

Born atoms in its element crystals prefer forming icosahedral B\textsubscript{12} cluster, where each boron atom connects five neighbors with intra-B\textsubscript{12} B-B bonds. In α-boron, equivalent icosahedral B\textsubscript{12} clusters connect to each other directly with inter-B\textsubscript{12} B-B bonds and each of them has 12 equivalent neighbouring B\textsubscript{12} clusters. In γ-boron, each icosahedral B\textsubscript{12} connects to ten equivalent neighbouring B\textsubscript{12} clusters directly with inter-B\textsubscript{12} B-B bonds and two secondly adjacent B\textsubscript{12} clusters indirectly by interstitial B\textsubscript{2} pairs. The connectivity between icosahedral B\textsubscript{12} clusters and interstitial atoms in β-boron becomes more complex.

α-boron is not the only phase of boron consisting of pure icosahedral B\textsubscript{12} clusters (without any interstitial atoms like those in β-boron and γ-boron). Very recently, Pickard et al. obtained\textsuperscript{\textsubscript{15}} a new meta-stable phase of boron by an ab initio random structure searching method. This new phase belongs to Cmcm space group and can be considered as a twinned polymorph of α-boron with new connectivity (different from that in α-boron boron) between icosahedral B\textsubscript{12} clusters which is 0.01 eV/atom less stable than α-boron and more favorable than β-boron. With remarkable energetic stability, such a phase of boron is a potential superhard material. But there is no further discussion about the structure, dynamical stability, mechanical and electronic properties of this new phase. In this paper, based on the density functional theory (DFT) method, we systematically study the structure, dynamical and mechanical stability, mechanical and electronic properties of this new boron phase (we call it α*-boron in the following) and compare them with those of α-boron.

I. COMPUTATIONAL DETAILS

All calculations are carried out using the density functional theory (DFT) with general gradient approximation (GGA)\textsuperscript{\textsubscript{13,14}} as implemented in Vienna ab initio simulation package (VASP)\textsuperscript{\textsubscript{13,15}}. The interactions between nucleus and the valence electrons are described by the projector augmented wave (PAW) method\textsuperscript{\textsubscript{15,16}}. A plane-wave basis with a cutoff energy of 500 eV is used to expand the wave functions of all the systems considered in present work. The Brillouin Zone (BZ) sample meshes for all systems are set to be denser enough (less that 0.2 1/Å) in our calculations. Crystal lattices and atoms positions for every systems are fully optimized (under different external pressure) up to the residual force on each atom less than 0.005 eV/Å through the conjugate-gradient algorithm. The vibrational properties of α-boron and α*-boron are studied by using the phonon package\textsuperscript{\textsubscript{17}} with the forces calculated from VASP. For the mechanical proper-
FIG. 1: Primitive view and crystal view of α-boron (a); Sketch maps showing the structural characters of α-boron (b) and α*-boron (c); Primitive view and crystal view of α*-boron (d); Simulated X-ray (ties calculations, different numbers of deformed α-boron, α*-boron and γ-boron are considered according to their crystal symmetries.

II. RESULTS AND DISCUSSIONS

A. Structures

The optimized structures of α-boron and α*-boron in both primitive cell (top) and crystal cell (bottom) are shown in Fig. 1(a) and (d), respectively. The hexagonal crystal cell of α-boron belongs to R-3m (166) space group. Under zero pressure, its lattice constants are a=b=4.9 Å and c=12.55 Å. Two inequivalent boron atoms B1 and B2 in α-boron locate at positions of (0.237, 0.119, 0.108) and (0.197, 0.803, 0.024), respectively. In α-boron, each B1 atom possesses five intra-B12 B-B bonds and single (S-) inter-B12 B-B bond (S-type, colored in blue). Each B2 atom possesses five intra-B12 B-B bonds and double (D-) inter-B12 B-B bonds (D-type, colored in brown). The orthorhombic α*-boron belongs to Cmcm (63) space group. Its equilibrium lattice parameters are a=4.88 Å, b=8.85 Å and c=8.06 Å, respectively. There are five inequivalent boron atoms B1, B2, B3, B4 and B5 in α*-boron. They locate at positions of (0.667, 0.334, 0.75), (0.818, 0.507, 0.75), (1.000, 0.563, 0.924), (0.797, 0.169, 0.639) and (0.500, 0.265, 0.568), respectively. Similar to those in α-boron, the five inequivalent boron atoms in α*-boron can be divided into two types: S-type where the three boron atoms (B1, B2 and B3) colored in blue have five intra-B12 B-B bonds and single (S-) inter-B12 B-B bonds and D-type where the two brown boron atoms (B4 and B5) possess five intra-B12 B-B bonds and double (D-) inter-B12 B-B bonds. Although α-boron and α*-boron contain different numbers of inequivalent boron atoms, both structures contain only one inequivalent icosahedral B12 cluster. That is the reason we refer them as twinned structures of element boron.

In both α-boron and α*-boron, each icosahedral B12 cluster possesses twelve neighboring B12 clusters distributing in different stacking manners. In α-boron, twelve neighboring B12 clusters distribute around the center B12 cluster with a "3S-6D-3S" connecting configuration. As indicated in Fig. 1(b), three top-position B12 clusters (indicated as 7, 8 and 9) connect to the center B12 cluster with single inter-B12 B-B bonds formed by S-type boron atoms, six middle-position B12 clusters (indicated as 1, 2, 3, 4, 5 and 6) connect to the center B12 clusters with double inter-B12 B-B bonds formed by D-type boron atoms and three bottom-position B12 clusters (indicated as 10, 11 and 12) connect to the center B12 clusters with double inter-B12 B-B bonds formed by S-type boron atoms, forming a "3S-6D-3S" configuration. In α*-boron, the twelve neighboring B12 clusters distribute around the center B12 cluster with a "2S-6D-4S" connecting configuration as indicated in Fig. 1(c). Two top-position B12 clusters (indicated as 7 and 8) connect to the center B12 cluster with single inter-B12 B-B bonds formed by S-type boron atoms, six middle-position B12 clusters (indicated as 1, 2, 3, 4, 5 and 6) connect to the center B12 cluster with double inter-B12 B-B bonds formed by D-type boron atoms and four bottom-position B12 clusters (9, 10, 11 and 12) connect to the center B12 cluster with inter-B12 B-B bonds formed by S-type boron atoms. In both α-boron and α*-boron, S-type atoms connect to D-type atoms only with intra-B12 B-B bonds and never meet each other in different B12 clusters.

Both α-boron and α*-boron contain equivalent icosahedral B12 clusters in their crystal structure. The different connecting configurations of "3S-6D-3S" and "2S-6D-4S" for α-boron and α*-boron result in different space group of R-3m (166) and Cmcm (63), respectively. The different structures of α-boron and α*-boron also result in different X-ray diffraction patterns. Fig. 1(e) shows the X-ray diffraction patterns of α-boron and α*-boron. We can see that almost all the diffraction peaks of α-boron can be found in the XRD of α*-boron with reduced intensities, such as the peaks at 4.5°, 7.2° and 8.6°. In addition, α*-boron possesses characteristic diffraction peaks forbidden in α-boron, which locate at 4.7°, 6.2°, 8.0°, 9.9°, 12.09°, 19.05° and 23.33°. These characteristic peaks are helpful for experimental identification of α*-boron.
TABLE I: The calculated values of elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Vicker’s hardness $H_v$ (GPa) of the $\alpha$-boron, $\alpha^*$-boron and $\gamma$-boron.

| Systems     | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $B$  | $G$   | $H_v$ |
|-------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|------|-------|------|
| $\alpha$-boron | 454.64   | 109.86   | 45.46    | 20.60    | -        | -        | 605.21   | 208.03   | -        | -        | 212.38| 201.63| 38.96|
| $\alpha^*$-boron| 466.22   | 53.99    | 77.49    | -        | 569.69   | 56.67    | 444.13   | 211.73   | 122.05   | 217.76   | 205.58| 190.91| 36.60|
| $\gamma$-boron | 604.58   | 80.26    | 37.65    | -        | 534.42   | 80.70    | 448.36   | 243.20   | 222.34   | 253.00   | 218.79| 235.26| 50.12|

C. Mechanical properties

The elastic constants of $\alpha$-boron and $\alpha^*$-boron are calculated as the second-order coefficient in the polynomial function of distortion parameter $\delta$ used to fit their total energies according to the Hooke’s law. In view of their differences in crystal symmetries, six and nine groups of deformations are applied on $\alpha$-boron and $\alpha^*$-boron ($\gamma$-boron) in our calculations, respectively. The elastic constants of $\alpha$-boron and $\alpha^*$-boron are summarized in Table I with those of $\gamma$-boron used for comparison. Our calculated elastic constants for $\alpha$-boron and $\gamma$-boron are in good agreement with those in previous first-principle calculations. Based on these results, we can see that the six independent elastic constants of $\alpha$-boron satisfy the corresponding mechanical stability criteria for a hexagonal crystal with $C_{66}=(C_{11}-C_{12})/2>0$, $C_{11}+C_{12}-2(C_{13})^2/C_{33}>0$, and $C_{44}>0$. The orthorhombic $\alpha^*$-boron possesses nine independent elastic constants. As listed in Table I, these elastic constants also satisfy the corresponding mechanical stability criteria for an orthorhombic crystal with $C_{11}+C_{12}-C_{21}>0$, $C_{11}+C_{33}-2C_{13}>0$, $C_{22}+C_{33}-2C_{23}>0$, $C_{11}>0$, $C_{22}>0$, $C_{33}>0$, $C_{44}>0$, $C_{55}>0$, $C_{66}>0$, and $C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23}>0$.

The bulk modulus ($B$) and shear modulus ($G$) are evaluated according to Hill’s formula based on the calculated elastic constants. The calculated $B$ and $G$ for $\alpha$-boron are 205.58 GPa and 190.91 GPa, respectively, which are very close to those of $\alpha$-boron. To further analyze the hardness of $\alpha$-boron and $\alpha^*$-boron, we adopt the recently introduced empirical scheme to evaluate their Vicker’s hardness ($H_v$) determined their $B$ and $G$ as $H_v=2(G/B)^{0.585}$-3. The calculated values of Vicker’s hardness for $\alpha$-boron and $\alpha^*$-boron are 38.96 GPa and 36.60 GPa, respectively. These values indicate that both $\alpha$-boron and $\alpha^*$-boron are potential superhard phases of element boron.
FIG. 3: The band structures of α-boron (a) and corresponding local density of state projected on the S-type (b) and the D-type (c) boron atoms. The band structures of α*-boron (d) and corresponding local density of state projected on the S-type (e) and the D-type (f) boron atoms.

FIG. 4: The charge difference density for α-boron (left) and α*-boron (right). Electrons transfer from the green-blue area to the red-yellow area.

D. Electronic properties

Both α-boron and α*-boron contain pure icosahedral B_{12} clusters with different connecting configurations. Such a structural difference may result in different electronic properties in α-boron and α*-boron. In Fig. 3 (a) and (d), we show the band structures of α-boron and α*-boron, respectively. From the band structures, we can see that both of them are indirect-band-gap semiconductors. Differently, the valence band maximum (VBM) and conduction band minimum (CBM) in α-boron locate at T-point (0.5, 0.5, 0.5) and Γ-point (0.0, 0.0, 0.0), respectively, separated by a forbidden band with a gap of 1.497 eV. But the VBM and CBM in α*-boron locate at Γ-point (0.0, 0.0, 0.0) and T-point (0.5, 0.5, 0.5), respectively, forming an indirect-band gap of 2.004 eV. Based on the local density of states (LDOS) projected on S-type and D-type boron atoms as shown in Fig. 3, we can see that the VBM states in both α-boron and α*-boron are contributed from the D-type boron atoms and their CBM states are derived from S-type boron atoms. In both α-boron and α*-boron the whole valence band is mainly contributed by the S-type boron atoms and the whole conduction band is mainly contributed by the D-type boron atoms. These results indicate that the valence electrons density mainly comes from the S-type boron atoms and the hole density mainly comes from the D-type atoms.

The corresponding charge difference density (CDD) of α-boron and α*-boron is shown in Fig. 4 to confirm and understand the electronic properties discussed above. From the CDD of α-boron shown in the left in Fig. 4, we can see that the D-type boron atoms (brown balls) lose electrons and the S-type boron atoms (blue balls) gain electrons. The CDD of α*-boron is shown in the right panel in Fig. 4. Similar to that of α-boron, the D-type boron atoms (brown balls) in α*-boron loss electrons and the S-type boron atoms (blue balls) gain electrons. These CDD results reveal that the bonding electrons in both α-boron and α*-boron prefer to distribute on the inter-B_{12} B-B bonds formed by the S-type boron atoms than those formed by the D-type boron atoms and the intra-B_{12} B-B bonds.

III. CONCLUSION

We have studied the structure, stability, mechanical and electronic properties of a new orthorhombic boron phase α*-boron and compared them with those of its twinned brother α-boron. Both α-boron and α*-boron consist of equivalent icosahedra B_{12} clusters with different connecting configurations of "3S-6D-3S" and "2S-6D-4S", respectively. Our results show that α*-boron is a dynamically and mechanically viable phase of element boron. The remarkable energetic stability and considerable hardness of 36.8 GPa of α*-boron indicate that it is a promising superhard material with potential applications in industry.
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