Predicting the Ground-state Structure of Sodium Boride

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(Received 2 October 2017; revised manuscript received 5 March 2018; published 26 March 2018)

Binary borides has been a subject of extensive research. However, the exact compositions and crystal structures of sodium borides remained controversial. Here, using the \textit{ab initio} variable-composition evolutionary algorithm, we utilized \textit{ab initio} evolutionary algorithm USPEX [12], performing searches with up to 40 atoms per primitive cell and searching for all stable stoichiometries and their corresponding structures simultaneously. A phase is deemed stable if its enthalpy of formation from either elements or any other possible compounds is negative, and such a method has been successfully applied to various bulk systems [13–16]. Structure relaxations and total-energy calculations used the all-electron projector-augmented wave [17] method as implemented in the \textit{VASP} package [18] with [1s2] cores for both Na and B atoms, the exchange-correlation energy was treated within the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE) [19]. In addition, the local density approximation (LDA) with the functional of Ceperley and Alder [20] as parametrized by Perdew and Zunger [21] was also employed to confirm the energetic stability. The plane-wave cutoff energy of 500 eV and uniform Γ-centered \textit{k}-point grids with a resolution of \(2\pi \times 0.04 \text{ Å}^{-1}\) were used. Denser \textit{k}-point grids were tested but produced indistinguishable results. The convergence for terminating the electronic self-consisting...
cycle and the force criterion for structure relaxation were set at $10^{-6}$ eV and $10^{-2}$ eV/Å, respectively. Phonon dispersion curves were calculated using the finite displacement method as implemented in the PHONOPY package [22] where the convergence criterion for the total energy was $10^{-8}$ eV. Elastic tensors were computed via stress-strain relations. Combined with the Voigt-Reuss-Hill approximation [23], the bulk and shear moduli were calculated by the CASTEP code at the GGA-PBE level [24]. Powder XRD patterns were simulated using the REFLUX software [24]. Topological properties were investigated by constructing maximally localized Wannier functions [25] using the WANNIER90 code [26].

The convex hull plotted in Fig. 1 showed two stable compounds at ambient pressure, Na$_2$B$_{20}$ and Na$_2$B$_{30}$, consistent with the available experimental reports. Especially, the predicted lattice constants and atomic positions for Na$_2$B$_{30}$ are in excellent agreement with the experimental values [9]. This illustrates the power, reliability, and accuracy of the USPEX method. However, the experimental $Imm2$-Na$_2$B$_{29}$ structure has a positive formation energy (3.03 meV/atom) and is far from the convex hull. Additionally, the structure search also found a new monoclinic Na$_2$B$_{29}$ (C2-Na$_2$B$_{29}$), which had lower formation energy (−2.45 meV/atom) than $Imm2$-Na$_2$B$_{29}$ but still above the convex hull formed by Na$_3$B$_{20}$ and Na$_2$B$_{30}$, indicating that both structures of Na$_2$B$_{29}$ are at best metastable phases. Unexpectedly, it was not the much-discussed $Imma$-Na$_2$B$_{30}$ but a new polymorph $I2\bar{1}2121$-Na$_2$B$_{30}$ that appeared on the convex hull and therefore predicted to be one of the true ground-state phases in the Na-B system because it has lower enthalpy than the mixture of elemental Na and B or any other mixtures. As shown in Table I, the GGA-PBE results show that $I2\bar{1}2121$-Na$_2$B$_{30}$ is more stable than $Imm2$-Na$_2$B$_{29}$ as a function of pressure. The LDA give the same ranking of structures by stability. Inclusion of zero-point energy from the GGA-PBE results only strengthens our conclusion: $I2\bar{1}2121$-Na$_2$B$_{30}$ is now more stable than $Imm2$-Na$_2$B$_{30}$ by −7.38 meV/atom. Moreover, the enthalpy difference (as a function of pressure; see the inset of Fig. 1) confirms that $I2\bar{1}2121$-Na$_2$B$_{30}$ is more stable than $Imm2$-Na$_2$B$_{30}$ at any pressure.

These two crystal structures are compared in Fig. 2. For the $Imm2$-Na$_2$B$_{29}$ structure, the Na atom sits at Na $(0.000,0.250,0.089)$, six inequivalent B sites are B1 $(0.202,0.089,0.915)$, B2 $(0.169,0.002,0.713)$, B3 $(0.395,0.250,0.144)$, B4 $(0.649,0.250,0.903)$, B5 $(0.000,0.250,0.497)$, and B6 $(0.915,0.250,0.796)$. Among them, Na, B3, and B5 are interstitial atoms, i.e., not belonging to any B$_12$ icosahedra. The icosahedra are connected either by direct intericosahedral B-B bonds (two-electron–two-center bonds with the lengths of 2.078 and 1.711 Å) or by three-center bonds with bond lengths of 2.078 and 1.746 Å [see Figs. 2(a) and 2(b)]. The $Imm2$-Na$_2$B$_{29}$ structure, as mentioned above, is just a modified version of $Imm2$-Na$_2$B$_{30}$, obtained by removing two interstitial B atoms from their interstitial triangular boron units in the unit cell, resulting in a 3.33% boron vacancy concentration. On the other hand, atomic positions in the $I2\bar{1}2121$-Na$_2$B$_{30}$ structure are completely different from those of $Imm2$-Na$_2$B$_{30}$ [see Figs. 2(c) and 2(d)]; Na $(0.000,0.250,0.149)$, eight inequivalent B atoms occupy sites B1 $(0.587,0.741,0.363)$, B2 $(0.332,0.996,0.039)$, B3 $(0.171,0.478,0.953)$, B4 $(0.191,0.095,0.953)$, B5 $(0.917,0.238,0.469)$, B6 $(0.189,0.419,0.339)$, B7 $(0.840,0.232,0.663)$, and B8 $(0.368,0.000,0.250)$. Among them, the interstitial B1 and B8 atoms form a peculiar hexagonal sublattice, linking B12 icosahedra by multicenter B-B-B bonds with varied bond lengths ranging from 1.711 to 2.058 Å.

Table I compares calculated properties of various models of Na$_2$B$_{20}$ and Na$_2$B$_{29}$ with experimental values. All three models have similar lattice constants and densities (compare lattice parameters of $I2\bar{1}2121$-Na$_2$B$_{30}$ with the experimental values [7,8], the maximum difference in lattice parameters $a$, $b$, and $c$ is 1.16%, 2.56%, and 2.25%), and all three are in good agreement with experimental results. It is unsurprising that $Imm2$-Na$_2$B$_{30}$ and $Imm2$-Na$_2$B$_{29}$ have similar lattice constants because they are just two versions of the

![Graph](image_url)

**FIG. 1.** The calculated convex hull for the Na-B system, using bcc-Na and α-boron phases for pure elements. Here, $\Delta H_{\text{formation}}(\text{Na}_x\text{B}_{1-x}) = H(\text{Na}_x\text{B}_{1-x}) - xH(\text{Na}) - (1 - x)H(\text{B})$. The inset shows the enthalpy difference between $Imm2$-Na$_2$B$_{30}$ and $I2\bar{1}2121$-Na$_2$B$_{30}$ as a function of pressure.

### Table I. Lattice constants, energy of formation ($\Delta E_f$ with units of meV/atom), density ($\rho$), shear modulus ($G$), and the calculated Vickers hardness ($H_v$) of sodium borides. Some experimental values (from Refs. [7,8]) are also listed for comparison.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$Na_2B_{20}$</th>
<th>$Na_2B_{30}$</th>
<th>$Na_2B_{29}$</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>10.42</td>
<td>10.29</td>
<td>10.34</td>
<td>10.40$^9$, 10.30$^7$</td>
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<tr>
<td>$b$ (Å)</td>
<td>5.70</td>
<td>5.84</td>
<td>5.82</td>
<td>5.86$^9$, 5.85$^7$</td>
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<tr>
<td>$c$ (Å)</td>
<td>8.23</td>
<td>8.42</td>
<td>8.31</td>
<td>8.33$^9$, 8.42$^7$</td>
</tr>
<tr>
<td>$\Delta E_f$ (GGA)</td>
<td>$-57.81$</td>
<td>$-51.44$</td>
<td>3.03</td>
<td>N/A</td>
</tr>
<tr>
<td>$\Delta E_f$ (LDA)</td>
<td>$-63.37$</td>
<td>$-45.23$</td>
<td>13.97</td>
<td>N/A</td>
</tr>
<tr>
<td>$\rho$ (g/cm$^{-3}$)</td>
<td>2.52</td>
<td>2.43</td>
<td>2.39</td>
<td>2.34$^a$, 2.44$^a$</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>189.02</td>
<td>162.50</td>
<td>142.03</td>
<td>N/A</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>190.05</td>
<td>179.32</td>
<td>167.22</td>
<td>N/A</td>
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<tr>
<td>$H_v$ (GPa)</td>
<td>37.40</td>
<td>30.23</td>
<td>25.53</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### Table I.

- $\Delta H_{\text{formation}}$: Formation energy difference.
- $\rho$: Density.
- $G$: Shear modulus.
- **Symmetry**: Crystal symmetry.
- **$Na_2B_{20}$**, **$Na_2B_{30}$**, **$Na_2B_{29}$**: Calculated properties.
- **Experiments**: Experimental values (from Refs. [7,8]).
FIG. 2. Structures of Imma-Na2B30 and I2212121-Na2B30. (a) Projection of Imma-Na2B30 along the [100] direction. (b) Projection of Imma-Na2B30 along the [010] direction. (c) Projection of I2212121-Na2B30 along the [100] direction. (d) Projection of I2212121-Na2B30 along the [010] direction. The Na and B atoms are colored in purple and brown, and the interstitial B atoms in the two structures are magnified for clarity.

same structure, whereas I2212121-Na2B30 has a completely different structural topology. Therefore, we simulated the x-ray-diffraction patterns of the Imm2-Na2B29, Imma-Na2B30, and I2212121-Na2B30 structures and compared them with the experimental results [8]. As shown in Fig. 3(a), there is good agreement, both for the positions and the intensities of most peaks for all of the three models and experiments, including the (200), (211), (301), (220), (312), (213), (321), and (325) peaks. The other simulated peaks with 2θ from 45° to 70° are too weak to be used for quantitative analysis [8]. Note that the (101) peak is absent in I2212121-Na2B30 and the intensities of the (011) and (002) peaks deviate from experimental values to some extent. We speculate that I2212121-Na2B30 may coexist with Imma-Na2B30 or Na2B29 at ambient conditions. Moreover, the comparison of the measured electron-diffraction pattern (TEM) along the [010] direction [Fig. 3(b)] showed that the diffraction spots of all three models again match well with the experimental data [8]. Since the I2212121-Na2B30 structure is very different from Imma-Na2B30 or Imm2-Na2B29, this example shows that very different structures can have very similar XRD and TEM patterns, making structure determination ambiguous, and in such cases the input from theory is invaluable.

FIG. 3. (a) Simulated XRD patterns of Imm2-Na2B29, Imma-Na2B30, and I2212121-Na2B30 with a wavelength of 1.54056 Å at ambient pressure compared with the experimental results. (b) Simulated TEM patterns of Imm2-Na2B29, (c) Imma-Na2B30, (d) I2212121-Na2B30, and (e) the experimental result at normal conditions.

Figure 4 shows band structures of Imma-Na2B30, Imm2-Na2B29, and I2212121-Na2B30 from the GGA-PBE calculations. Previously, Imma-Na2B30 was thought to be a metal [11]. However, our calculations show that valence and conduction bands exhibit linear dispersion at the Fermi level [Fig. 4(a)]. Further band analysis of Imma-Na2B30 indicates that the crossing points form two perpendicular nodal rings [Fig. 4(b)], which are dominantly originated from the p orbitals of B atoms. Therefore, Imma-Na2B30 is a topological nodal line semimetal. The particular nodal rings should be protected by the combination of inversion and time-reversal symmetry [27], which are expected to have more intensive nonlinear electromagnetic response than Dirac semimetals with a single cone and thus possess a higher efficiency of carrier transport at the Fermi level via multiple Dirac channels [28]. In Imm2-Na2B29, due to very close structure similarity, the nodal rings could be preserved. However, because of the minor concentration of B vacancies, the Fermi level is shifted down by 0.62 eV to the valence band [Fig. 4(c)], consequently the hybridized bonding states located at the valence band are partially filled, hence Imm2-Na2B29 is metallic. In contrast, I2212121-Na2B30 is an indirect-gap semiconductor with a band gap of 1.6 eV [Fig. 4(d)]. Therefore, as mentioned above, in view of the energetic stability, we see the order of stability I2212121-Na2B30 > Imma-Na2B30 > Imm2-Na2B29, which is in accordance with the electronic stability among the three compounds, that is, the semiconducting I2212121-Na2B30 > semimetallic Imma-Na2B30 > metallic Imm2-Na2B29.

Phonon densities of states (PDOS) of I2212121-Na2B30 and Imma-Na2B30 phases are shown in Fig. 5(a), both of them...
are dynamically stable at ambient pressure. In addition, the temperature dependence of the free energy of I212121-Na2B30 and Imm2-Na2B29 is shown in Fig. 5(b): I212121-Na2B30 is always more stable than Imm2-Na2B29 at least up to the temperature of 1000 K.

In conclusion, we performed a systematic search for stable compounds of sodium and boron and identified semiconducting I212121-Na2B30 as a new ground-state structure, which has an unprecedented three-dimensional boron framework with the peculiar interstitial helical structure. Recently, a new silicon allotrope with a quasidirect band gap was synthesized by using a novel two-step synthesis methodology [33] (consisting of the synthesis of Na4Si24 and then removing the Na atoms from the open-framework Na4Si24 structure by the thermal “degassing” process). Since the channel-like boron host structure is also present in I212121-Na2B30 (along the b axis), one can attempt to synthesize a new boron allotrope (I212121-B30) by using the same approach.

This Rapid Communication was supported by the National Science Foundation of China (Grants No. 11674176 and No. 51772263), the Tianjin Science Foundation for Distinguished Young Scholars (Grant No. 17JCQJC44400), and the 111 Project (Grant No. B07013). A.R.O. thanks Russian Science Foundation (Grant No. 17-73-20038), and the Foreign Talents Introduction and Academic Exchange Program (Grant No. B08040). Q.Z. is grateful for support from the National Nuclear

FIG. 4. (a) The band structure of Imm2-Na2B30 at ambient pressure. (b) Several high-symmetry points in the Brillouin zone of Imm2-Na2B30 are labeled. The multiple nodal rings center at the Z point, and the color bar indicates the energy of each nodal point. (c) and (d) show the band structures of Imm-Na2B29 and Imma-Na2B30 at ambient pressure. (e) and (f) show the band crossings (indicated by the yellow dotted lines) of Imm2-Na2B30 formed by the valence and conduction bands in the vicinity of the Z point.
Security Administration under the Stewardship Science Academic Alliances Program through DOE Cooperative Agreement No. DE-NA0001982. X.D. acknowledges the computing resources of Tianhe II and the support of Chinese National Supercomputer Center in Guangzhou. Q.S.W. acknowledges support by the NCCR MARVEL.