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Predicting the ground-state structure of sodium boride

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Binary borides has been a subject of extensive research. However, the exact compositions and crystal structures of sodium borides remained controversial. Here, using the ab initio variable-composition evolutionary algorithm, a new stable Na2B30 with I212121 symmetry (I21;2121-Na2B30) is found, which is −7.38 meV/atom lower in energy than the Imma-Na2B30 structure reported by experimentalists. Interestingly, the Imma-Na2B30 structure is predicted to be a topological nodal line semimetal, which may result in superior electronic transport. In contrast, I21;2121-Na2B30 is a ultrahard semiconductor with an unprecedented open-framework structure, whose interstitial helical boron sublattice enhances its hardness and energetic stability.

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The discovery of high-temperature superconductivity, superhardness, ferromagnetism, and quantum topological properties in metal borides has attracted much attention owing to many interesting fundamental issues and huge potential applications [1–6]. For alkali–metal borides, only a few compounds have been precisely determined with regard to their compositions and structures. This is mainly limited by the synthesis and characterization of these materials, e.g., it is difficult to conduct a controlled reaction between the low-melting alkali metals with boron under ambient pressure, and their products are often microcrystalline powders rather than single crystals [7–10]. So far, there are only two sodium borides, orthorhombic Na3B20 and Na2B30 (or monoclinic Na2B29), which were successfully synthesized at ambient pressure [7–9]. However, the exact structure and composition of “Imma-Na2B30” are still controversial. Previously, Naslain and Kasper refined the structure as orthorhombic Na3B20 (designated as the φ phase) [7]. This structure consists principally of B12 icosahedra with interstitial boron triangular units, with Na atoms accommodated in the cages formed by icosahedra [7]. Since the unit cell of Na2B30 contains four formula units, it could be written as 4(NaB3B12). However, by using x-ray diffraction (XRD), neutron diffraction, electron microscopy, and solid-state NMR spectroscopy, Albert et al. revised the structure as monoclinic Na2B30 (2(NaB3B12 + NaB2B12)) with two interstitial B atoms per unit cell unoccupied (Cm′-Na2B30) [8]. To study the controversy, we performed ab initio calculations for the two structural models and found that: (1) the relaxed Na2B30 had orthorhombic symmetry (I2mm-Na2B30), which is inconsistent with the reported monoclinic symmetry [8]; (2) Imma-Na2B30 is energetically more favorable than I2mm-Na2B30 in the Na–B system; (3) the band structure shows that Imma-Na2B30 is a topological nodal line semimetal rather than a metal [11]. These intriguing results inspire us to further explore the polymorphism, phase diagram, and properties of this important compound.

To find stable Na–B compounds and structures, we utilized the 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 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 k-point grids with a resolution of 2π × 0.04 Å−1 were used. Denser k-point grids were tested but produced indistinguishable results. The convergence for terminating the electronic self-consisting
The inset shows the enthalpy difference between \( \text{Imma-Na}_2\text{B}_{30} \) and \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) as a function of pressure. Here, \( \Delta H_{\text{formation}}(\text{Na}_2\text{B}_{1-x}) = H(\text{Na}_2\text{B}_{1-x}) - xH(\text{Na}) - (1 - x)H(B) \). The inset shows the enthalpy difference between \( \text{Imma-Na}_2\text{B}_{30} \) and \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) as a function of pressure.

The convex hull plotted in Fig. 1 showed two stable compounds at ambient pressure, \( \text{Na}_3\text{B}_{20} \) and \( \text{Na}_2\text{B}_{30} \), consistent with the available experimental reports. Especially, the predicted lattice constants and atomic positions for \( \text{Na}_2\text{B}_{30} \) are in excellent agreement with the experimental values [9]. This illustrates the power, reliability, and accuracy of the USPEX method. However, the experimental \( 1\text{mm}2\text{-Na}_2\text{B}_{30} \) 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 \( \text{Na}_2\text{B}_{29} \) (\( C2\text{-Na}_2\text{B}_{29} \)), which had lower formation energy (−2.45 meV/atom) than \( 1\text{mm}2\text{-Na}_2\text{B}_{30} \) but still above the convex hull formed by \( \text{Na}_3\text{B}_{20} \) and \( \text{Na}_2\text{B}_{30} \), indicating that both structures of \( \text{Na}_2\text{B}_{29} \) are at best metastable phases. Unexpectedly, it was not the much-discussed \( \text{Imma-Na}_2\text{B}_{30} \) but a new polymorph \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) 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 \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) is −6.37 and −60.84 meV/atom lower in formation energy than the \( \text{Imma-Na}_2\text{B}_{30} \) and \( 1\text{mm}2\text{-Na}_2\text{B}_{29} \) structures. The LDA calculations show the corresponding values are −18.14 and −77.34 meV/atom accordingly, i.e., both the GGA-PBE and the LDA give the same ranking of structures by stability. Inclusion of zero-point energy from the GGA-PBE results only strengthens our conclusion: \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) is now more stable than \( \text{Imma-Na}_2\text{B}_{30} \) by −7.38 meV/atom. Moreover, the enthalpy difference (as a function of pressure; see the inset of Fig. 1) confirms that \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) is more stable than \( \text{Imma-Na}_2\text{B}_{30} \) at any pressure.

These two crystal structures are compared in Fig. 2. For the \( \text{Imma-Na}_2\text{B}_{30} \) structure, the Na atom sits at \( \text{Na}_3\text{B}_{20} \) (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, \( \text{Na} \), \( B3 \), and \( B5 \) are interstitial atoms, i.e., not belonging to any \( \text{B}_{12} \) icosahedra. The icosahedra are connected either by direct intericosahedral \( B \)-B bonds (two-electron–two-center bonds with the lengths of 1.766 and 1.755 Å) or by three-center bonds with bond lengths of 2.078 and 1.746 Å [see Figs. 2(a) and 2(b)]. The \( 1\text{mm}2\text{-Na}_2\text{B}_{29} \) structure, as mentioned above, is just a modified version of \( \text{Imma-Na}_2\text{B}_{30} \), 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 \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) structure are completely different from those of \( \text{Imma-Na}_2\text{B}_{30} \) [see Figs. 2(c) and 2(d)]; \( \text{Na} \) (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, 0.337), \( B5 \) (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 helical sublattice, linking \( B12 \) icosahedra by multiconcentric \( B-B-B \) bonds with varied bond lengths ranging from 1.711 to 2.058 Å.

Table I compares calculated properties of various models of \( \text{Na}_3\text{B}_{20} \) and \( \text{Na}_2\text{B}_{29} \) with experimental values. All three models have similar lattice constants and densities (compare lattice parameters of \( \text{I}2\_2\_2\_2\_\text{Na}_2\text{B}_{30} \) with the experimental values [7,8], the maximum difference in lattice parameters \( a, b, c \) is 1.16%, 2.56%, and 2.25%), and all three are in good agreement with experimental results. It is unsurprising that \( \text{Imma-Na}_2\text{B}_{30} \) and \( 1\text{mm}2\text{-Na}_2\text{B}_{29} \) have similar lattice constants because they are just two versions of the...
same structure, whereas $I2\overline{2}121-Na2B30$ has a completely different structural topology. Therefore, we simulated the x-ray-diffraction patterns of the $Imm2$-$Na2B29$, $Imma-Na2B30$, and $I2\overline{2}121-Na2B30$ 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 $2\theta$ from 45$^\circ$ to 70$^\circ$ are too weak to be used for quantitative analysis [8]. Note that the (101) peak is absent in $I2\overline{2}121-Na2B30$ and the intensities of the (011) and (002) peaks deviate from experimental values to some extent. We speculate that $I2\overline{2}121-Na2B30$ 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 $I2\overline{2}121-Na2B30$ 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.

Figure 4 shows band structures of $Imma-Na2B30$, $Imm2-Na2B29$, and $I2\overline{2}121-Na2B30$ 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, $I2\overline{2}121-Na2B30$ 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 $I2\overline{2}121-Na2B30 > Imma-Na2B30 > Imm2-Na2B29$, which is in accordance with the electronic stability among the three compounds, that is, the semiconducting $I2\overline{2}121-Na2B30$ > semimetallic $Imma-Na2B30$ > metallic $Imm2-Na2B29$.

Phonon densities of states (PDOS) of $I2\overline{2}121-Na2B30$ and $Imma-Na2B30$ phases are shown in Fig. 5(a), both of them...
FIG. 4. (a) The band structure of Imma-Na2B30 at ambient pressure. (b) Several high-symmetry points in the Brillouin zone of Imma-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 Imm2-Na2B29 and I212121-Na2B30 at ambient pressure. (e) and (f) show the band crossings (indicated by the yellow dotted lines) of Imma-Na2B30 formed by the valence and conduction bands in the vicinity of the Z point.

are dynamically stable at ambient pressure. In addition, the temperature dependence of the free energy of I212121-Na2B30 and Imma-Na2B30 is shown in Fig. 5(b): I212121-Na2B30 is always more stable than Imma-Na2B30 at least up to the temperature of 1000 K. We also calculated charge distributions of Imma-Na2B30 and I212121-Na2B30. Bader charges show significant differences for the interstitial B atoms: In Imma-Na2B30, they are +0.38 and −1.15 e for B3 and B5 atoms, whereas they are +0.03 and +0.07 e for the interstitial B1 and B8 atoms of the I212121-Na2B30 structure. More homogeneous Bader charges in the interstitial sublattice correlate with their greater thermodynamic stability at ambient pressure, in agreement with the proposed correlations between local bonding configurations and energetic stability [29,30]. Hence the free energy, electronic stability, formation energy, and charge transfer support that I212121-Na2B30 is a true thermodynamic ground state, unlike Imm2-Na2B29 and Imma-Na2B30. Furthermore, boron-rich sodium borides are expected to have superior mechanical properties, e.g., high hardness. According to models [31,32], Vickers hardness was estimated as $H_v = 0.92k^{1.37}G^{0.708}$ and $k = G/B$, where $G$ and $B$ are the shear modulus and the bulk modulus. The calculated hardesses for Imm2-Na2B29, Imma-Na2B30, and I212121-Na2B30 (see Table I) are 25.5, 30.2, and 37.4 GPa, respectively. Thus the semiconducting I212121-Na2B30 phase is harder than semimetallic Imma-Na2B30 or metallic Imm2-Na2B29, owing to its special interstitial helical structure, which enhances the energetic stability and hardness.

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.

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