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Prediction of a multicenter-bonded solid boron hydride for hydrogen storage

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A layered solid boron hydride structure (B_2H_2) consisting of a hexagonal boron network and bridge hydrogen which has a gravimetric capacity of 8 wt% hydrogen is predicted. The structural, electronic, and dynamical properties of the proposed structure are investigated using first-principles electronic structure methods. The absence of soft phonon modes confirms the dynamical stability of the proposed structure. Charging the structure significantly softens hydrogen related phonon modes. Boron modes, in contrast, are either hardened or not significantly affected by electron doping. Furthermore, self-doping the structure considerably reduces the energy barrier against hydrogen release. These results suggest that electrochemical charging or self-doping mechanisms may facilitate hydrogen release while the underlying boron network remains intact for subsequent rehydrogenation.

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I. INTRODUCTION

Hydrogen fuel cells are attractive for their very high efficiency. Beyond the technology of the cells themselves, these systems present two major challenges: economic large-scale hydrogen production and practical small-scale on-board hydrogen storage.[1] The storage problem, in particular, demands fundamentally new transformative science and engineering. Most current hydrogen storage technologies (e.g., cryogenic liquid, high-pressure gas cells, low-temperature adsorbates, metal hydrides, and chemical storage) suffer from one or more major deficiencies in cost, thermodynamic efficiency, volumetric capacity, kinetics, gravimetric density, long-term storage, and reversibility.[2] Although there are some recent encouraging progresses,[3–6] the challenge is far from being solved. As a result, progressive optimization of the existing material systems alone may not be able to solve this grand challenge. An equally important direction is to explore completely new materials. A recent US Department of Energy (DOE) annual report[7] on hydrogen storage documents in details the progress achieved as well as the need to investigate new materials to overcome existing problems.

An ideal material for on-board hydrogen storage must release hydrogen at practical temperature and pressure and also must be regenerated efficiently under similarly gentle conditions. Therefore, thermodynamically, the hydride material must lie within a narrow range near the hydrogenation/dehydrogenation phase boundary. Materials involving only conventional bonding mechanisms normally do not meet these requirements. In contrast, materials containing certain frustrated bonding are designed to be on the verge of frustration-induced phase transition, and they may be better suited for hydrogen storage. Here we propose a layered solid boron hydride which has a gravimetric capacity of 8 wt% H_2 and show its potential for hydrogen storage.

It is interesting that all three major classes of hydrogen storage materials investigated so far (i.e., low-temperature adsorbates, metal hydrides, and chemical storage) overlap with regards to only boron. Examples include physical adsorption systems with boron-doped carbons,[8–10] chemical systems using ammonia borane derivatives,[11–14] and light metal borohydrides.[15] Boron is distinguished from the remainder of the periodic table by an *electronic frustration*. As a result, boron-based materials are well known for their rich and highly unconventional chemistry. Having only three valence electrons, boron cannot form a sufficient number of traditional covalent bonds to reach a close-shell configuration. Being a small, tight first-row *p*-block element, it is insufficiently electropositive to participate strongly in traditional metallic bonding, yet also insufficiently electronegative to be dominated by highly stable ionic configurations. These properties force boron to assume unusual multicenter bonding configurations in many of its compounds. One of the most famous examples, and a distinct feature of electron deficiency, is the three-center two-electron (3c2e)[16] bonding found in many boranes. Chemically frustrated boron, when properly deployed in a supporting chemical framework, provides an intriguing opportunity to attain an intermediate bonding with hydrogen. In this paper, we exploit the rich chemistry of boron and hydrogen to propose a solid boron hydride structure which contains intermediate strength 3c2e-like multicenter B−H bonds and investigate its potential for on-board hydrogen storage.

II. MODEL

Although the rich boron chemistry explored to date has been dominated by three dimensional cage structures,[17–19] computational and experimental studies[20–23] have begun to uncover a latent planar aspect in boron-rich materials. Using a combination of photoelectron spectroscopy (PES) technique and *ab initio* calculations,[24,25] a stable planar structure of boron clusters containing 10 to 15 atoms are shown to exist. Furthermore, a new class of planar boron sheets is predicted to exist through a self-doping mechanism.[26] The stability of these sheets is explained with a bonding mechanism which arises from the competition of two- and three-center bondings. The possibility of using planar boron sheets with alkali-metal intercalation for hydrogen storage has also been investigated.[27]

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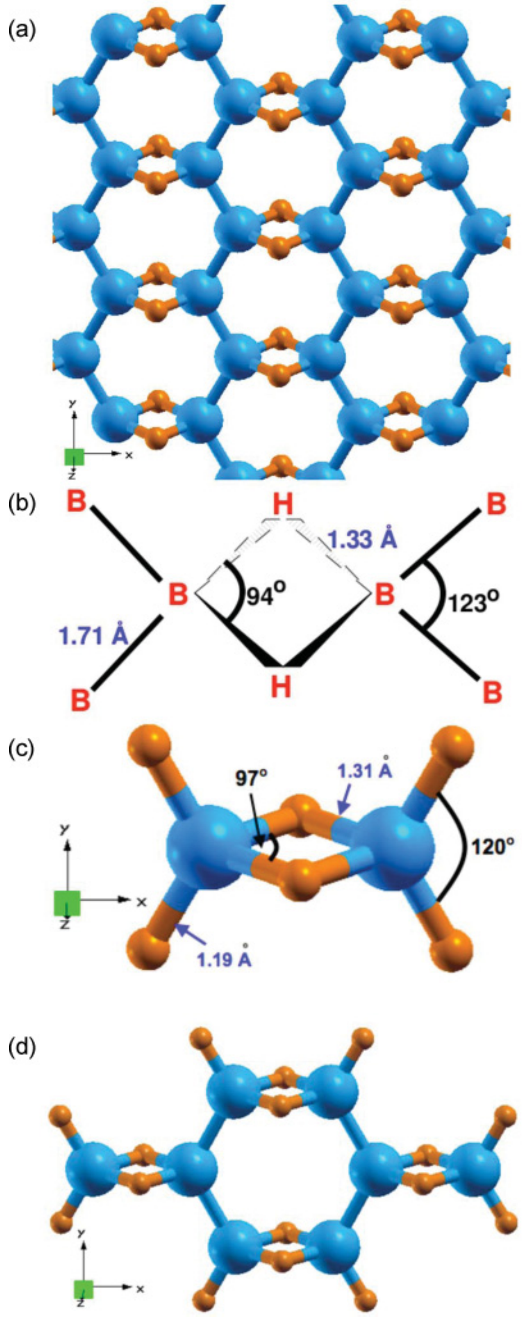

FIG. 1. (Color online) Structure of single-layer B_2H_2, (a) The relaxed structure. (b) The corresponding bond angles and bond lengths. (c) The structure of diborane. (d) Structure of octaborane. Boron is blue (big spheres) and hydrogen is orange (small spheres).

Pure hexagonal boron layer, although not stable alone due to electron deficiency, can be stabilized by intercalating electron donors such as Mg and Al to form MgB_2 and AlB_2. The hexagonal boron sheet has a much greater structural flexibility than graphine. For example, the in-plane lattice constant expands from 3.01 Å in AlB_2 to 3.17 Å in ZrB_2. In this work, we propose that the electron-deficient hexagonal boron network can be stabilized in part or whole through the formation of 3c2e bonds with hydrogen atoms. In fact, nature finds a way to stabilize the electron-deficient molecule diborane through the formation of 3c2e bonds. The 3c2e BH bonds have also been proposed to stabilize boron hydride fullerenes.[28] It is plausible that the electron-deficient hexagonal boron network can be stabilized in part or whole through the formation of 3c2e bonds with hydrogen, as shown in Fig. 1(a), which we denote as B_2H_2. The boron atoms in B_2H_2 form borane-like 3c2e bonds with bridging hydrogen atoms and connect to other in-plane boron atoms via a conventional sp^2 hybridization. The hydrogen atoms are bound to the hexagonal boron plane in pairs, one above and the other below the plane. These weakly bonded hydrogens are crucial to stabilize the boron network and are desirable for the release of hydrogen at practical conditions. The extended boron framework in this solid boron-hydride structure is quite distinct from a collection of individual diborane molecules [Fig. 1(c)]. Preservation of the backbone boron structure over cycling (by means of kinetic barriers against framework decomposition) would be extremely advantageous for regeneration as compared to traditional boron hydrides, i.e., boranes.

III. COMPUTATIONAL DETAILS

We employ density functional theory (DFT) based first principles electronic structure methods as implemented in the Quantum Espresso package[29] to investigate the structural, electronic, and dynamical properties of the proposed solid boron hydride B_2H_2. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof[30] is used for the exchange and correlation terms. Ultrasoft pseudopotentials[31] are used to describe the electron-ion interactions. The plane-wave energy cutoff is set at 50 Ry for the wave functions expansion and 500 Ry for the charge density. All structures are relaxed until the forces on each atom are less than 10^{-5} Ry/a.u. and the stress less than 1 GPa. The charge density for a single layer B_2H_2 is sampled with a k-point set of $24 \times 24 \times 24$ in the Brillouin zone. The phonon dispersion is calculated using the density functional perturbation theory[33]. We first calculate the dynamical matrices on a $6 \times 6 \times 6$ q-point. Next, the force constant matrices in the real space are obtained by Fourier-transforming the dynamical matrices. Finally, the dynamical matrix at any q-point is obtained by inverse Fourier transformation of the force constant matrices. All results presented in this work are calculated at zero temperature. Long-range van der Waals interaction is significant in layered structures. In this work, we focus our discussion on the properties of isolated (single layer) system. For the bulk structure (multilayer), interlayer binding will be investigated in the near future using a recently developed method for efficient calculations of the van der Waals energy.[32] In the following sections, we discuss the electronic, structural, and dynamical properties for the proposed solid boron hydride B_2H_2.

IV. STRUCTURAL AND ELECTRONIC PROPERTIES OF SINGLE LAYER B_2H_2

The proposed B_2H_2 layered structure has a D_{2h} symmetry which is the same as that of diborane. The structure has a gravimetric capacity of 8 wt% H_2. The calculated bond angles and bond lengths of B_2H_2 [Fig. 1(b)] are close to those in diborane [Fig. 1(c)]. The boron–boron (B–B) distance of the

3c2e bond is 1.82 Å, to be compared with 1.76 Å in diborane. The sp^2 B–B bond length (1.71 Å) is substantially shorter than the 3c2e B–B bond. For comparison, the theoretical B–B bond length in MgB_2 calculated within the GGA is 1.77 Å. The hydrogen–boron (H–B) bridge bond length is 1.33 Å. This is essentially the same as that in diborane (1.31 Å) and is substantially longer than the sp^2 H–B bond (1.19 Å). The B–H–B bridge bond angle is 86°, to be compared with 83° in diborane. These hydrogen bridge bonds are crucial to stabilize the boron network.

Although it is difficult to predict a viable pathway for synthesizing this material, we propose that one possibility is through the atomic exchange with metal borides such as Li_2B_2. Compared with a stable structure of Li_2B_2, α-Li_2B_2,[34] the B_2H_2 structure is thermodynamically stable as suggested by the following reaction: $E[\alpha\text{-}Li_2B_2] + E[H_2(\text{gas})] \rightarrow 2E[\text{Li}] + E[B_2H_2]$. The enthalpy for this reaction is $\Delta H_o = -97.5\,\text{KJ/mol}(0.17\,\text{eV/atom})$. Therefore, the reaction is exothermic.

The B_2H_2 structure may also be viewed as a result of polymerization of a planar octaborane (B_8H_{16}) molecule shown in Fig. 1(d). This molecule is also surprisingly stable compared to diborane as suggested by the following reaction: $E[B_8H_{16}] + 4E[H_2(\text{gas})] \rightarrow 4E[B_2H_6]$. The calculated enthalpy for this reaction is about 12 kcal/mol. We would like to mention that although there is evidence for the existence of the B_8H_{16} molecule, no structural data are known. It would be interesting to investigate the nuclear magnetic resonance (NMR) spectra of this molecular structure and compare with available experimental data. Furthermore, compared with the recently discovered stable planar boron structure, B(α sheet),[26] the B_2H_2 structure is also slightly more stable. The calculated enthalpy is $\Delta H_o = -8.3\,\text{KJ/mol}$ for the reaction: $2E[\text{B}\ (\alpha\text{-sheet})] + E[H_2\ (\text{gas})] \rightarrow E[B_2H_2]$.

We mention that the hexagonal boron network can be further stabilized by charging through alkali intercalation or self-doping.[26] The boron layer becomes less electron deficient upon acquiring extra electrons. The stabilization of the boron network in turn weakens the hydrogen-boron bridge bonds and facilitates the hydrogen release which will be discussed later. All results presented here are calculated at zero temperature and we have not considered the temperature (entropy) effects. We realize that the compensating effects from the entropy term may change the Gibbs free energy significantly. We plan to address these issues in a follow-up paper with first-principles molecular dynamics calculations as well as quasiharmonic calculations of the phonon contribution to the free energy. However, we emphasize that an ideal material for hydrogen storage should not bind hydrogen too strongly. Otherwise the dehydrogenation temperature would be impractically high. Therefore, a relative weak bonding between hydrogen and boron is desirable for the release of hydrogen at practical conditions. In addition, this system is more likely stabilized by the kinetic constraints instead of being more stable thermodynamically.

The band structure of the single-layer B_2H_2 is shown in Fig. 2. It is interesting to compare the band structure of planar B_2H_2 to MgB_2. Like MgB_2, the system is metallic. However, unlike that of MgB_2, the degeneracy of the p-σ bands at the Γ point in MgB_2 is now removed due to lowering of the symmetry from D_{6h} to D_{2h}. As a result, only one of the p-σ bands crosses the Fermi level and the hole pocket near the Γ point comes from the upper p-σ band. The degeneracy of the p-π bonding and antibonding states near the Fermi level is also removed. Similar to that in MgB_2, the Fermi surface of B_2H_2 also consists of both a p-σ derived hole pocket and a p-π derived electron pockets.

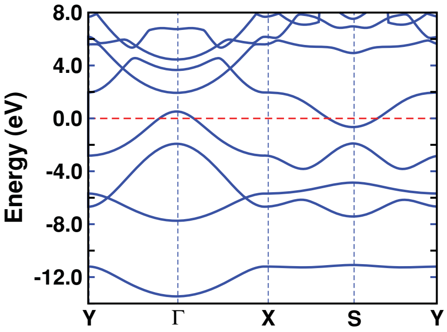

FIG. 2. (Color online) Band structure of a single-layer of B_2H_2. The Fermi level is at 0 eV and shown with the dotted line.

V. PHONON DISPERSION AND DYNAMICAL STABILITY

To investigate the dynamical stability of the proposed structure, we carry out phonon calculations using density functional perturbation theory.[33] The calculated phonon dispersion [shown in Fig. 3(a)] reveals no soft phonon modes (i.e., imaginary phonon energies), thus verifying the dynamical stability of the B_2H_2 structure. The nine optical phonon modes can be classified using group theory analysis:

$$\begin{aligned}\Gamma_{\text{vib}} = {} & A_g^1[\text{H–H}(z)] + A_g^2[\text{B–B}(x)] + B_{1g}[\text{B–B}(y)] \\ & + B_{2g}[\text{H–H}(y)] + B_{3g}^1[\text{H–H}(x)] + B_{3g}^2[\text{B–B}(z)] \\ & + B_{1u}[\text{H–B}(z)] + B_{2u}[\text{H–B}(x)] + B_{3u}[\text{H–B}(y)].\end{aligned}$$

The two A_g modes will mix so that the polarization vectors of the eigenmodes with the A_g symmetry will involve both hydrogen and boron motions. We denote the mode with primarily hydrogen motion as A_g^*. Similarly, the two B_{3g} modes will mix and we denote the one with primarily hydrogen motion as B_{3g}^*. The phonon polarization vectors for the nine optical phonon modes at Γ are also shown in Fig. 3(b).

The highest energy mode (A_g^*) is a symmetric stretching of H atoms perpendicular to the boron plane (i.e., along the z direction), whereas the B_{1u} mode involves H–B vibrations in the z direction. The next two phonon modes (B_{3g}^* and B_{2u}) are H–H and H–B vibrations along the direction of the bridging bonds (x direction). The B_{1g} and A_g modes are similar to the E_{2g} modes in the AlB_2 structure and involve boron motions in the boron plane (x-y plane). Note that the energies of these two modes are very close to the energy of the E_{2g} phonon in AlB_2 but substantially higher than that in MgB_2. The B_{2g} and B_{3u} modes involve H–H and H–B vibrations in the y direction whereas the low energy B_{3g} mode consists primarily of boron vibration in the y direction admixed with hydrogen motion in the x direction.

In addition to the dynamical stability, we have also investigated the thermodynamical stability of the B_2H_2 structure

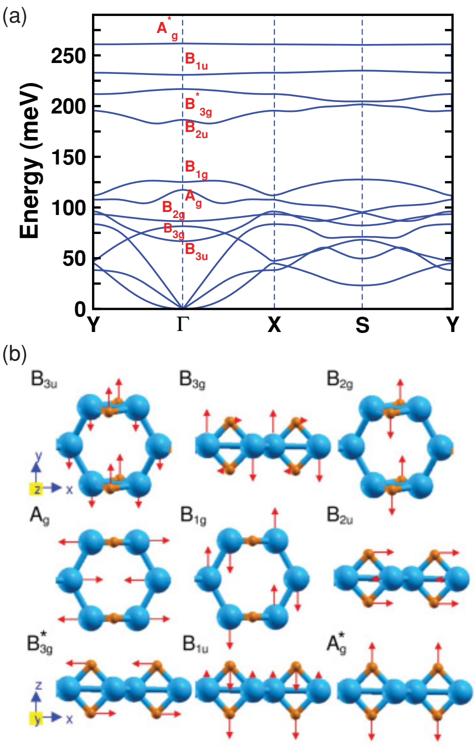

FIG. 3. (Color online) Phonon dispersion: (a) The calculated phonon dispersion for single-layer B_2H_2. The labels at Γ are the nine optical phonon modes. (b) The corresponding phonon polarization vectors of the optical phonons at Γ. Boron is blue (big spheres) and hydrogen is orange (small spheres).

using a long time *ab initio* molecular dynamics (MD) simulation in a temperature range of 300 K–400 K. For the MD calculation, we consider several supercell sizes up to a 6×6 B_2H_2 supercell to account for the statistics. The simulation is carried out for 50000 MD steps (about 1.2 ps simulation time). In this temperature range, we find that the energies of the system remain the same throughout the simulation time, indicating that no phase separation occurs within this temperature range. The hydrogen atoms showed fluctuation about their original position but not significant enough to break the bridge bond with the boron. These results suggest that B_2H_2 structure is sufficiently stable for the purpose of hydrogen storage.

We note that one of the known issues with molecular dynamics calculation is the simulation time which is needed to obtain a reliable information regarding the dynamics and phase separation. Molecular dynamics calculations are extremely time consuming and we have done our best to ensure that the MD simulation results presented here give a reliable statistics. In addition, we have carried out simulations with different supercell sizes in which the largest supercell contains 288 atoms. These considerations certainly improve the reliability of our simulation results. Furthermore, the small mass of hydrogen and the small time step needed to integrate the equations of motion in the molecular dynamics simulations are other serious limitations, which restrict the total simulation time. However, in most cases, molecular dynamics simulations of few ps are found to be sufficient to get the dynamics of the system. We will present more details of our MD results in a follow-up paper.

One key aspect of the present work is to assess the feasibility of the B_2H_2 structure for hydrogen storage. This requires not only a stable backbone structure that binds hydrogen with intermediate strength but also a structure that releases hydrogen under practical conditions. In the next section, we investigate the charging effects and self-doping mechanism[26] on the dynamical properties of B_2H_2 and discuss their implication for dehydrogenation.

VI. CHARGE DOPING EFFECTS

Utilizing B_2H_2 for hydrogen storage requires not only a stable boron framework but also a practical hydrogen release mechanism. As discussed earlier, a planar hexagonal boron layer is not stable alone due to electron deficiency. If additional electrons are introduced to the B_2H_2 system (for example, by intercalation of Li or self-doping[26]), the boron network will be less electron deficient. As a result, the hydrogen bridge bonds should weaken with charging. The hexagonal boron backbone structure, on the other hand, should remain stable with charging. Therefore, one may be able to control the strength of the hydrogen bridge bonds by controlling the degree of electron deficiency of the boron network. This, when combined with thermal activation, may facilitate dehydrogenation and/or rehydrogenation.

Here we investigate this possibility by studying the effects of charging on the zone center phonon energies. Our results reveal that some of the phonon modes (especially those involving vibrations of hydrogen) are significantly softened by charging. Figures 4(a) and (b) show the softening of the hydrogen-related phonon modes, namely the A_g^*, B_{1u}, B_{3g}^*, and B_{3g} phonons. The softening of these hydrogen-related phonons is a result of the weakening of the hydrogen bridge bonds upon charging, which in turn should enhance hydrogen release.

In-plane boron modes (A_g and B_{1g}) shown in Fig. 4(c) show more subtle charging dependence. The B_{1g} mode hardens significantly at low charging levels, reflecting a strengthening of the boron network. When charging level exceeds 0.5 electrons per cell, the B_{1g} mode softens slightly. At this charging level, excess electrons start to occupy high energy antibonding states. Although the system is still dynamically stable, thermodynamically it may prefer to release hydrogen in exchange for stabilizing the boron network. The A_{1g} mode, on the other hand, softens at low charging levels. Since this mode involves the stretching of both the B–B bonds and hydrogen bridge bonds, the initial softening of this mode shows the combined effects of strengthening the boron network and weakening the hydrogen bridge bonds. Clearly, at low charging level, the weakening of the bridge bonds dominate.

Alkali-metal intercalation is the most common technique to introduce charge into layered materials. The rich chemistry of boron allows a new way of introducing charge to the system through a self-doping mechanism.[26] The self-doping mechanism has been shown to stabilize the electron deficient boron framework to yield a stable planar boron framework.[26]

For a B_2H_2 sheet, although the electron deficiency is reduced compared with the pure hexagonal boron sheet, the

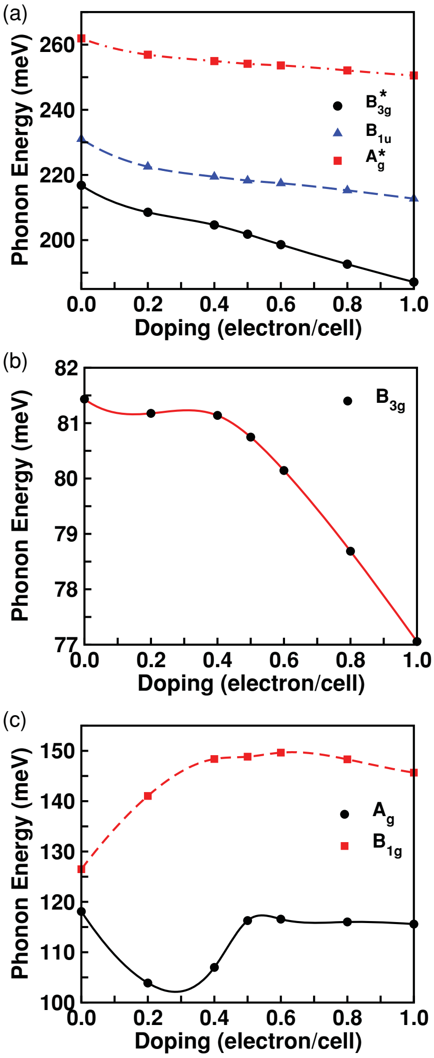

FIG. 4. (Color online) Phonon energy change as a function of charging for four hydrogen phonon modes and two boron phonon modes at Γ for single-layer B_2H_2: (a) Phonon energy change for the three higher energy H phonon modes B^*_{3g}, B_{1u}, and A^*_g. (b) Phonon energy change for lower energy H phonon mode B_{3g}. (c) Phonon energy change for boron phonon modes A_g and B_{1g}.

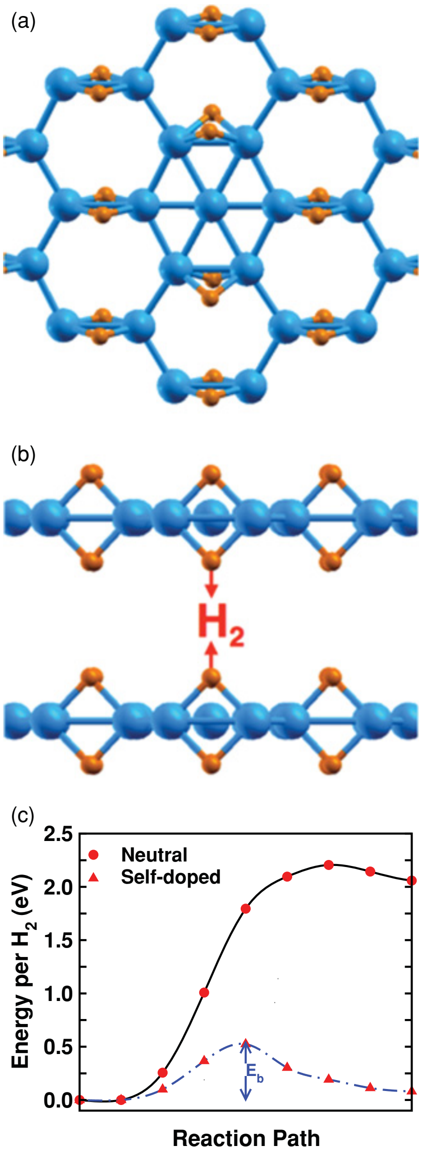

FIG. 5. (Color online) Reduction of the kinetic energy barrier (E_b) against hydrogen release by self-doping. (a) Self-doped B_2H_2 structure. (b) Side view of the self-doped B_2H_2 structure with a possible H release pathway. (c) Kinetic energy barrier as a function of a reaction path for such a process for both self-doped and neutral B_2H_2 structures. The kinetic energy barrier is calculated using a 4 × 4 supercell of B_2H_2 structure. Boron is blue (big spheres) and hydrogen is orange (small spheres).

formation energy of a self-doped boron is still negative. In the dilute limit, we find that the formation energy of a self-doped boron in a B_2H_2 sheet is −2.4 eV. The energy gain by self-doping reduces with increasing self-doping (defect) concentration. At certain self-doping concentration when the underlying B_2H_2 sheet is no longer electron deficient, the defect formation then turns positive. Therefore, if the B_2H_2 material is synthesized, it is likely that it will be produced with extra boron, i.e., the materials will likely be $B_{(2+x)}H_2$ instead of stoichiometric B_2H_2. This will both stabilize the boron backbone network as well as facilitate the hydrogen release.

Here we considered one particular hydrogen release pathway from the B_2H_2 by self-doping as shown in Fig. 5(b). The hydrogen atoms in the vicinity of the self-doped boron migrate laterally to merge with another hydrogen coming from the neighboring plane to form H_2. Using a nudged elastic band (NEB) method,[29] we calculate the kinetic energy barrier (E_b) for such a process and compared the results for the same process in the absence of boron self-doping as shown in Fig. 5(c). Without self-doping, it would be very difficult to release the hydrogen through this particular mode (path). With a self-doping boron, the hydrogenated and dehydrogenated states have comparable energies and are separated by a relatively small kinetic barrier. Therefore, by changing the self-doping level, the B–H bonding strength can be systematically tuned to match the target bonding strength for practical applications. These results demonstrate the flexible and tunable nature of this structure. The strength of the B–H bridge bonds may also be tuned through alkali metal, or a combination of both methods.

Although the NEB method is widely used to determine the transition state, depending on the complexity of the system, it may not yield a correct transition state. However, our focus here is to use the NEB method to estimate the kinetic barrier and our results should give the upper bound of this quantity. We have used a large number of images and reasonable force constants to ensure that the forces on the individual images are small enough. We would like to point out that the transition state may not be exact but it is within the margin of error.

VII. SUMMARY

In summary, we predict a layered solid boron hydride structure (B_2H_2) and investigate its structural, electronic, and phonon properties using density functional based first-principles electronic structure methods. The structure consists of a graphene-like hexagonal boron network and bridge hydrogens which form 3c2e-like multicenter B–H bonds. The phonon dispersion of single-layer B_2H_2 does not show any soft phonon modes, thus confirming the dynamical stability of the proposed structure. We also investigate the effects of charging on the dynamical properties and hydrogen release kinetics of B_2H_2. With the presence of extra electrons, the boron network becomes less electron-deficient therefore reducing the strength of the multicenter B–H bonds. Charge may be introduced by either alkali-metal intercalation or through self-doping mechanism. Softening of the hydrogen related phonon modes upon charging suggests a weakening of the hydrogen bridge bonds. The boron network, however, remains stable upon charging. This conclusion is further substantiated by the calculation of the kinetic energy barrier against the hydrogen release with and without self-doping.

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