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Boron-hydrogen complexes in diamond

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Boron in diamond traps hydrogen forming passive B_s-H pairs. Boron trapping two deuterium atoms has been speculated as forming a shallow donor (0.23–0.34 eV below the conduction band). We present the results of first-principles calculations of boron complexes with 2–4 hydrogen atoms. The binding energy of the second and subsequent H atoms is small and none of the structures found are shallow donors. We also present the structure of interstitial boron, the boron-vacancy complex, and their interaction with hydrogen.

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I. INTRODUCTION

Diamond appears rapidly be becoming a realistic electronic material in terms of crystalline quality,[1] and it is well known that *p*-type material can be formed with very high boron concentrations, high mobilities, and low activation energies. However, *n*-type material has proved difficult to manufacture, and it is the relatively deep phosphorus donor ($E_c-0.6$ eV,[2] E_c being the conduction band minimum) that is considered the most reliable "shallow" donor at this time. For room-temperature operation of devices such as *p*-*n* junctions, a shallower donor is required, and considerable effort is being made to attain this goal.

Recent experimental data of electrical characteristics of heavily boron doped ($[B]\sim10^{19}\ \mathrm{cm}^{-3}$) and deuterated diamond[3] have been interpreted in terms of shallow donor levels due to boron-deuterium complexes. A negative Hall-effect coefficient indicates *n*-type behavior although impurity band conduction might lead to anomalous behavior.[4] This seems unlikely in light of the rather high carrier mobility. The electronic infrared absorption measurement of the material shows the passivation of the boron by deuterium in this study, and indicates that the *n*-type material does not exhibit the transitions at 2450 cm^{-1} and 2800 cm^{-1}, characteristic of substitutional boron.[3] No infrared transitions around 1800–1900 cm^{-1} arising from the shallow donor were reported. The electron concentration is comparable to that of the boron in the samples, perhaps suggesting an efficient conversion of the boron acceptors into donors. The value of $E_c-0.23$ eV for the donor level is close to that predicted from effective-mass theory and, if reproducible, this material shows promise of resolving the long-standing problem of shallow donors in diamond. Material with a lower boron concentration ($[B]\sim10^{17}\ \mathrm{cm}^{-3}$) apparently also exhibits the *n*-type conductivity, albeit with a deeper level at around $E_c-0.34$ eV.[5] It is not clear from the current data what defect mechanism might give rise to this apparent donor level.

Secondary ion mass spectroscopy (SIMS) data after exposure to the D-plasma at 550°C are consistent with more than one D per boron acceptor, and this has been interpreted as suggestive of B_sD_2 complexes (B_s representing substitutional boron) being responsible for the shallow donor level.[3] Furthermore, low concentrations of impurity species other than B and D relative to the carrier concentration strongly suggest that if the donor level is due to an impurity, it must involve these constituents.

Regrettably, the effect is not particularly thermally stable. Half-hour anneals of the *n*-type material at 520°C reduce the free-electron concentration dramatically and the donor activity is removed completely after annealing at 600°C for 15 min. *p*-type behavior is re-established after subsequent higher-temperature treatments, where the passivating D has been lost from the sample. From the available experimental data the stability (e.g., the binding energy or migration barrier) of the donor species is not clear—no isochronal annealing studies have been performed to the authors' knowledge. However, it seems likely that the *n*-type conductivity is stable at room temperature, and indeed, for the effect to be technologically useful this is essential.

Although very little data are available for the donor species, much has already been discovered regarding other B and B_s-H defects. Individual substitutional boron acceptors possess an acceptor level at $E_v+0.37$ eV,[6] (E_v is the valence-band top) but for high [B] the acceptors form an impurity band and the activation for hole conduction is very low. Indeed, when the *n*-type deuterated samples are annealed to 750°C a hole conductivity with an activation of just 90 meV is reported.[3]

Boron-hydrogen and boron-deuterium pairs are believed to be passive: electronic infra-red absorption[7] and capacitance-voltage measurements[8] have independently determined the passive nature of hydrogenated B-doped diamond, and theory predicts that the B_s-H pair should have no gap levels.[9–12] The structure of the B_s-H pair has been calculated using empirical methods to lie in a pucker bond-centered site,[9] but density-functional-theory (DFT) calculations yield a more complex structure with the H atom lying along approximately [001] from the B atom,[10,11,13] and involving three-center bonding.[10] The dissociation energy of the B_s-H pair is measured to be around 2.5 eV,[12] which can be viewed as being made up from the sum of the binding energy and H-migration barrier. However, the migration barrier for positively charged H in diamond is believed to be very small, with an experimental estimate of 0.35 eV,[14,15]

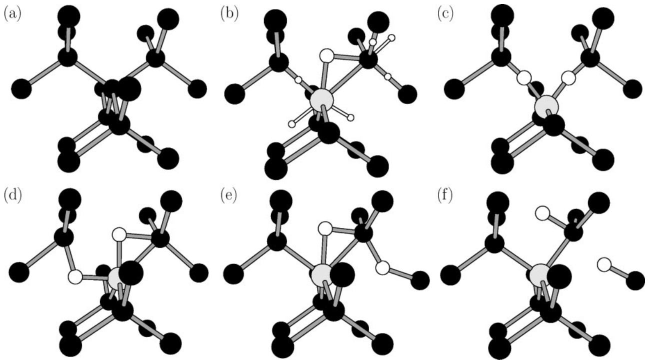

FIG. 1. Schematic representations of the structures of B_sH_2 described in the text. Black, gray, and white atoms are C, B, and H, respectively. (a) shows a section of bulk diamond for comparison. (b) initial configurations related to B_s-H, with the small white circles representing the approximate starting location of the second H atom. (c) is the {B,H,H} structure and (d)–(f) are the ground-state structures in the positive, neutral, and negative charge states, respectively. The structures depicted in (b) and (c) have had a carbon atom removed in comparicon to (a) to facilitate a better view of the location of the H atoms.

and theory predicting similarly low values.[9,10] Theoretical estimates of the binding energy of B_s-H vary widely, with the DFT values in reasonable agreement with experiment.[10–12]

Complexes made up from two boron and up to two hydrogen atoms have also been investigated as a potential deep trap for hydrogen in heavily doped material. However, these centers all represent either acceptors in the lower half of the band gap, or in the case of B_2H_2, a passive center,[12] and do not yield shallow donor levels.

On simple chemical grounds it is hard to see why a single substitutional B center would trap more than one hydrogen atom. However, this is believed to be the case in silicon, where theory predicts that the passive B_s-H pair can trap a second bond-centered H with a binding energy of 2.23 eV.[16] The two equivalent H atoms lie in different B–Si bonds, and this geometry is termed the {B,H,H} defect.[16] This has C_{2v} symmetry and is shown schematically in Fig. 1(c), but care must be taken in transplanting such systems from silicon to diamond due to the difference in lattice constant and bond strengths. Recent cluster based DFT calculations for neutral B_sH_2 defects yielded a structure made up from B_s-H with a second H atom in a nearby bond center.[11] This structure was calculated to be unstable with respect to dissociation into B_s-H and isolated interstitial H. Furthermore, even if this defect was to be formed, it has deep gap levels, presumably as indicated by the Kohn-Sham eigenvalues.

It is worth considering why one might expect B_sD_2 complexes to form a shallow donor level. An argument has been made for the formation of shallow dopants via codoping.[17] Within this scheme a system of two or more dopants combine to produce the shallow dopant, such as a double-donor-acceptor complex yielding a shallower donor level than the double-donor alone, or a complex of three impurities as a donor-acceptor-donor complex, with the same effect.[17] Now, interstitial H is theoretically a donor,[10,18–20] so H-B-H might be expected to yield a shallower donor level than H on its own. However, one must take care in drawing this type of analogy. The donor-acceptor-donor complex may well yield a shallower donor level than that of the donor, but this is likely to be most effective where the isolated donor is already reasonably close to the conduction band. For example, the complex N-Al-N is theoretically expected to have a significantly shallower donor level than N on its own.[17] H, on the other hand, is a very deep donor, so it is not at all obvious that one would expect H-B-H to form a shallow donor level.

The existing theoretical study of B_sH_2 in diamond did not examine the effects of charge on the structures and energetics of the complexes. In view of the potential importance of this material we have therefore examined the geometry and energetics of B_sH_n ($n=2$, 3, and 4) using DFT supercell methods, as outlined in Sec. II. The potential involvement of carbon-based defects in the donor has also been investigated in the form of B-H complexes associated with self-interstitials and vacancies. We present the results of the calculations in Sec. III and conclude in Sec. IV.

II. METHOD

All calculations were carried out using the local-density-functional technique as implemented in AIMPRO (Refs. 21,22) (*ab initio* modeling program). To model the various defects, 64 and 216 atom cubic unit cells of side length 2 and $3a_0$ have been used. The calculations have been performed using the Monkhorst-Pack[23] scheme for sampling the Brillouin zone with a mesh of $2\times2\times2=8$ special *k* points. For a representative sample of the structures (in fact those we shall indicate below as the lowest energy structures for B_sH_2) we checked the total energies for the superior $4\times4\times4=64$-point mesh, which indicated that the absolute total energies are converged to around 10 meV. Structures are optimized via a conjugate-gradients scheme until the change in energy between iterations is less than 10^{-5} Ha. The optimization of the structures does not include the mass of the atoms, and hence the results presented here apply equally to hydrogen and deuterium. The zero-point motion and associated energy are unlikely to lead to a qualitative change in the conclusions. However, one must keep in mind that the processes involving a light impurity such as hydrogen are quantum mechanical in nature, and tunneling rates, for example, *are* mass dependent. Although the use of deuterium in the experiment is to facilitate the SIMS experiments, it is not clear from the experiment if it is necessary to use deuterium to generate the *n*-type conductivity, i.e., no hydrogen-related data are available.

Norm-conserving pseudopotentials[24,25] enabled core electrons to be eliminated. In a few cases different pseudopotentials[26] were used to establish that the results are independent of which type we use, and we found that relative energies of different structures varied by less than 0.1 eV. The wave function basis consists of independent sets of *s*, *p*, and *d* Gaussian orbitals with four different exponents, sited at each C, or B, site and the H atoms are treated using four independent sets of *s* and *p* Gaussians. The charge density is Fourier transformed using plane waves with a cutoff of 300 Ry. We performed tests with the plane-wave cutoff being doubled to 600 Ry which altered the total energy by around 1 meV, suggesting that the lower value was sufficiently convergerd. The lattice constant and bulk modulus of diamond using these bases are within ~1% and 5%, respectively, of the experimental values, while the direct and indirect band gaps are close to previously published plane-wave local-density approximation values[27] (5.68 and 4.18 eV).

There are two principal physical quantities derived in this study. Both can be obtained from the formation energy, $E^f(X,q)$, of a defect X in charge state q made up from atoms with chemical potentials μ_i:[28]

$$E^f(X,q)=E(X,q)-\left(\sum \mu_i\right)+q(E_v^{X,q}+\mu_e)+\chi(X,q). \tag{1}$$

Here $E(X,q)$ is the total energy of the supercell containing the defect, and the sum is over all atoms in the supercell. $E_v^{X,q}$ and μ_e are the valence-band top (for the defect cell) and electron chemical potentials, respectively. Finally, $\chi(X,q)$ is a term correcting for the electrostatic and multipole interactions due to the periodic nature of the calculation,[29] although this approach is not universally accepted, in part due to the approximation of the charge to a point. The value taken for $E_v^{X,q}$ can be approximated by that of bulk diamond, or evaluated from the appropriate defect cell by aligning the bottoms of the band structures of the defect and bulk cells.[30] The latter correction typically yields a change in the formation energy of the order of $0.1q$ eV.

The donor and acceptor levels can be derived by determining the thermodynamically most stable charge state for all values of μ_e, but since all such levels are then referenced to the valence-band top, the underestimation of the band gap under DFT yields problems in interpreting the locations of levels with respect to the conduction band minimum, as required for shallow donors.

A more pragmatic approach is to compare the ionization energies and electron affinities of different systems with one another—we term this the marker method since we are using a second level as a marker for the defect we are interested in. For example, the location of the donor level of system X in comparison to that of system Y is simply given as

$$X(0/+)=Y(0/+)+[\{E(X,0)-E(X,+)\} \\ -\{E(Y,0)-E(Y,+)\}],$$

where the energies are derived from calculations of the different systems within the same cell geometries. Similar equations can be constructed for any electronic transition. Y could be another defect for which a similar level is known[31] (e.g., P for shallow donors[32]) or bulk diamond.[33]

The second quantity that can be estimated from the formation energy is the binding energies. The binding energy of complex A made up from components B and C can be written as

$$E^b(A)=E^f(B)+E^f(C)-E^f(A), \tag{2}$$

which will not depend on the chemical potentials of the impurity species, but only on the supercell total energies and the carbon chemical potential (in practical terms one typically requires the total energy of a defect-free supercell of the same size as used for systems A, B, and C). However, one should note that the binding energy may include the formation energies of *charged* defects. In cases where B and C are both charged (e.g., in the reaction $B^-+H^+\rightarrow BH$), E^b will include potentially large contributions from the Madelung component of $\chi(X,q)$ in Eq. (1), since equal contributions arise from each component. The Madelung term in the binding energy for a 64 atom cubic unit cell is then numerically around q^2 eV. Using Eq. (2), a positive value represents A bound with respect to B and C.

III. RESULTS

A. B_sH_2 complexes

We have examined complexes made up from B_s with two hydrogen atoms lying in various starting structures and symmetries. Several structures were examined where one H atom is added to a relaxed B_s-H pair. The additional H atom was placed (i) antibonding to the B atom in the plane of the B_s-H defect (this represents two different sites) (ii) H in a bond center between B and a C atom, (iii) H bond centered in a site between a nearest and next-nearest C neighbors, and (iv) antibonded to a neighboring C atom. The sites where the second H were placed are shown schematically by the small white circles in Fig. 1(b). The {B,H,H} structure from silicon, shown in Fig.1(c), was also relaxed, but the C_{2v} geometry produced a high-energy structure, nearly 2 eV above the lowest energy structure in the neutral charge state. With a sufficiently large initial <HBH the structure in fact relaxes to a configuration with the two H atoms antibonded to B, around 1 eV above the ground-state neutral structure. The contrast with silicon is most probably due to the fact that boron is tensile in silicon and the presence of the two H atoms relieves some of the local strain, whereas in diamond the presence of H in B-C bonds is not favorable due to the small lattice constant. We also considered the possibility of adding the most stable hydrogen dimer, H_2^*, to B_s, or at a nearby site, which relaxed into a range of low-energy structures. (H_2^* consists of a bond centered hydrogen and antibonding H along $\langle 111\rangle$, C-H_{BC}–C-H_{AB}, and is seen experimentally via infrared absorption in Si and Ge, but was first proposed as a stable structure for diamond.[34]) Finally, we also examined the possibility of a hydrogen *molecule* in the vicinity of B_s, but such configurations always resulted in high-energy structures.

Significantly we found that the lowest-energy structure is strongly dependent on the charge state of the system. The neutral defect consists of one H atom lying approximately as with the isolated B_s-H pair, and the second lies in a C-C bond site close-by with a C-H-C bond-angle of around 138°. This is in broad agreement with previous calculations.[11] In the negative charge state we find that a configuration resembling H_2^* in a C-C bond neighboring the B site is lowest in energy, whereas for the positive charge state the lowest-energy structure has a puckered bond-centered H in a B-C bond. The three structures are shown schematically in Figs. 1(d)–1(f).

TABLE I. Binding energy E^b (eV) for the BH_2^q complexes in diamond relative to various dissociation products. None of the reactions listed involve the addition of a Madelung energy.

Reaction	E^b
$(B_s)^- + H_2^* \rightarrow (B_sH_2)^-$	-0.1
$B_sH + (H_i)^- \rightarrow (B_sH_2)^-$	2.1
$(B_s)^0 + H_2^* \rightarrow (B_sH_2)^0$	0.8
$B_sH + (H_i)^0 \rightarrow (B_sH_2)^0$	0.5
$B_sH + (H_i)^+ \rightarrow (B_sH_2)^+$	0.7

The reactions and associated binding energies for the various charge states of the B_sH_2 system are listed in Table I. Table I shows that the binding energies are relatively modest for these complexes with the exception of $B_sH + H^- \rightarrow B_sH_2^-$. The large difference between E^b for the two processes for BH_2^- arise largely because of the difference in the acceptor levels of B_s and H_i. Both dissociation paths involve relatively immobile species: H_i^- theoretically has an activation barrier of around 2 eV (Ref. 10)–2.5 eV,[9] whereas the migration of H_2^* is estimated at >3.5 eV.[10]

The *activation* energy for the dissociation of these complexes can be approximated by the sum of the binding energy and migration barrier. We previously calculated the binding energy of H_2^* to be around 2.5 eV and the migration barriers of positive, neutral, and negative bond-centered hydrogen to be <0.2 eV, 1.6 eV and 2 eV, respectively,[10] which are broadly in line with other calculations (see Ref. 35 and references therein). Then the dissociation of H_2^*, for example, would have an activation energy around 4.1 eV. For the more pertinent case of $B_sH_2^+$, the release of a proton will then be of the order of 0.9 eV. This is inconsistent with a thermally stable donor. Using the expression $\nu = \omega \exp(E/k_BT)$ for the hopping rate ν, with ω the attempt frequency, E the activation barrier, k_B Boltzmann's constant, and T the absolute temperature, one can estimate the thermal stability of a defect, at least in the absence of quantum-mechanical effects. With ω set to a typical C-H vibrational frequency $(\sim 90\ \mathrm{THz})$, the barrier $E = 0.9$ eV, and setting the hop rate ν to 1 Hz this yields a value of T around room temperature. Admittedly this procedure is rather crude, but for $E = 0.9$ eV one requires $\omega \approx 10^5$–10^6 Hz for dissociation at 520°C, whereas for $\omega \approx 10^{13}$ Hz and $T = 520°\mathrm{C}$, the activation barrier for dissociation is $E \approx 2$ eV, and we conclude that B_sH_2 is less stable than the measured electrical activity.

A further, more critical problem in assigning the $E_c - 0.23$ eV level to B_sH_2 arises upon estimation of the electrical levels. Using the formation energy approach [Eq. (1)], and for each charge state taking the lowest energy structure we have thus far obtained, the donor level lies at $E_v + 1.65$ eV. Hence B_sH_2 in the form we have found energetically most favorable is most definitely not a shallow donor. Interestingly an acceptor level lies at $E_v + 1.50$ eV, making B_sH_2 a so-called negative-U system. The formation energy is plotted as a function of the electron chemical potential in Fig. 2.

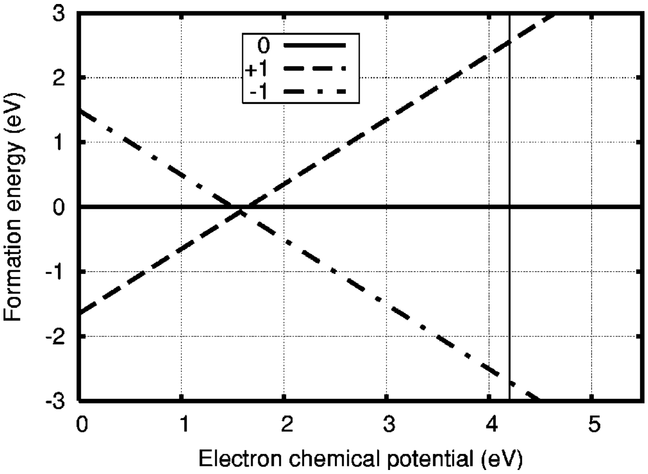

FIG. 2. Formation energy for B_sH_2 in three charge states. The vertical zero is defined by choosing the atomic chemical potentials μ_i such that $E^f(B_sH_2^0) = 0$ eV. The theoretical (indirect) band gap is indicated by the vertical line at ~ 4.2 eV.

We have also obtained the levels using the marker method. For the acceptor level we have used the electron affinity of a bulk cell and the boron acceptor for first-principles and empirical approaches, respectively. These yield $E_c - 3.6$ eV and 1.4 eV above the B_s acceptor level, i.e., $E_v + 1.8$ eV $(E_c - 3.7\ \mathrm{eV})$. All three methods for calculating the acceptor level are therefore in close agreement with the complex forming a very deep acceptor in the region of 1.6–1.9 eV above E_v.

The donor level has also been obtained via the marker method, in this case using the ionization potentials of bulk diamond and N_s (experimentally $E_c - 1.7$ eV (Ref. 36)). These yield $E_v + 2.6$ eV and $E_c - 3.0$ eV, respectively. Thus the marker method donor levels are mutually consistent, but around 1 eV higher in the gap than predicted using the formation energy approach. There is some evidence that the marker method is more reliable than using the formation energies,[37,38] but in any case there is no evidence that B_sH_2 acts as a shallow donor.

The above calculations of the electrical levels assume that when the charge state changes the constituent atoms are free to adopt the appropriate ground-state structure. This may not be the case, especially for conversion between the neutral and positive charge states where the geometries are quite distinct, requiring the hop between different bonds for one H atom. However, one can also calculate the donor level of the lowest-energy structure in the neutral charge state, as depicted in Fig. 2(e), where the positively charged state is relaxed from the neutral geometry. This indeed yields a shallower donor since we have raised the energy of the positive charge state, but the effect is only a few tenths of an eV, and this cannot explain the shallow donor behavior seen experimentally. The same is true for the instantaneous donor level of the geometry of the positively charged defect [Fig. 1(d)].

It therefore seems highly unlikely that a shallow donor can be obtained from B_s and two hydrogen (or deuterium) atoms unless there is a lower-energy structure we have missed or there is a large barrier to the formation of the

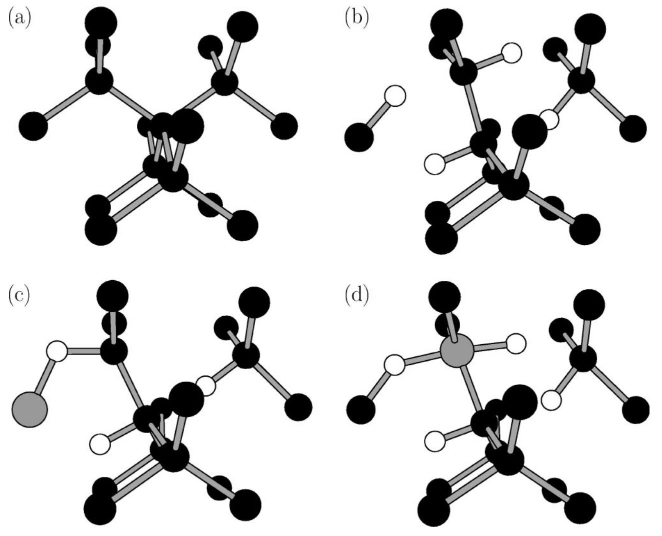

FIG. 3. Schematic representations of the structures of (b) H_4, (c) B_sH_3, and (d) B_sH_4. Black, gray, and white atoms are C, B, and H, respectively. (a) shows a section of bulk diamond for comparison.

ground-state structures that we have obtained. In the latter case one could envisage there to be a structure with a shallow donor level which is comprised of B_s-H and a more remote H atom, but it seems hard to believe that this would lead to levels very far from the deep levels of isolated interstitial H. We have therefore looked at higher degrees of hydrogen aggregation.

B. B_sH_3 and B_sH_4 complexes

The large number of components makes an exhaustive examination computationally expensive, so we have focused on a small number of possible geometries to estimate the binding energy and electrical levels.

For B_sH_3, we have examined two structures where H is directly bonded to the boron acceptor: one with three bond-centered H, and one with three antibonding H. In the light of the results presented for B_sH_2, these would be expected to be high-energy structures, and indeed they are much higher in energy than an isolated B_s-H pair and H_2^*. Of the two directly bonded structures the antibonding system is lower in energy, but is around 4 eV higher in energy than $B_sH + H_2^*$. Even if this defect could be formed, the Kohn-Sham eigenvalues suggest a deep donor.

Perhaps a more likely structure is related to the H_4 complex proposed from theory.[39] In this geometry two H_2^* defects combine with a substantial relaxation to form a strongly bound system [Fig. 3(b)]. Replacing one of the C-H bonds with the B impurity seems a reasonable step, and we have examined the structures derived by placing the B atom at various sites. Calculations based on H_4 were performed using a 216 atom supercell. The lowest-energy structure is shown schematically in Fig. 3(c). This and similar structures are not candidates for shallow donors, being essentially electrically passive, as one might expect: the bulk marker method yields donor levels within 0.2 eV of the valence-band top, although there may be an acceptor level around 0.5–0.9 eV below the conduction-band minimum, depending on the structure. In the neutral charge state the lowest-energy structure we have found is bound by around 0.9 eV with respect to H_2^* and B_s-H, and the reactions $(B_sH_2)^0+(H)^0 \rightarrow (B_sH_3)^0$, $(B_sH_2)^- + (H)^+ \rightarrow (B_sH_3)^0$, and $(B_sH_2)^+ + (H)^- \rightarrow (B_sH_3)^0$ are exothermic by 3.5 eV, 3.8 eV, and 5.0 eV, respectively. Including the activation barriers for the motion of H_i or H_2^* renders this complex rather stable, with the lowest-energy path being the ejection of a proton at around 4 eV.

For B_sH_4, the situation is very similar to that of B_sH_3. We examined as a reference a complex made up from on-site substitutional B with bond-centered or antibonded hydrogen tetrahedrally arranged about it. As before the lower-energy structure contained the antibonded H, but this was much higher (~ 4 eV) than H_2^* and a neutral B_sH_2 complex. Starting from a configuration made up from close-by B_sH_2 and H_2^* defects resulted in a low-energy structure with gap states similar to those of B_sH_2, but with a positive U. The complex made up from H_4 and B_s [Fig. 2(d)] is the lowest-energy structure we have found and is bound by just 0.5 eV relative to those constituents. The binding energy with respect to B_sH_2 and H_2^* is ~ 1.4 eV and 0.9 eV relative to B_sH_3 and H^0. The charged complexes are similarly relatively weakly bound, with the reactions $(B_sH_3)^0 + H^q \rightarrow (B_sH_3)^q$ liberating around 0.7 eV in both $q=-1$ and $q=+1$ cases. This is particularly important in the positive charge state since the migration barrier of the proton is very low, and this therefore represents low activation energy for dissociation. Using the bulk marker method the $(-/0)$ and $(0/+)$ levels lie at $E_c - 3.0$ eV and $E_v + 1.8$ eV, respectively.

Although we have examined a rather limited number of structures with three and four hydrogen atoms, it seems likely that such defects are relatively weakly bound. More significantly we find no propensity for the formation of shallow donor levels.

C. Boron-hydrogen complexes with native defects

Self-interstitials in diamond have a very high formation energy,[40,41] but the aggregation of impurities can sometimes liberate sufficient energy to promote their formation, such as one mechanism proposed for the formation of platelets in diamond via nitrogen aggregation.[41,42] In the presence of large concentrations of both boron and hydrogen it is possible that boron may be incorporated as an interstitial species, or indeed form complexes with lattice vacancies, both of which would be likely to interact with the hydrogen.

We have examined a wide range of interstitial boron structures (split-interstitials, bond-centered, and nonbonded) and find that the lowest-energy configuration for interstitial boron (B_i) is that of a split-interstitial aligned along [001] with C_{2v} symmetry [Fig. 4(b)]. However, we find that the total energy of a self-interstitial adjacent to substitutional boron is lower in energy by around 0.25 eV in the neutral charge state. (This is in contrast to previous Tersoff potential calculations, which suggested the split-interstitial configuration lower in energy by 0.14 eV.[43]) The structure of this pseudo-interstitial boron defect is shown schematically in

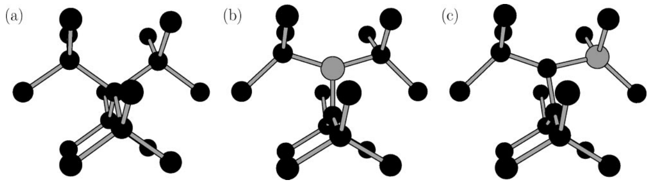

FIG. 4. Schematic representations of the structures of (b) the B_i and (c) B_sI complexes in diamond. Black and gray atoms are C and B, respectively. A section of bulk material is shown in (a) for comparison.

Fig. 4(c). Separating the boron and self-interstitials by a lattice site increases the total energy very slightly in the 64 atom cell. The B_s-I complex [Fig. 3(c)] is also the most stable in the positive and neutral charge states, and possesses an acceptor and donor level at E_c-1.8 eV and $E_v+2.2$ eV, respectively, using the bulk cell as a marker. The C_{2v} B_i defect [Fig. 3(b)] also has deep levels, and in particular the $(0/+)$ level lies at $E_v+2.4$ eV. It therefore seems unlikely that interstitial boron is responsible for the $E_c-0.23$ eV level.

The binding energy of a [001]-split self-interstitial (I) to B_s can be calculated as indicated in Sec. II. This yields around 2.8 eV for neutral reactants, and around 1.4 eV for the reaction $B_s^- + I^+ \rightarrow B_sI$, the latter of which includes a contribution of around 1 eV from the Madelung term. (We find that the self-interstitial is a [001]-split structure in all stable charge states, and that in particular it possesses donor and acceptor levels around $E_v+2.5$ eV and $E_c-1.9$ eV, respectively, close to those of B_s-I.[38]) The B_s-I complex is most likely bound via a Coulombic interaction. B_s-I has a very high formation energy, equal to that of the substitutional B atom plus around 9 eV, where we have taken the Fermi level to be pinned by the B_s acceptor level.

One can take either the metastable form of the boron-interstitial [Fig. 3(b)] or the lower energy B_s-I complex and add one or more H atoms. Indeed the presence of dangling bonds in these defects renders them prime sites for trapping H atoms. In all cases examined, the preferential site for the hydrogen is saturating a *carbon* dangling bond. For example, B_iH with a B-H bond is 2.2 eV higher in energy than where the H saturates carbon. For the neutral species the binding energies for B_iH and B_s-IH are 4.4 and 4.6 eV, respectively, with this large energy being consistent with the passivation of a carbon dangling bond. The effect of adding the H to B or C in B_i can be seen in the Kohn-Sham levels, shown in Fig. 5. The B-H bonded clearly has a deeper occupied level than the C-H system, and indeed a Mulliken analysis shows that the highest occupied level for the B-H complex is dominated by the B-H bond with the mid-gap empty level being localized on the dangling bond on the interstitial carbon atom. For the lowest-energy structure we determine an acceptor level at about $E_c-1.9$ eV, but there is no donor level. Therefore the presence of such a defect would compensate any shallow donors in the material, as one might expect.

The addition of a second H atom is desirable in the case of B_s–IH with the binding energy being 2.4 eV for the reaction $B_s-IH+H \rightarrow B_s-IH_2$. However, there is a much less substantial binding for the B_iH+H reaction where the second H atom binds to the B atom, at around 1 eV. According to our calculations B_iH_2 is 1.8 eV higher in energy than B_s-IH_2. This latter defect possesses a B-related acceptor level in the bottom half of the band gap since the self-interstitial component is passivated. Indeed, this complex can be viewed as a strongly perturbed B_s.

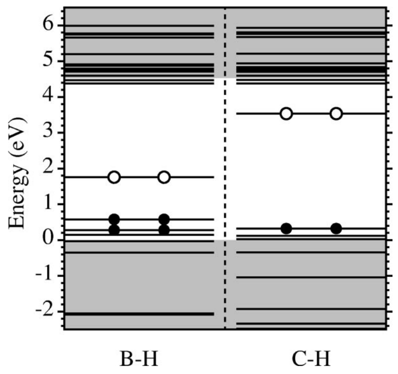

FIG. 5. Kohn-Sham eigenvalues at Γ in the vicinity of the band gap for the B_i [001]-oriented split-interstitial with a single H atom. The shaded areas indicate the bulk valence and conduction bands with the valence-band top being at zero energy. The black and white circles indicate filled and empty levels, respectively.

We have also examined boron adjacent to a lattice vacancy. The defect is bound by around 1.8 eV relative to V and B_s. Here $E^f(V)=6$ eV is taken from quantum Monte Carlo calculations due to the complications inherent in the multiplet structure of this defect.[44] The electronic structure of B_s-V is similar to that of the well known N_s-V complex which gives rise to 1.945 eV and 2.156 eV optical features and the W15 paramagnetic signature in CVD diamond. In the neutral charge state of B_s-V the three C-related dangling bonds give rise to a doubly degenerate, e level, which is lower in energy than an empty a_1-level associated with the sp^3 dangling bond on the B atom. This is in fact the reverse of N_s-V, but the $e^1a_1^0$ and $e^2a_1^0$ one-electron configurations for the neutral and negative charge states closely resemble those of N_s-V in character ($a_1^2e^1$ and $a_1^2e^2$), which is as one would expect since in both cases they arise from the three C-related dangling bonds. In the negative charge state we find that B_s-V is likely to be paramagnetic, with a ${}^3A_2$ ground state, as is the case for N_s-V (the W15 EPR center). However, we have only treated the diamagnetic states approximately, and we cannot be certain regarding the energy of the ${}^1E$ and ${}^1A_1$ multiplets. Using the bulk marker approach, B_s-V has a donor level at around $E_v+1.1$ eV and an acceptor level at around $E_c-3.8$ eV. These are close to those calculated for N_s-V at $E_v+1.5$ eV and $E_c-3.3$ eV for the $(0/+)$ and $(-/0)$ levels, respectively.[38]

In the B_s-V case, as with the self-interstitial, the *carbon* dangling bonds are preferentially saturated by hydrogen before the boron. For one or two H atoms the defects possess mid-gap acceptor levels, and donor levels close to the valence band top. For B_s-V-H_3 the defect does not possess a donor level, consistent with all electrons residing in bonding states. However, the empty sp^3 orbital on the B site remains an electron trap, and this defect has an acceptor level around

$E_c - 2.5$ eV (obtained using the bulk marker method). In the case of trigonal B_s-V-H_4 complex where the fourth H atom lies along $\langle 111 \rangle$ from the B atom, the defect is a deep acceptor and donor, with the activity arising from the B-H-related orbital pointing into the vacancy, as determined from a Mulliken bond population analysis. For one to three H atoms, the binding energy per H (relative to bond-centered hydrogen and in the neutral charge state) is around 6 eV, and therefore these complexes represent thermally stable defects. The binding of the fourth H atom to B_s-V-H_3 is much less at around 2 eV.

In summary, our calculations for B-H complexes with lattice vacancies and self-interstitials have yielded only deep levels, consistent with the electrical activity expected for carbon (or in some cases boron) dangling bonds. In any case, it seems difficult to understand how a supersaturation of hydrogen (or deuterium) would yield a mechanism by which such defects would be formed *reversibly*. Ignoring for a moment the details of the structure of the shallow donor, one can envisage reactions of the type

$$B_s + nH \rightarrow B_s - IH_n + V$$

and

$$B_s + nH \rightarrow B_s VH_n + I,$$

where the boron-containing defect is a shallow donor. For such a mechanism to work the emitted I or V must be removed a considerable distance from the donor to prevent electrical compensation, or alternatively they could be hydrogen terminated. In either case, the energies involved are inconsistent with the loss of donors and return to *p*-type material at relatively modest temperatures (the binding energy for B_s-V-H_n complexes is around 6 eV per H atom, and the self-interstitial is relatively strongly bound to B_s). Furthermore, it appears that such processes would necessarily require many more H atoms than boron, which appears to be inconsistent with the SIMS data.

D. B_s-H pairs revisited

Finally, one possible solution to the formation of a shallow donor might be sought in the simple B_s-H complex. In silicon the electronic properties of of the C_s-H pair is sensitive to the location of the H atom.[45–49] Here the donor level for the C_s-H pair is calculated to change from around the valence band top for H neighboring C_s, to around 0.2 eV below the conduction band when the H atom is in a bond center more distant from the C atom.[48,49] The binding energy of this more distant complex is rather small (the infrared absorption associated with the H-stretch modes of the partially dissociated pair anneal out at about 220 K, with the intimate pair surviving up to about 400 K).[48] Importantly, the metastable structures can generally be characterized as possessing electrical levels consistent with bond-centered hydrogen, whereas the intimate pair has electrical levels associated with a Si dangling bond.[49]

The C_s-H system is unlike B_s-H in diamond in two important ways: (1) C_s-H is not made up from a donor–acceptor pair, and (2) it is electrically active in the nearest-neighbor pair configuration. There remains a likelihood, however, that a more distant, metastable pairing of B_s and H (or D) yield electrical levels quite different from the intimate pair. We have rexamined these partially dissociated defects, and indeed find that moving the H atom by a lattice constant from the B atom introduces new gap states. However, these are very deep, and can be simply understood as arising from a bond-centered hydrogen defect that has been ionized by the presence of the near-by acceptor. There is no evidence for a donor level anywhere in the band gap, but an acceptor level lies around mid gap. We conclude that the shallow donor level is unlikely to arise from a metastable B_s-D complex.

We note that, in the absence of a constraint, moving the H atom to the nearest C-C back-bond is unstable and we find that this complex spontaneously relaxes back to the B_s-H intimate pair.

IV. DISCUSSION AND CONCLUSIONS

We have examined a range of complexes of a single B impurity with interstitial hydrogen (or equivalently within our calculations, deuterium) in the light of the experimental identification of a shallow donor most probably made up from these constituents. We find no evidence for any structure made up from B_s and two H atoms that gives rise to a shallow donor level. B_s-H_2 are thermally unstable in comparison to the 550°C annealing temperatures used in the experimental study, although it should be noted that the activation energy for dissociation is yet to be established experimentally. B_sH_3 and B_sH_4 complexes are passive or possess deep levels in all configurations studied, as do complexes made up from interstitial boron, B_i-hydrogen, and vacancy-boron-hydrogen complexes.

Of course, we cannot completely rule out the possibility that there exists a defect configuration that we have missed, made up from boron, carbon, and deuterium, which gives rise to a shallow donor level. However, if one accepts that there is no B-H point defect that acts as a shallow donor, then there are a number of possible explanations for the measured conductivity that one might consider, such as inhomogeneous doping or an anomalous Hall effect.[4] Furthermore, one should consider the nature of van der Pauws Hall measurement, which has all contacts on the same surface of the sample. For materials such as GaAs it is usual to diffuse the contact into the material, but this is not possible for diamond. It is not clear that a surface conductive channel (not necessarily due to adsorbates) might be present, qualitatively affecting the experiment.

In conclusion, there is no evidence from first principles calculations that a small complex of boron and hydrogen (or deuterium) gives rise to a shallow donor level. Alternative interpretations that we have suggested require additional experimental investigation to lead to an understanding of this potentially highly significant breakthrough in the development of *n*-type diamond.

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