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Theory of boron aggregates in diamond: First-principles calculations

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It is well known that nitrogen forms aggregates in diamond. However, little is known regarding aggregation of boron, an impurity that can be incorporated in very high concentrations. In this paper we present the results of first-principles calculations regarding the structure and properties of boron-aggregates, and simple complexes with native defects. We find that certain complexes are shallower acceptors than B_s, and that pairs of boron interstitials, suggested as having a role in the recently observed low-temperature superconduction in B-doped diamond, are unstable and do not provide the shallow acceptor states required.

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I. INTRODUCTION

Diamond, a wide-gap insulator, can be doped with high concentrations of boron acceptors (B_s) rendering it *p*-type. For modest [B] the activation energy for hole conduction is 0.37 eV,[1] dropping for higher concentrations so that for $[B] \sim 10^{20}-10^{21}$ cm^{-3} the conduction becomes metallic.[2,3] However, it seems that many boron atoms incorporated into diamond do not act as acceptors, and some estimates using a combination of infrared-absorption (IR) and secondary-ion mass spectroscopy (SIMS) suggest that as much as 90% of the impurities are electrically inactive.[4] This might arise if in some form boron acts as a deeper acceptor, is passive or even acts a donor. Alternatively, boron may segregate into highly defective regions of the material or within inclusions.

Multiboron complexes, boron-interstitials, and complexes of B with vacancies would be candidate structures for point defects resulting in a reduction in doping efficiency. Indeed, there is experimental evidence that heavily B-doped diamond contains nearest-neighbor-pair complexes which act as deep traps for hydrogen,[5] and may be associated with a vibrational band around 500 cm^{-1}.[6] Additionally, a paramagnetic center has previously been tentatively assigned to a vacancy-boron pair,[7] although recent theoretical treatment of this center casts doubt over this model.[8]

It has been observed that at low temperature [$\sim$4 K (Ref. 9) or lower[10,11]] and for $[B] > 5-7 \times 10^{20}$ cm^{-3}, diamond superconducts, sparking great interest in this material.[9–21] It has been suggested that above 0.01 atomic %, boron is taken up *interstitially*,[22] and a model has been proposed where pairs of interstitial boron atoms lying in cage sites are at the heart of the superconducting properties of diamond.[23]

Given the lack of data regarding aggregated boron, it is instructive to briefly review what is known for nitrogen.[24,25] Nitrogen aggregation is used to categorize natural diamond.[26] Neutral substitutional $N(N_s^0)$ has one unpaired electron detectable via electron paramagnetic resonance (EPR): the P1 center.[27] Over geological time scales and temperatures, N_s migrates to form nearest-neighbor pair complexes (*A*-centers). Note, although these aggregates do not form in significant concentrations in as-grown synthetic material, they have been detected.[28] The production of *A*-centers can be achieved in the laboratory with the considerable activation energy of 4.8–6.2 eV.[29,30] *A*-centers have a filled level close to E_v associated with the lone pairs on the N-atoms, but are electrically active.[31]

A-centers can be further converted into *B*-centers by thermal treatment. *B*-centers are complexes of four N_s defects surrounding a lattice vacancy (V). Indeed, aggregation is driven by the energy reduction associated with the removal of carbon dangling bonds: *A*- and *B*-centers are chemically satisfied, with all carbon and nitrogen atoms appropriately coordinated.

There are a range of other vacancy-nitrogen complexes, typically seen in irradiated diamond, but of particular interest is the N_1V complex which is seen in as-grown CVD material. This center is electrically and optically active and in the negative charge state is responsible for the W15 EPR center.[32] The electronic structure of partially N-terminated vacancies can be understood from the band-gap states associated with an ideal (T_d) vacancy,[33] where the four dangling bond orbitals yield a $a_1^2t_2^2$ one-electron configuration. Replacement of C by N, increases the number of electrons and for 1–3 impurities splits the t_2 level. Splitting the t_2 level admits optical transitions with zero-phonon lines at 2.156 eV, 2.463 eV (H3) and 2.985 eV (N3) for 1–3 N atoms, respectively. All three centers are predicted to be electrically active with donor and acceptor level.[34] For the *B*-center the one-electron configuration is $a_1^2t_2^6$: the t_2 level represents combinations of lone-pairs lying close to E_v.

Qualitatively, one might expect similar behavior for boron aggregates as for the nitrogen equivalents. For instance, *B*-nearest-neighbor pairs theoretically resemble *A*-centers,[5] with the B-B separation being around 27% longer than the host bond length. B_nV complexes, in contrast to N_nV, would depopulate the vacancy-related gap levels, so that B_2V would be $a_1^2t_2^0$ (neglecting symmetry-related splittings) and for a B_4V-complex analogous to the *B*-center, one would expect the a_1 level also to be empty. The details the electrical levels (i.e., the stable charge states) of B_nV therefore depend critically on the location of the dangling-bond levels relative to E_v.

Finally, as suggested previously boron may not be sited substitutionally, but instead lie interstitially.[22,23] Previous calculations using Tersoff potentials suggest that interstitial boron (B_i) would be a [001]-split configuration,[35,36] but we have shown using first-principles methods that a self-interstitial (I) neighboring B_s is around 0.2 eV lower in energy.[37] In either case, since these defects are both donors, incorporation would lead to compensation of acceptors, and lower the doping efficiency. Again, guided by what is found for interstitial nitrogen, one might envisage the formation of aggregates containing interstitials and boron. However, given the theoretical structure of individual B_i centers, it seems unlikely that interstitial boron would form the dumbbell pairs of tetrahedral interstitials suggested for superconducting material,[23] but more likely forms akin to the known self-interstitial pairs bonding into the lattice and satisfying the valence of all atoms.[8]

In heavily doped material it is plausible that defects involving boron might contain more than one B impurity, and it is not clear what behavior or contribution to the electrical conductivity any of these complexes might have. Therefore, we present in this paper the results of first-principles calculations regarding the structure, electrical levels, and binding energies of simple boron-boron, boron-vacancy, and boron-self-interstitial complexes in diamond.

II. METHOD

Calculations were carried out using the local-spin-density-functional technique, implemented in AIMPRO.[38] To model the defects, 64–216 atom, cubic supercells of side length 2 or $3a_0$ have been used. The Brillouin zone is sampled using the Monkhorst-Pack scheme,[39] generally with a uniform mesh of $2\times2\times2$ special k-points. For representative cases we have compared total energies with a $4\times4\times4$ mesh, and the results suggest our values from the smaller mesh are converged to the order of 10 meV. Core electrons are eliminated by using norm-conserving pseudopotentials.[40,41]

The wave function basis consists of atom-centered Gaussians.[42] We use independent s, and p Gaussians with four widths, plus one further set of d Gaussians. The charge density is Fourier transformed using plane waves with a cut-off of 300 Ry, yielding total energies converged to ~1 meV. The lattice constant and bulk modulus are within ~1% and 5%, respectively, of experimental, while the direct and indirect band gaps at 5.68 eV and 4.26 eV, respectively, are close to previously published plane-wave values.[43]

The formation energy of X in charge-state q is calculated using[44]

$$E^f(X,q) = E(X,q) - \sum \mu_i + q(E_v^X + \mu_e) + \chi(q), \qquad (1)$$

where E is the total energy, μ_i and μ_e are the chemical potentials of the atoms and electrons, respectively, E_v^X is the energy of E_v in the defect cell and χ is the correction for periodic boundary conditions, for which we include only the Madelung term,[45] which for cubic supercells of side length $2a_0$ and $3a_0$ is around $0.53q^2$ eV and $0.35q^2$ eV, respectively. Donor or acceptor electrical levels may be estimated using the formation energy method (FEM), or instead by use of the marker method[42] (MM) with comparison of the ionization potential or electron affinity of a bulk supercell as suggested previously,[46] and discussed in detail for application to defects in diamond.[34]

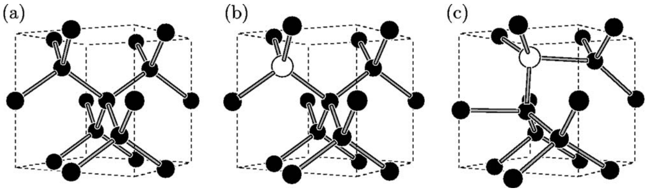

FIG. 1. Diffusion of B_s. (b) and (c) show B_s and saddle point structures, with (a) being a defect free section of diamond for comparison. Black and white circles represent C and B atoms, respectively.

Finally, we define a binding energy by $E^b(XY)=E^f(X)+E^f(Y)-E^f(XY)$.

III. RESULTS

A. Substitutional boron

We find B_s^0 possesses one 2% bond shorter than the others, yielding C_{3v} symmetry.[5,8] This distortion can be understood as a depletion of the charge preferentially from one covalent bond. For B_s^-, the number electrons can provide full covalency, yielding a T_d structure. By finding the equilibrium lattice constant for the supercell containing a single B_s center, we may estimate the dilatation effect of this impurity.[47] The effect is modest, yielding a modified lattice constant, a', which depends on $[B_s]$ as $a'=(1+0.1[B_s]/[C])a_0$, or an increase of ~0.1% for 1 at. % boron. This is in line with previous findings.[9,17]

MM and FEM estimates of the B_s acceptor level are $E_c-5.0$ eV and $E_v+0.2$ eV, respectively, in good agreement with experiment. This gives us some confidence in subsequent calculations.

We have calculated the barrier to migration for B_s using a dimer method[48] to determine a saddle point structure and energy. We have assumed that B_s diffuses via concerted exchange, and the resulting saddle point is structure shown schematically in Fig. 1. The barrier is 7.6(9.9) eV for the neutral (negative) charge state. Similar calculations for N_s yielded a similar value of 7.9(10.8) eV for the neutral (positive) charge state.[49] This implies that if boron migrates via concerted exchange it will diffuse only at very high temperatures, much higher than typical in CVD processes and probably in high-pressure growth techniques. Therefore if boron aggregates form, it seems likely that they are grown in, or that migration is mediated by some other defect, such as V or I.

B. B_s-B_s complexes

Heavily B-doped diamond, even if only via random chance, will contain B_s at nearby sites. Statistically, the number of pairs formed at various distances is given by

$$\frac{n_m[B]^2}{2[C]}, \qquad (2)$$

where $[X]$ represents the concentration of X, and n_m is the number of possible configurations of a second B atom in the

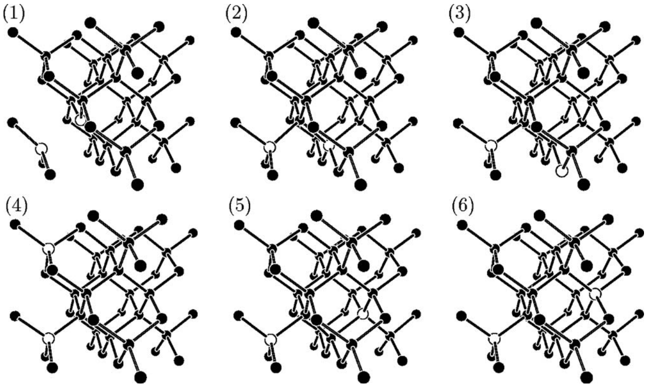

FIG. 2. Structures of B_s-B_s for the first six shells of neighbors. Black and white circles represent C and B atoms, respectively. There are $n_m=4$, 12, 12, 6, 12, and 24 equivalent versions of (1)–(6), respectively.

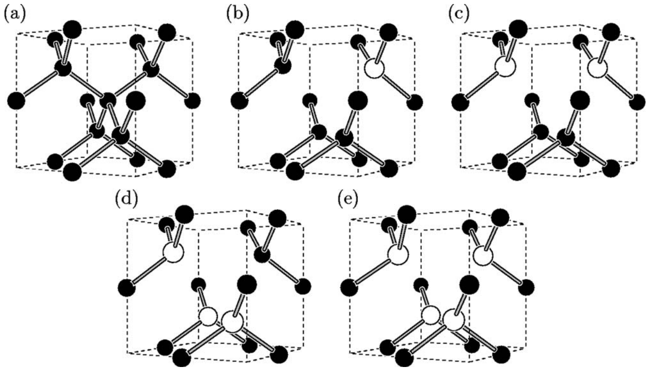

FIG. 4. Schematic structures for B_nV, $n=1,2,3$ and 4 in diamond, (b)–(e). Black and white circles represent C and B, respectively, and the dashed lines are the cubic axes. (a) shows a section of defect-free diamond for comparison.

*m*th concentric shell of host sites around the first.[50] The closer they lie, the greater the elastic and electrostatic interaction is likely to be.

We previously reported the properties of nearest-neighbor B pairs.[5] Here, we present the results for B pairs at various separations in 216-atom cubic unit cells. Placing a second B_s in one of the six concentric shells of host sites surrounding B_s (Fig. 2), reduces the formation energies by 0.8, 0.6, 0.3, 0.3, 0.6, and 0.4 eV, respectively. The fifth-shell pair [Fig. 2(5)] shows a particularly large interaction between the B atoms due to the direct interaction mediated by the intervening C-C bond.

The calculated acceptor levels relative to that calculated for B_s are shown in Fig. 3. We note that the 216-atom supercell represents $[B]\sim 10^{21}$ cm^{-3}, in the region of the onset of metallic conduction. In all cases, B-pairs result in *deeper* acceptor levels than B_s: this can be understood qualitatively from the inset in Fig. 3, showing the acceptor states of two nearby B_s giving rise to even and odd combinations split by 2Δ. The lower-energy combination is filled and the acceptor level must be related to the higher energy state. In our calculations, only the empty level lies in the band gap, but even if the lower level was to appear in the band gap it would not be able to contribute to the hole concentration since it is filled. Although the absolute location of the acceptor levels of the boron pairs may be accurate to a few tenths of an eV, the relative locations of electrical levels may be expected to be more accurate, the principle which forms the cornerstone of the marker method.[42] We therefore conclude that the boron pairs all give deeper acceptor levels than isolated B_s. In summary and in variance to the suggestion of Mamin and Inushima,[51] we find no evidence that individual boron pairs can lead to a lower activation energy than B_s. In heavily B-doped diamond, if nearest-neighbor B pairs are formed, they will tend to contribute less to conduction than isolated impurities, and may contribute to the reduction[4] in the activation fraction for heavily B-doped diamond. However, most B_s pairs would behave in a fashion similar to two isolated B_s, and then contribute to a Mott-mechanism for metallization.[52]

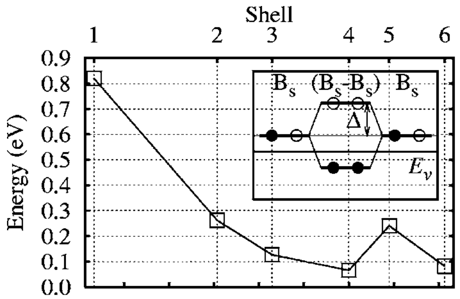

FIG. 3. Calculated B_s-B_s acceptor levels for various separations [$R(B_s$-$B_s)$], relative to the computed level of B_s. The inset shows a schematic one-electron picture for the combination of B_s acceptor states, with Δ showing the increase in the acceptor level due to the interaction.

C. B_nV complexes

Schematics of geometries for B_nV, $n=1-4$, are shown in Fig. 4. As outlines in the introduction, the electronic structure can be understood by extension of the vacancy model, with electronic configurations $(a_1t_2)^{4-n}$. We find that the a_1 level lies below E_v, so that for $n>2$, holes are introduced into the valence band. The Kohn-Sham levels of the systems at the Brillouin-zone center are shown in Fig. 5, with levels in the band gap being components of the vacancy t_2 level localized on dangling bonds.

For $n>1$, only empty levels lie in the band gap, so these complexes are unlikely to give rise to *sharp* optical transitions, in contrast to the analogous nitrogen defects. Band-edge related transitions may occur, but are likely to be rather broad.

The high symmetry and electronic degeneracies of B_1V^- and B_4V lend them to the possibility of having effective spins of $S=1$. As explained previously,[8] it is difficult to be precise about the ground spin states of such systems. However, we find the paramagnetic state of B_1V^- is more stable than $S=0$, whereas the paramagnetic and diamagnetic forms of B_4V are practically degenerate.

The electrical levels obtained using the MM are listed in Table I. With the exception of B_1V, the donor levels lie be-

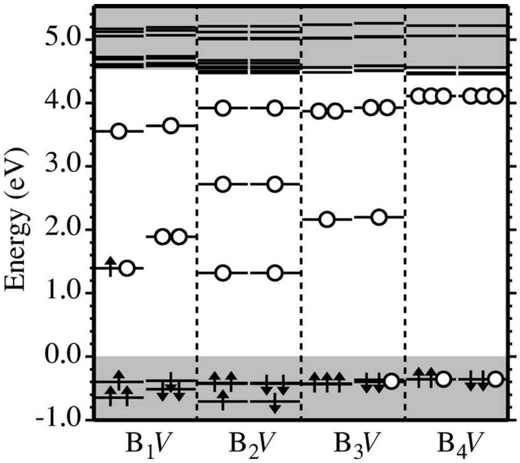

FIG. 5. Kohn-Sham eigenvalues for B_nV, $n=1,2,3$, and 4 in diamond. Arrows and circles represent filled and empty levels, respectively, and the shaded areas represent the valence and conduction bands of pure diamond.

low E_v and can be ignored. The deep B_1V donor level would compensate B_s, whereas B_3V and B_4V are *shallower acceptors* than B_s and would *decrease* the activation energy for conduction. Indeed, if present in large concentrations B_3V and B_4V may contribute to the metallic conduction in heavily doped material.

The stability of neutral B_nV complexes can be estimated by comparison of the formation and binding energies relative to B_s and V. $E^f(V)$ is difficult to obtain using DFT-based techniques due to multiplet effects, so we have used the value of 6 eV taken from quantum Monte Carlo calculations.[53] The formation and binding energies are listed in Table I. Of particular note is that B_4V is *more* stable than B_s.

Migration of B_1V may proceed as a hop of B along $\langle 111\rangle$ and subsequent motion of the vacancy, as illustrated in Fig. 6. Step (a) is bounded by the energy of the split-vacancy structure which lies around 1 eV above the ground state.[8] V is known to migrate with a barrier of 2.3 eV,[54] so that an estimate of the migration barrier (b)–(f) may be obtained approximately by $E^b(B_1V)+E^a(V)=4.2$ eV, which is greater then step (a) and would be the rate limiting barrier.

TABLE I. Formation and binding energies and electrical levels for B_nV complexes in diamond (eV). For E^f, the μ(C) and μ(B) are taken from diamond and the condition $E^f(B_s)=0$ eV, respectively. E^b refers to the energy released per B atom in $(n\times B_s+V)\rightarrow B_nV$. The donor and acceptor levels are with respect to E_v and E_c, respectively.

n	1	2	3	4
$(0/+)$	1.0			
$(-/0)$	3.6	3.9	5.6	5.6
E^f	4.0	1.3	0.1	−1.1
E^b/n	1.9	2.3	2.0	1.8

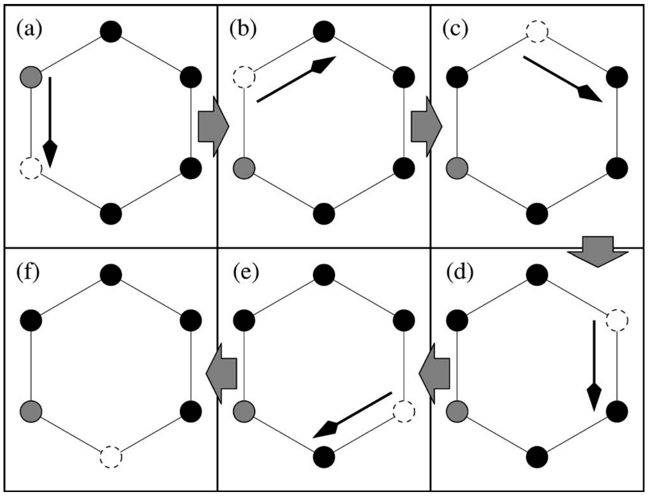

FIG. 6. Schematic of B_1V migration. Black gray and white circles represent B, C and vacant sites in a hexagonal ring.

Indeed, this relates to the migration of B_s via the transient interaction with V. We shall return to this in the discussion below.

D. B_nI complexes

An alternative to the formation of multiboron complexes with lattice vacancies involves excess boron occupying interstitial locations. Indeed, this has been suggested as significant to the superconducting properties of heavily B-doped material, with nonbonded interstitial-pairs forming in the lattice.[23] Although the formation energy of isolated self-interstitials has been calculated to be very high (~12–13 eV),[47,55] gas-phase growth is inherently nonequilibrium, and it is possible that particularly stable interstitial-impurity defects might be taken up by a growing surface, especially where the concentration of the impurities is large.

Previously, we indicated that B favors a substitutional site neighboring I.[37] The total energies for B_i at the T, H, bond-centered and [001]-oriented split-interstitial configurations are listed in Table II relative to the energy of B_sI. Neutral and negatively charged bond-centered B_i is lowered in energy by decreasing the C-B-C bond angle from 180° to around 120–130°. This puckered bond-centered configuration spontaneously reconstructs into the [001]-split interstitial configuration in the positive charge state.

All configurations are found to be donors, and would compensate B_s. The formation energy of B_i is 10 eV or more above that of B_s, and so to incorporate large concentrations would be highly nonequilibrium. The reaction $I+B_s\rightarrow B_sI$ liberates 3.1(4.1) eV in the neutral (positive) charge states, suggesting that the activation energy for dissociation is around 4.8(5.8) eV using the 1.7 eV migration barrier for I.[55–57]

The migration of B_sI is likely to involve the [001]-split configuration in a transient sense: $B_sI\rightarrow B_i\rightarrow B_i\rightarrow IB_s$, including a through-bond migration step of B_i analogous to that of interstitial nitrogen.[58] We have estimated these steps for the neutral and positive charge states, with an overall

TABLE II. Total energies (eV) for B_i in diamond relative to the B_sI complex of Ref. 37. The donor and acceptor levels (eV) are with respect to E_v and E_c, respectively.

		Energy				
	Sym.	+	0	−	(0/+)	(−/0)
T	T_d	5.3	7.9	9.6	4.8	0.1
H	D_{3d}	1.5	4.1	5.7	4.8	0.2
Bond centered	D_{3d}	0.9	2.9	4.4	4.2	0.4
Off bond centered	C_{1h}		1.8	2.8	3.9	0.8
[001] split	C_{2v}	0.0	0.3	1.0	2.4	1.1
B_sI	C_{1h}	0.0	0.0	0.0	2.2	1.8

activation energy of 2.1 and 1.4 eV, respectively, where the rate limiting step is the migration of B_i in both cases. This suggests that B_sI would migrate well before it would dissociate, and most likely be mobile under growth conditions.

We now turn to aggregates involving B_i.

We find the lowest energy $2B_s+I$ complex is a [110]-oriented self-interstitial bordered by two substitutional B defects [Fig. 7(b)]. This is 1.5 eV lower in energy than the [100]-oriented split-interstitial configuration shown schematically in Fig. 7(c), which is the most stable form in silicon.[59] Although the higher energy structure has threefold coordinated B in line with their valence, boron is well known to form structures with fivefold coordination, such as the B_s-H complex in diamond[60]. Other structures are competative in energy, and in particular that shown in Fig. 7(d) is just 0.2 eV higher in energy than Fig. 7(b). As with other low energy models, all host atoms are fourfold coordinated, but in this case there are both three- and five-fold coordinated B atoms. B_s-B_i is bound by 4 eV relative to B_s and B_sI. This defect is likely to be less mobile than B_sI, so that if formed during growth it is likely to be frozen in.

The [110]-oriented B_s-B_i does not have a donor level, but does have an acceptor level deep in the band gap. However, the Fig. 7(d) structure *does* have a donor level above the acceptor level of B_s, and is the most stable form of this complex that we found for the positive charge state. Therefore, it is possible that as-grown diamond contains a mixture of these complexes, and that each one in the (d)-form would remove *three* boron atoms from the uncompensated B_s concentration (two in the complex and one compensated B_s).

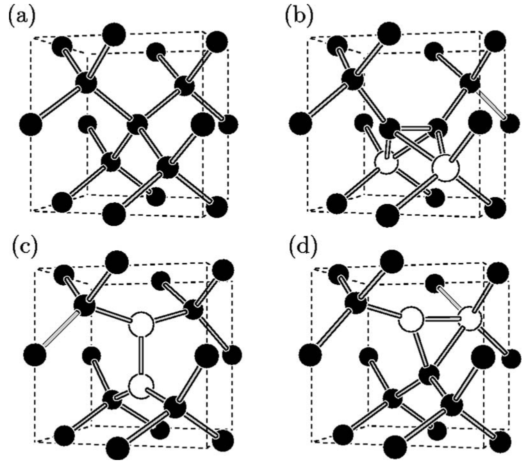

FIG. 7. Schematic of B_s-B_i pairs in diamond. (b) C_{2v}, [110]-oriented split-interstitial, (c) D_{2d}, [001]-oriented split-interstitial, and (d) a planar B_s-B_i complex. (a) shows the comparable section of defect free material. Colors and axes are as in Fig. 4.

Finally, following suggestions in the literature,[23] di-interstitial complexes have also been examined. Structures resembling the native R1, 3H and π-bonded di-interstitials[55] were relaxed where the threefold-coordinated C-atoms are replaced by boron, and are shown in Fig. 8. These structures are also the most stable structures found for interstitial nitrogen.[58] We also examined structures made up from two nearby B_i in T sites, which relaxed into a metastable structure similar to the R1-form [Fig. 8(e)]. This is more than around 4 eV higher in energy than (c) and is made up from two spacially separated threefold coordinated C atoms. No fivefold coordinated structures we examined were found to be stable, and exchanging C and B atoms in the structures in Fig. 8 increases the energy considerably. Figure 8(c) was found to be the lowest in energy, 0.6 eV, 2.2 eV, and 4.4 eV below (b), (d), and (e), respectively. This is in contrast to nitrogen interstitials where we found structure (b) to be most stable.[58] B_i-B_i is bound with respect to two separated B_sI by around 5 eV, but has a formation energy of 14 eV more than two B_s centers.

The two low energy (b) and (c) structures exhibit simple electronic structures characterized by an empty level associ-

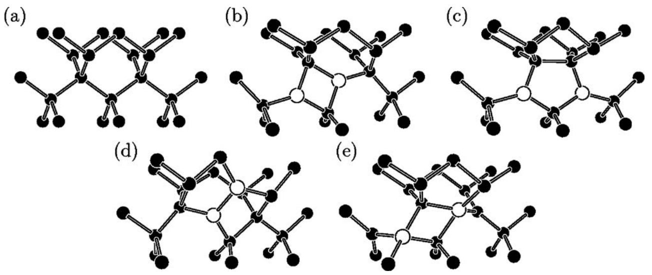

FIG. 8. Schematic of B_i-B_i pairs in diamond. (b) C_{2h} (R1), (c) C_{2v} (3H), (d) C_{2h} (π-bonded) and (e) C_2 structure obtained from relaxing two T-site B_i defects. (a) shows the comparable section of defect free material. Colors and axes are as in Fig. 4.

ated with *p*-orbitals on the B atom, lying close to E_c. There is no evidence of occupied gap levels. Specifically, in contrast to the suggestions of Pogorelov *et al.*,[23] there is no suggestion that pairs of interstitial boron would act as shallow acceptors.

IV. DISCUSSION AND CONCLUSIONS

At least on total energy grounds, aggregation of boron would be expected in diamond. For substitutional pairs, the binding energy is modest in comparison with the case of nitrogen, but the reaction $B_s+B_s \rightarrow (B_s)_2$ is exothermic by around 0.8 eV. In contrast to the suggestion[51] that such defects would be acceptors as shallow as 60 meV, we find that all B_s pairs we have looked at are *deeper* than B_s. Indeed, we find other complexes such as B_s-N_s-B_s, also suggested[51] to be shallow are not significantly different from B_s. Furthermore, we find that B_i pairs are also not shallow acceptors.[23]

We estimate that the diffusion barrier for B_s via concerted exchange is extremely high (7.6 eV), with activation somewhat lower for the migration for neutral B_1V and B_sI at around 4.2 and 2.1 eV, respectively. These values belie the true cost of V and I mediated migration of B_s, because these activation barriers do not include the formation of the native defect. If there is no lower energy source of the native defects (for example, voids or interstitial aggregates) in the material, the cost of the reactions are heavily influenced by the formation energies of these species: 6 eV for V and 12–13 eV for I. Our first-principles results are in stark contrast to the Tersoff potential results of Hu *et al.*[35] who suggested that the activation for interstitial-mediated migration is just 0.23 eV. Our high barriers are consistent with the 1600 °C needed to indiffuse boron.[61] Once formed, we predict that B_sI would be mobile at these high temperatures, as would B_1V.

Structures comprised of complexes of boron with lattice vacancies (other than B_4V) or self-interstitials have a higher formation energies than B_s, and would be unlikely to occur in diamond under equilibrium conditions. However, there is evidence that nonequilibrium concentration of impurities are now relatively routinely incorporated, as in the case of phosphorus doping: theory predicts that substitutional phosphorus has a very high formation energy, but there are surface effects during growth that allow the incorporation into diamond.[62] Additionally, simple defects such as complexes of lattice vacancies with silicon and nitrogen grow into CVD material despite their relatively high formation energies.[8] Therefore under the growth conditions commensurate with heavy doping, it seems plausible that boron may be incorporated in high energy structures.

We predict that B_3V and B_4V are extremely shallow acceptors, but in the absence of boron migration under grown conditions, this would require the simultaneous incorporation of three or four boron impurities along with the lattice vacancy during growth. Even for doping concentrations of atomic %, this represents a statistically unlikely event unless there are growth mechanisms that preferentially incorporate these defects. However, it is a intriguing observation that B_4V is both highly stable and a shallow acceptor, and in highly boron-doped material they may be present, and may contribute to the superconducting material. As neutral or negatively charged open spaces, these centers would be ideal candidates for investigation via positron annihilation spectroscopy.

B_1V and boron-interstitial defects generally act as compensating defects, and where they are formed would lead to a reduction in the doping efficiency. In addition to these high energy compensating defect, nearest-neighbor B_s pairs show relatively deep acceptor levels, and represent a fraction of the boron that is incorporated in substitutional sites that do not contribute to the free-hole concentration.

Neutral B_1V should give rise to optical transitions around 2 eV, but would be inactive in the positive charge state. Since it is likely to be produced only in *p*-type material, this renders the complex hard to detect optically or via EPR, although it would be possible in material which is co-doped with more donors than boron. Indeed, since most of the centers we have examined are anticipated to be diamagnetic in *p*-type material, this problem of EPR detection is likely to be wide spread.

An inactive fraction of boron might be explained in terms of the nonequilibrium incorporation of passive boron (e.g., B_2V), boron-related donors (e.g., B_sI) and deep acceptor levels (e.g. B_s-B_s pairs). However, we note that the 90% estimate of Chen *et al.*[4] relies on the IR bands associated with the oscillation of B_s, rather than on the electronic infrared transitions or a direct measurement of the hole concentration. Additionally SIMS is not spacially sensitive and cannot be used to determine if the concentration of boron is uniform or involves local clustering of impurities, and IR measurements are problematic in the case of opaque diamond samples where [B] is high. Nevertheless, a 90% loss of *isolated* uncompensated B_s requires only a minority of boron to be incorporated in other sites. For example, if 45% of boron goes into a mixture of B_sI and B_1V donors, then this would compensate more than 80% of the remaining B_s and leave only 10% of [B] as uncompensated B_s.

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[1] P. A. Crowther, P. J. Dean, and W F. Sherman, Phys. Rev. **154**, 772 (1967).

[2] K. Thonke, Semicond. Sci. Technol. **18**, S20 (2003).

[3] C. Johnston, A. Crossley, M. Werner, and P. R. Chalker, in *Properties, Growth and Applications of Diamond*, No. 26 in EMIS Datareviews Series, edited by M. H. Nazaré and A. J. Neves (INSPEC, Institute of Electrical Engineers, London, 2001), Chap. B3.3, pp. 337–347.

[4] Y.-H. Chen, C.-T. Hu, and I.-N. Lin, Appl. Phys. Lett. **75**, 2857 (1999).

[5] J. P. Goss, P. R. Briddon, R. Jones, Z. Teukam, D. Ballutaud, F. Jomard, J. Chevallier, M. Bernard, and A. Deneuville, Phys. Rev. B **68**, 235209 (2003).

[6] M. Bernard, C. Baron, and A. Deneuville, Diamond Relat. Mater. **13**, 896 (2004).

[7] J. M. Baker and M. E. Newton, Appl. Magn. Reson. **7**, 209 (1994).

[8] J. P. Goss, P. R. Briddon, M. J. Rayson, S. J. Sque, and R. Jones, Phys. Rev. B **72**, 035214 (2005).

[9] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, and S. M. Stishov, Nature (London) **428**, 542 (2004).

[10] J. Kačmarčik, C. Marcenat, C. Cytermann, A. Ferreira de Silva, L. Ortega, F. Gustafsson, J. Marcus, T. Klein, E. Gheeraert, and E. Bustarret, Phys. Status Solidi A **202**, 2160 (2005).

[11] E. Bustarret, J. Kačmarcik, C. Marcenat, E. Gheeraert, C. Cytermann, J. Marcus, and T. Klein, Phys. Rev. Lett. **93**, 237005 (2004).

[12] J. F. Prins, Semicond. Sci. Technol. **18**, S131 (2003).

[13] X. Blase, C. Adessi, and D. Connetable, Phys. Rev. Lett. **93**, 237004 (2004).

[14] L. Boeri, J. Kortus, and O. K. Andersen, Phys. Rev. Lett. **93**, 237002 (2004).

[15] K. W. Lee and W. E. Pickett, Phys. Rev. Lett. **93**, 237003 (2004).

[16] Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, and H. Kawarada, Appl. Phys. Lett. **85**, 2851 (2004).

[17] H. J. Xiang, Z. Li, J. Yang, J. G. Hou, and Q. Zhu, Phys. Rev. B **70**, 212504 (2004).

[18] V. A. Sidorov, E. A. Ekimov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, V. Fritsch, J. D. Thompson, S. M. Stishov, A. E. Alexenko, and B. V. Spitsyn, Diamond Relat. Mater. **14**, 335 (2005).

[19] V. A. Sidorov, E. A. Ekimov, S. M. Stishov, E. D. Bauer, and J. D. Thompson, Phys. Rev. B **71**, 060502(R) (2005).

[20] J. S. Tse, Y. M. Ma, and H. M. Tutuncu, J. Phys.: Condens. Matter **17**, S911 (2005).

[21] T. Yokoya, T. Nakamura, T. Matsushita, T. Muro, Y. Takano, M. Nagao, T. Takenouchi, H. Kawarada, and T. Oguchi, Nature (London) **348**, 647 (2005).

[22] A. N. Utyuzh, Yu. A. Timofeev, and A. V. Rakhmanina, Izv. Akad. Nauk SSSR, Neorg. Mater. **40**, 1062 (2004) [Inorg. Mater. **40**, 926 (2004)].

[23] Yu. G. Pogorelov and V. M. Loktev, Phys. Rev. B **72**, 075213 (2005).

[24] R. Jones and J. P. Goss, in *Properties, Growth and Applications of Diamond*, No. 26 in EMIS Datareviews Series, edited by M. H. Nazaré and A. J. Neves (INSPEC, Institute of Electrical Engineers, London, 2001), Chap. A5.1, pp. 127–129.

[25] I. Kiflawi and S. C. Lawson, in *Properties, Growth and Applications of Diamond*, No. 26 in EMIS Datareviews Series, edited by M. H. Nazaré and A. J. Neves (INSPEC, Institute of Electrical Engineers, London, 2001), Chap. A5.2, pp. 130–133.

[26] G. S. Woods, in *Properties and Growth of Diamond*, No. 9 in EMIS Datareviews Series, edited by G. Davies (INSPEC, Institute of Electrical Engineers, London, 1994), Chap. 3.1, pp. 83–84.

[27] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).

[28] K. M. McNamara, Appl. Phys. Lett. **83**, 1325 (2003).

[29] T. Evans and Z. Qi, Proc. R. Soc. London, Ser. A **381**, 159 (1982).

[30] I. Kiflawi, H. Kanda, D. Fisher, and S. C. Lawson, Diamond Relat. Mater. **6**, 1643 (1997).

[31] G. Davies, J. Phys. C **9**, L537 (1976).

[32] M. E. Newton, in *Properties and Growth of Diamond*, No. 9 in EMIS Datareviews Series, edited by G. Davies (INSPEC, Institute of Electrical Engineers, London, 1994), Chap. 5.2, pp. 153–158.

[33] C. A. Coulson and M. J. Kearsley, Proc. R. Soc. London, Ser. A **241**, 433 (1957).

[34] J. P. Goss, P. R. Briddon, S. J. Sque, and R. Jones, Diamond Relat. Mater. **13**, 684 (2004).

[35] X. J. Hu, Y. B. Dai, H. S. Shen, and X. C. He, Solid State Commun. **132**, 557 (2004).

[36] X. J. Hu, Y. B. Dai, R. B. Li, H. S. Shen, and X. C. He, Physica B **327**, 39 (2003).

[37] J. P. Goss, P. R. Briddon, S. J. Sque, and R. Jones, Phys. Rev. B **69**, 165215 (2004).

[38] R. Jones and P. R. Briddon, in "Identification of defects in semiconductors," in *Semiconductors and Semimetals*, edited by M. Stavola (Academic, Boston, 1998), Vol. 51A, Chap. 6.

[39] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[40] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[41] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).

[42] J. P. Goss, M. J. Shaw, and P. R. Briddon, Top. Appl. Phys. (to be published).

[43] D. A. Liberman, Phys. Rev. B **62**, 6851 (2000).

[44] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).

[45] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[46] J.-W. Jeong and A. Oshiyama, Phys. Rev. B **64**, 235204 (2001).

[47] J. P. Goss, R. Jones, and P. R. Briddon, Phys. Rev. B **65**, 035203 (2002).

[48] G. Henkelman and H. Jónsson, J. Chem. Phys. **111**, 7010 (1999).

[49] S. Papagiannidis, P. R. Briddon, and J. P. Goss (unpublished).

[50] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[51] R. F. Mamin and T. Inushima, Phys. Rev. B **63**, 033201 (2001).

[52] N. F. Mott, Philos. Mag. **19**, 835 (1969).

[53] R. Q. Hood, P. R. C. Kent, R. J. Needs, and P. R. Briddon, Phys. Rev. Lett. **91**, 076403 (2003).

[54] G. Davies, S. C. Lawson, A. T. Collins, A. Mainwood, and S. J. Sharp, Phys. Rev. B **46**, 13157 (1992).

[55] J. P. Goss, B. J. Coomer, R. Jones, T. D. Shaw, P. R. Briddon, M. Rayson, and S. Öberg, Phys. Rev. B **63**, 195208 (2001).

[56] S. J. Breuer and P. R. Briddon, Phys. Rev. B **51**, 6984 (1995).

[57] D. C. Hunt, D. J. Twitchen, M. E. Newton, J. M. Baker, T. R. Anthony, W. F. Banholzer, and S. S. Vagarali, Phys. Rev. B **61**, 3863 (2000).

[58] J. P. Goss, P. R. Briddon, S. Papagiannidis, and R. Jones, Phys. Rev. B **70**, 235208 (2004).
[59] J. Adey, J. P. Goss, R. Jones, and P. R. Briddon, Phys. Rev. B **67**, 245325 (2003).
[60] J. P. Goss, R. Jones, M. I. Heggie, C. P. Ewels, P. R. Briddon, and S. Öberg, Phys. Rev. B **65**, 115207 (2002).
[61] O. B. Krutko, P. B. Kosel, R. L. C. Wu, S. Fries-Carr, S. J. Heidger, and J. Weimer, Appl. Phys. Lett. **76**, 849 (2000).
[62] Y. Yan, S. B. Zhang, and M. M. Al-Jassim, Phys. Rev. B **66**, 201401(R) (2002).