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Interaction of hydrogen with boron, phosphorus, and sulfur in diamond

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The production of *n*-type doped diamond has proved very difficult. Phosphorus, and possibly sulfur, when in substitutional sites in the lattice, forms a donor which could be used in electronic devices. Boron, which is a relatively shallow acceptor, can be passivated by hydrogen, and it is possible that some of the difficulties in producing electrically active donors could be due to their passivation by the hydrogen which is present during the chemical vapor deposition growth of diamond. We report *ab initio* modeling of these dopants and their complexes with hydrogen in diamond and show that it is energetically favorable for hydrogen to be trapped and to passivate boron and phosphorus. We predict that sulfur with one hydrogen atom produces shallow donor levels in the band gap of diamond with a previously unconsidered configuration being the most stable and producing the shallowest level. We show that the S-H pair is stable under conditions of limited H availability. Further, we show that it is energetically favorable for both P-H and P-H_2 to dissociate forming H_2^*. H diffusion in *n*-type P-doped diamond is inhibited by this formation of immobile H_2^*. This is in contrast to B-doped diamond, where we predict that H_2^* will dissociate in the presence of substitutional B atoms, forming B-H complexes. We demonstrate that the recently observed shallow *n*-type conductivity is unlikely to arise from B-D_2 complexes, because these complexes would dissociate into B-D plus a distant deuterium interstitial. We also predict that they would induce deep levels in the band gap.

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I. INTRODUCTION

Diamond has been suggested as a material for semiconductor devices for high temperature and high power applications, due to its large band gap, high breakdown field, and other extreme properties.[1] However, impurity incorporation and doping are not yet well controlled; in particular, it has proven difficult to find a suitable donor. Boron can be grown into diamond or implanted successfully to produce *p*-type layers, with an activation energy of 0.37 eV.[2] The only successful donor, so far, has been phosphorus with an activation energy of 0.6 eV,[3,4] although there has been a very recent report[5] of shallow donors with high *n*-type conductivity and activation energy of around 0.23 eV in deuterated homoepitaxial boron-doped diamond layers. However, the production of reliable *n*-type diamond is still at an early stage.[4] Sulfur-doped diamond has had a controversial history;[6,7] much research will be required before the production of *n*-type diamond is routine.

Hydrogen is a very common impurity in natural diamond.[8] It is a major component in the gas phase of most synthetic diamond grown by the chemical vapor deposition (CVD) processes. It appears that, as for silicon, interstitial hydrogen binds strongly to impurities in diamond,[9] and it is probable that multiple trapping of hydrogen at donors and acceptors in diamond may occur, as is seen in silicon. It is therefore important to understand the interaction of hydrogen with dopants in diamond and the role it plays in passivating them.

The interaction of a single hydrogen atom with boron, phosphorus, and sulfur in diamond has been modeled previously,[9–11] although not all the likely structures have been considered. For example, we show that the most stable configuration of the hydrogen-sulfur complex has the hydrogen at an antibonding site behind a carbon neighbor to the sulfur atom, rather than bonded to the sulfur itself as previously suggested.[11]

In silicon, further hydrogen atoms are trapped by dopants,[12] leading to the nucleation of platelets; we therefore model the complexes of the dopants with two hydrogen atoms, to our knowledge, none of which have been reported before. A recent paper showed that under some conditions deuterated boron-doped diamond could display *n*-type conductivity with an activation energy of around 0.23 eV.[5] The experimental results cannot show what kind of defect the donor is, although a B-D_2 complex was considered consistent with the results. Our calculations show that several B-D_2 complexes are stable, but it is energetically favorable for them to dissociate into B-D and a deuterium interstitial atom. Moreover B-H_2 complexes do not have shallow donor levels, therefore the identification of a B-H_2 complex with the shallow dopant is unlikely.

After a brief review of the experimental properties of the systems to be considered, we use *ab initio* density functional theory (DFT) methods (described in Sec. II) to investigate the properties of boron, phosphorus, sulfur, and hydrogen (Sec. III) and the interaction of these dopants with one (Sec. IV) or two hydrogen atoms (Sec. V).

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A. Experimental properties of B, P, and S in diamond

Boron and nitrogen are among the most common impurities and the easiest to incorporate into diamond. Nitrogen has a donor level at 1.7 eV and is thus too deep to be a useful donor in diamond. Boron is an effective-mass-like acceptor[2] with an optical ionization energy of 0.382 eV and thermal activation energy of 0.368 eV; its properties have recently been reviewed.[13]

Despite many difficulties in achieving *n*-type doping in diamond, success has recently been attained using phosphorus as a donor in CVD diamond grown at NIMS (Ref. 14) and CNRS Grenoble.[4] The excitation has also been studied optically,[3] where an ionization energy of 630 meV has been found. In the manufacture of these thin-film CVD doped diamond samples, growth conditions were optimized to minimize the hydrogen codoping with phosphorus. The quality of *n*-type doped material has been steadily improving, with Hall mobilities of 240 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ having been reported.[15] Constant photocurrent measurements[16] showed two defect levels at 0.56 eV (ionization of the phosphorus) and a compensation level at 0.81 eV. Gheeraert *et al.*[17] showed that the thermal activation energy is 610 meV, together with an optical ionization energy of 600 ± 20 meV, and its properties are described by the effective-mass approximation, implying that phosphorus behaves as a conventional effective-mass-like shallow donor in diamond.

The first reports of high mobility, low resistivity, *n*-type sulfur-doped diamond[6] were disputed, since the samples showed unintentional boron contamination.[7] Some sulfur-doped samples have shown *n*-type conductivity with an activation energy of 0.19–0.33 eV,[18] while recently a sulfur related activation energy of 0.5–0.75 eV has been observed.[19] However, the results have been difficult to reproduce and boron contamination was identified as a prevalent problem.[4,20]

B. Experimental data on hydrogen in diamond

Identification of the structure of single hydrogen interstitials in diamond has come from muon spin-resonance experiments.[21,22] In common with many other semiconductors, two stable sites have been identified for μ^+e^- (called muonium, a hydrogen atom analog). "Normal muonium" occupies the tetrahedral interstitial site, but the more common species is "anomalous muonium" which occupies a bond-centered site.[23] In other semiconductors a hydrogen molecule has been identified, but so far this has not been detected in diamond. Similarly, the H_2^* species has not been observed in diamond, although it has been predicted by theory[24] to be the most stable form of H in undoped diamond.[9] It consists of a bond-centered hydrogen atom with an additional hydrogen atom at an antibonding site to the carbon neighbor along the same axis. Hydrogen is known to diffuse rapidly in boron-doped diamond[25,26] with the activation energy varying from 0.35 eV for an rf-plasma treated sample to 1.4 eV for a microwave-plasma treated sample. Modeling identifies the low-energy migration energy with the H^+ ion, associated with excess deuterium introduced during the more aggressive rf-plasma treatment, while the higher migration energy is associated with the diffusion of deuterium governed by the trapping-detrapping of deuterium on boron.[9,26] Neutral or negatively charged hydrogen atoms or ions have higher migration energies. In contrast, H_2^* is expected to be immobile at temperatures below 1000 °C.[9]

C. Experimental properties of hydrogen-dopant complexes

Boron can be passivated when hydrogen (or deuterium) diffuses into a heavily B-doped sample.[25–27] For diffusion temperatures as high as 480 °C, with hydrogen (deuterium) introduced by a microwave plasma, the hydrogen plateau concentration follows the boron concentration very closely, with H diffusion governed by trapping-detrapping of H at B; a cohesive energy of 2.5 eV has been determined for the boron-hydrogen pair.[28] The boron-hydrogen complexes appear to dissociate above 550 °C. Since theoretical studies[29] predicted that H induces an electronic level above the boron acceptor level, Chevallier *et al.*[25] proposed that neutral H atoms entering diamond become ionized, providing their electrons first to compensate holes arising from the few ionized B acceptors and second to ionize neutral boron atoms. The resulting B ion is expected to attract the mobile H^+ ions by a Coulomb interaction, eventually forming B-H complexes. This is in contrast to lightly B-doped diamond, where D diffusion has been found to be inhibited by the formation of deep traps.[28]

More recently,[5] high *n*-type conductivity with an activation energy of about 0.23 eV has been observed in homoepitaxial boron-doped diamond layers after deuterium plasma treatment. Prior to deuteration, the samples were *p*-type due to the boron. After deuteration, clear *n*-type conductivity was observed with high electron mobility. This conductivity was ascribed to the possible formation of boron-multideuterium complexes. These complexes were found to break up under thermal annealing, with, first, the *n*-type conductivity decreasing, followed by a stage with no clear *n*-type or *p*-type conductivity. After annealing above 600 °C, there was a partial recovery of the *p*-type conductivity, associated with the breakup of B-D pairs, followed by the out-diffusion of D at annealing temperatures above 750 °C.

Experiments to investigate whether hydrogen is trapped by, or diffuses to, phosphorus donors in diamond have shown no measurable hydrogen diffusion in phosphorus-doped diamond.[30] Low solubility of hydrogen in phosphorus-doped diamond, high migration energy of the H^- ion, or strong phosphorus-hydrogen interactions were suggested as possible causes. Studies of diamond doped with phosphorus during growth[31] showed that hydrogen is bound to phosphorus leading to most of the phosphorus atoms being electrically inactive. The concentration of hydrogen was seen to increase with increasing dopant concentration.[31] Therefore for the successful growth of *n*-type diamond using phosphorus as a dopant, growth conditions had to be optimized to minimize the hydrogen incorporation[14] by using a high substrate temperature during growth. Similarly, growth of *n*-type CVD diamond, using D_2 in the plasma, found much smaller quantities of deuterium incorporated in the sample than for similar undoped diamond.[30] We are not aware of reports of similar experiments on sulfur-doped diamond.

II. THEORETICAL METHOD

Boron, phosphorus, and sulfur, and their hydrogen complexes in diamond, were modeled using the local-density approximation (LDA) methods with norm-conserving Bachelet-Hamman-Schlüter pseudopotentials,[32] as implemented in the AIMPRO code.[33] Finite 123 C atom clusters bounded by hydrogen atoms (denoted C_{123}), as well as 165 C atom clusters bounded by $\langle 111\rangle$ hydrogen-terminated surfaces (C_{165}), were used. An optimized lattice constant was used, which was determined using a C_{123} cluster in which all atoms were allowed to relax. The C-C bond length from the center of this cluster was used to create a second C_{123} cluster in which all atoms were kept fixed at the lattice site optimizing the positions of only C atoms at the core of the cluster. The C-C bond length at the core of this cluster of 1.58 Å was used to determine the final lattice constant which was used in all subsequent calculations.

All calculations of substitutional dopants were performed using both 123 and 165 C atom clusters with the substitutional impurity atom X at a central site (denoted XC_{164}). Impurity-hydrogen complexes were initially modeled using 123 C atom clusters, with the most stable impurity-hydrogen configurations then modeled using clusters of 165 C atoms (XHC_{164} and XH_2C_{164}).

In the initial geometries, the additional H atoms were shifted away from high symmetry positions[34] so that no preconceptions of the symmetry of a complex affected the results. For all clusters, full geometry optimizations were performed. For the 123-atom calculations, all impurity and carbon atoms were allowed to relax, while for the 165-atom calculations, all carbon atoms up to third neighbors from the impurity were allowed to relax; the remaining carbon atoms were kept fixed at their lattice sites.

This method has had considerable success in the calculation of the structure and electronic properties of defects in diamond in the past, including some of those modeled in this paper [B,[35] H, H_2^* and BH (Refs. 9, 24, and 36)]. We have repeated some of those calculations in this work with the larger clusters described above, so that all our calculations are comparable in terms of the size and shape of the clusters.

To verify that the results were not dependent on the basis sets used, selected impurities were modeled using additional bond-centered Gaussians between the impurity atom and its neighbors, as well as larger basis sets. Using additional bond-centered Gaussians, the optimized geometry differed by less than 0.03 Å; using larger basis sets, the bond lengths changed by less than 0.6%, while the electronic band structure remained unchanged.

The Kohn-Sham band gap of the C_{165} cluster was 4.9 eV. LDA calculations often underestimate band gaps, but in this case the band gap, compared with the experimental value of 5.49 eV, does not show a serious discrepancy.

The formation energy E_f^q of a system in charge state q and a Fermi level at E_F is given by

$$E_f^q = E_t^q - \left(\sum_i \mu_i\right) + q(E_v + E_F), \tag{1}$$

where E_t^q is the total energy of the system in charge state q, as determined by a quantum-mechanical calculation; μ_i are the chemical potentials of the atomic species of which the system is composed; E_v is the valence-band top; and the Fermi level E_F is measured relative to the valence-band top.[37] The last term corrects for charge neutrality and corresponds to a system of charge q in equilibrium with an electron reservoir of energy E_F.[38] For periodic supercells an additional term should be added corresponding to the interaction of periodic charged impurities. Using the cluster approach, it is possible to model the properties of charged dopants without the complications of infinite periodic charges.

The binding energies u of a single H atom to an impurity X were determined using

$$u = E_t^0(XHC_{164}) - E_t^0(XC_{164}) - E_t^0(HC_{165}) + E_t^0(C_{165}), \tag{2}$$

where E_t^0 refers to the total energy of a relaxed cluster in the neutral charge state, relative to the energies of the constituent atoms. A subsitutional atom X is represented by $E_t^0(XC_{164})$,for example, or an interstitial hydrogen atom by $E_t^0(HC_{165})$.The binding energy relative to charged H and impurity atoms may be calculated in an equivalent manner, using charged impurity and H clusters. Similarly, the binding energy of two hydrogen atoms to an impurity atom X can be expressed in a directly analogous way, either with respect to the energy of two HC_{165} clusters or with respect to the XH complex and one H interstitial. In all cases, a more negative u corresponds to a greater binding energy. The binding energy corresponds to the enthalpy component of the chemical potential of the complex compared to that of the constituents, and therefore gives an indication of the stability of the complex. The chemical potential (and hence solubility) of the complex also includes a term dependent on the comparative entropies (both configurational and vibrational), which we have made no attempt to calculate here. The solubility of hydrogen in diamond, which depends on the chemical potential in each of its complexes, is the subject of a future paper.

Several approaches have been proposed for the calculation of energy levels in the band gap using finite clusters. Often optical ionization spectra have been analyzed by direct comparison with Kohn-Sham one-electron eigenvalues,[37] despite Kohn-Sham eigenvalues not having a strict physical significance (except for the highest occupied eigenvalue, which is equal to the ionization potential of the system[39]).

A more rigorous approach for establishing donor/acceptor levels is by determining the thermodynamic transition levels, which are the position of the Fermi level for which the most stable state of the system changes from one charge state to another. For example, the donor level $(0/+)$ is the value of the Fermi level for which $E_f^{+1}=E_f^0$.

For a donor X, from Eq. (1), setting $E_f^0=E_f^{+1}$ we have

$$(0/+) = E_t^0(XC_{164}) - E_t^{+1}(XC_{164}) - E_v. \tag{3}$$

Since it is not possible to determine the value of E_v accurately, we make use of the fact that minus E_v is equal to the first ionization energy of the system,[37,39]

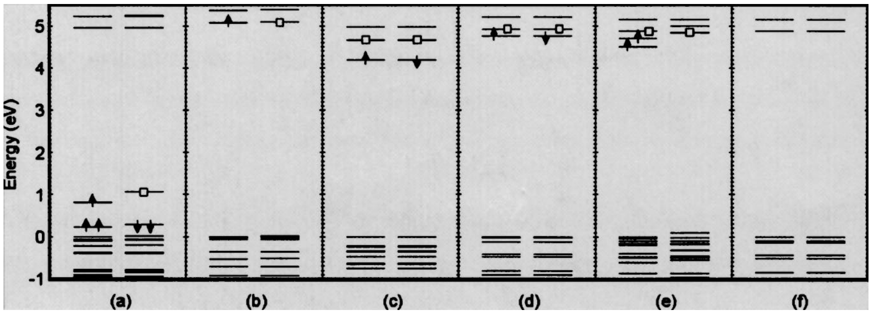

FIG. 1. The Kohn-Sham energy levels associated with (a) boron with T_d symmetry, (b) neutral phosphorus, (c) neutral sulfur, spin--0, in a C_{3v} configuration, (d) neutral sulfur, spin--0, in a T_d configuration, (e) neutral sulfur, spin–1, (f) compared to those for pure diamond.

$$E_v = E_t^0(\mathrm{C}_{165}) - E_t^{+1}(\mathrm{C}_{165}), \tag{4}$$

where C_{165} refers to impurity free diamond.

Equation (3) then becomes

$$(0/+) = E_t^0(X\mathrm{C}_{164}) - E_t^{+1}(X\mathrm{C}_{164}) - E_t^0(\mathrm{C}_{165}) + E_t^{+1}(\mathrm{C}_{165}). \tag{5}$$

Similarly, for acceptors,

$$(-/0) = E_t^{-1}(X\mathrm{C}_{164}) - E_t^0(X\mathrm{C}_{164}) - E_t^{-1}(\mathrm{C}_{165}) + E_t^0(\mathrm{C}_{165}) + E_g, \tag{6}$$

where E_g is the diamond band gap. Since in LDA the band gap is underestimated, the experimental value is used,[37] with $E_g = 5.49$ eV. The thermodynamic transition levels are relative to the top of the valence band.

An alternative approach[40] has also been proposed, which calculates the donor and acceptor levels from the ionization potential and electron affinity of clusters containing the defects.

Another reliable strategy which has been developed to determine the thermodynamic transition levels used in Ref. 41, for example, determines the donor (acceptor) ionization energy by finding the ionization potential (IP) (or electron affinity) of the impurity. This is then compared to that of a known donor/acceptor level energy modeled using a similar cluster. The calculated ionization energies are scaled according to the known level using

$$(0/+)_d = (0/+)_s + \mathrm{IP}_d - \mathrm{IP}_s, \tag{7}$$

where $(0/+)_d$ is the sought for donor level, $(0/+)_s$ is the donor level of a standard defect, taken from experiment, together with the calculated ionization energies of the unknown ($\mathrm{IP_d}$) and standard defects ($\mathrm{IP_s}$). Electron affinities are used in the same way to determine acceptor levels. A standard defect is used which assumes the same structure in all charge states. This approach uses entirely ground-state properties of each system. By comparing ionization energies of defects calculated using similar clusters, the systematic shift in the calculated levels originating from the overlap of delocalized wave functions with the cluster surface can be reduced.[41] The Slater transition state argument may be used[42] to calculate ionization potentials, with clusters relaxed in either the $-\frac{1}{2}e$, $+\frac{1}{2}e$, or $+\frac{3}{2}e$ charge states to determine the $(-/0)$, $(0/+)$, and $(+/++)$ thermodynamic transition levels, respectively.[33,41] Using the relaxed geometry of the transition state takes into account, to first order, the difference in structures between the neutral and ionized clusters.[41] We found that electron affinities and ionization potentials for pure diamond calculated directly differed by less than 0.003 eV from the Slater transition state values.

This scaled Slater transition state approach has had considerable success in estimating the position of thermodynamic transition levels in the band gap[41] and we use this approach to determine electrical levels in the band gap. We use the boron acceptor level, $(-/0) = E_v + 0.37$ eV,[2] and the phosphorus donor level, $(0/+) = E_c - 0.60$ eV (Refs. 3 and 4) as our reference levels. Since in much previous work on these dopants in diamond only the Kohn-Sham one-electron eigenvalues have been quoted, we include these Kohn-Sham eigenvalues for a direct comparison, together with the scaled thermodynamic transition levels.

We also determine the charge and spin densities within the cluster. The eigenvectors associated with the Kohn-Sham energy levels cannot be interpreted as wave functions in general, but since the differences between the spin-up and spin-down charge densities do determine the total spin density around the defect, we are able to associate the Kohn-Sham eigenvector distribution of an unpaired orbital with the spin distribution.

III. MODELS OF THE IMPURITIES IN DIAMOND

A. Substitutional boron

Substitutional boron in the diamond cluster (BC_{164}) was modeled, using the procedure outlined above. We find boron relaxes to a structure with C_{3v} symmetry, where one of the B-C bonds elongates by 18%, with the remaining B-C bonds elongating by 1%. Two Kohn-Sham one-electron levels were induced in the band gap, one doubly degenerate fully occupied level at $E_v + 0.24$ eV, together with a nondegenerate, partially occupied level at $E_v + 0.81$ eV [see Fig. 1(a)].

The geometry obtained for neutral boron was quite sensitive to the size as well as shape of the cluster, obtaining either T_d or C_{3v} symmetry; we ascribe this behavior to the delocalized nature of the boron acceptor level. This is similar to previous theoretical studies of boron, where either T_d (Refs. 35 and 43) or C_{3v} (Ref. 44) symmetry was found for substitutional boron. Negatively charged boron was found to relax to a structure with T_d symmetry, the B-C bond lengths elongating 3% to 1.63 Å. A triply degenerate, fully occupied one-electron level is induced in the band gap at $E_v + 0.81$ eV. Tables I and II summarize the results for boron, along with phosphorus and sulfur.

TABLE I. Summary of the symmetry and Kohn-Sham eigenvalues of B, P, and S in stable and metastable charge and symmetry states.

Impurity	Spin state	Defect symmetry	Kohn-Sham eigenvalues Degeneracy	Occupancy	KS-Level (eV)
Neutral B	$\frac{1}{2}$	C_{3v}	1	$1h^+$	$E_v+0.81$
			2	$4e^-$	$E_v+0.24$
Ionized B^-	0	T_d	3	$6e^-$	$E_v+0.81$
Neutral P	$\frac{1}{2}$	T_d	1	$1e^-$	$E_c-0.27$
Ionized P^+	0	T_d			
Neutral S	0	C_{3v}	1	$2e^-$	$E_c-0.48$
	0	T_d	1	$2e^-$	$E_c-0.16$
	1	C_{3v}	1	$1e^-$	$E_c-0.17$
			1	$1e^-$	$E_c-0.36$
Ionized S^+	$\frac{1}{2}$	C_{3v}	1	$1e^-$	$E_c-0.76$
	$\frac{1}{2}$	T_d	1	$1e^-$	$E_c-0.60$
Doubly ionized S^{++}	0	T_d			
Nitrogen	$\frac{1}{2}$	C_{3v}	1	$1e^-$	$E_c-0.71$
H_{bc}	0	D_{3d}	1	$1e^-$	$E_c-1.78$

B. Substitutional phosphorus

The substitutional phosphorus atom had a minimum energy at the lattice site (T_d symmetry). The nearest neighbors of P relaxed outwards, the P-C bond lengths increasing by 12% to 1.77 Å, similar to that found by Wang and Zunger.[38] The final geometry is illustrated in Fig. 2(a). We find that singly ionized P^+ in diamond also has T_d symmetry, with a geometry identical to that of neutral P^0. Phosphorus induces a shallow, nondegenerate, singly occupied one-electron level in the band gap at $E_c-0.27$ eV [see Fig. 1(b)]. This is similar to the value found by Kajihara *et al.*,[45] though other calculations have also found the one-electron level to lie deeper in the band gap.[10,46] As was the case for boron, the wave function of the partially occupied level is delocalized, indicating that phosphorus behaves as a shallow donor in diamond, as is observed experimentally.[17] For ionized P^+, no partially occupied one-electron levels were observed in the band gap.

TABLE II. Scaled thermodynamic transition levels of most stable states of impurities in diamond.

Impurity	Transition levels
Boron	$(-/0): E_v+0.37$ eV[a]
Phosphorus	$(0/+): E_c-0.60$ eV[a]
Sulfur (C_{3v})	$(0/+): E_c-1.12$ eV; $(+/++): E_c-3.73$ eV
Nitrogen	$(0/+0): E_c-1.40$ eV
H_{bc}	$(0/+): E_c-3.00$ eV; $(-/0): E_c-1.45$ eV

[a] Experimental P(0/+) and B(−/0) levels are used as markers, relative to which other donor or acceptor levels are calculated.

C. Substitutional sulfur

Neutral sulfur has six valence electrons compared to the four valence electrons of carbon, and could therefore exist in either a spin-0 or spin-1 configuration. Ionized sulfur was also modeled, for S^+ singly ionized (spin $\frac{1}{2}$) and doubly ionized S^{++} (spin 0) using the finite clusters described above.

1. Neutral sulfur

Neutral S^0 in a spin-0 configuration was found to undergo a strong C_{3v} distortion after a full geometry optimization. One carbon neighbor (C_1) moves away from the S^0 atom in a $\langle 111\rangle$ direction, while the S atom itself relaxes in the opposite direction towards the plane of its remaining carbon neighbors. The unique S-C_1 bond elongates by 30% to 2.06 Å. The bonds to the C atoms basal to the sulfur atom elongate by 15%. This is illustrated in Fig. 2(b). An occupied, nondegenerate Kohn-Sham level appears in the band gap at $E_c-0.48$ eV [Fig. 1(c)]. The eigenfunction of this energy level [Fig. 3(a)] has a node between the sulfur and C_1 atom, leading to a buildup of charge close to these atoms. This antibonding behavior causes the S-C_1 bond to break. The electron density associated with this electrically active state is more localized than the corresponding states of boron and phosphorus.

In addition to the C_{3v} configuration of substitutional sulfur in diamond, we also find geometries with T_d and C_{2v} symmetries to be metastable. Modeling neutral, spin-0 sulfur with S^0 initially at the lattice site, the S atom remains on the lattice site, giving a center of T_d symmetry which is 0.27 eV less stable than the C_{3v} configuration, in close agreement with Ref. 38. The carbon neighbors of the sulfur atom undergo a strong outward distortion, the S-C bond lengths in-

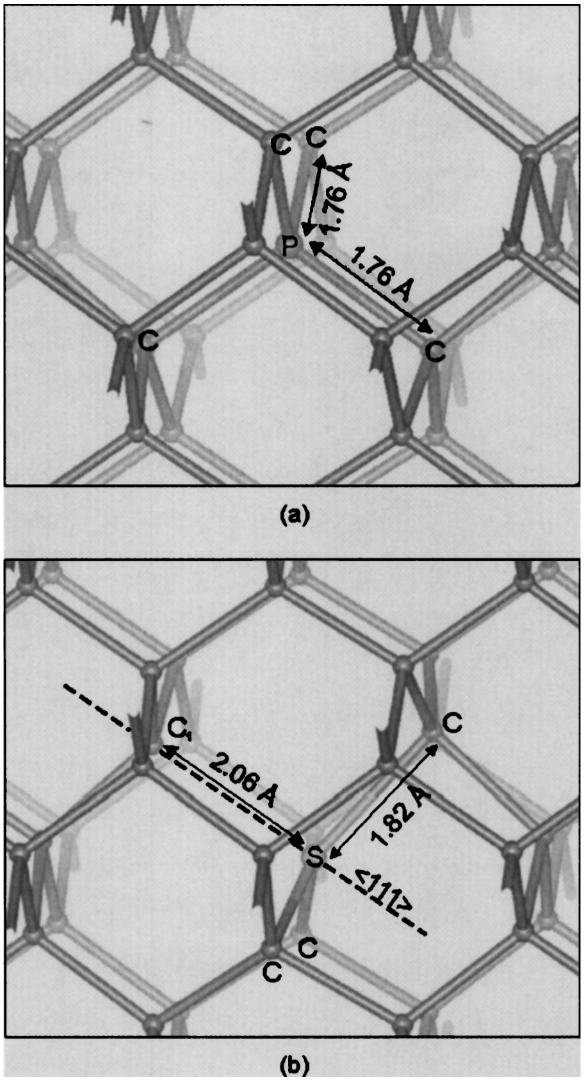

FIG. 2. The relaxed structures showing the dopants and neighbors around (a) phosphorus (T_d symmetry) and (b) sulfur with $C_{3\nu}$ symmetry about ⟨111⟩ axis passing through the impurity.

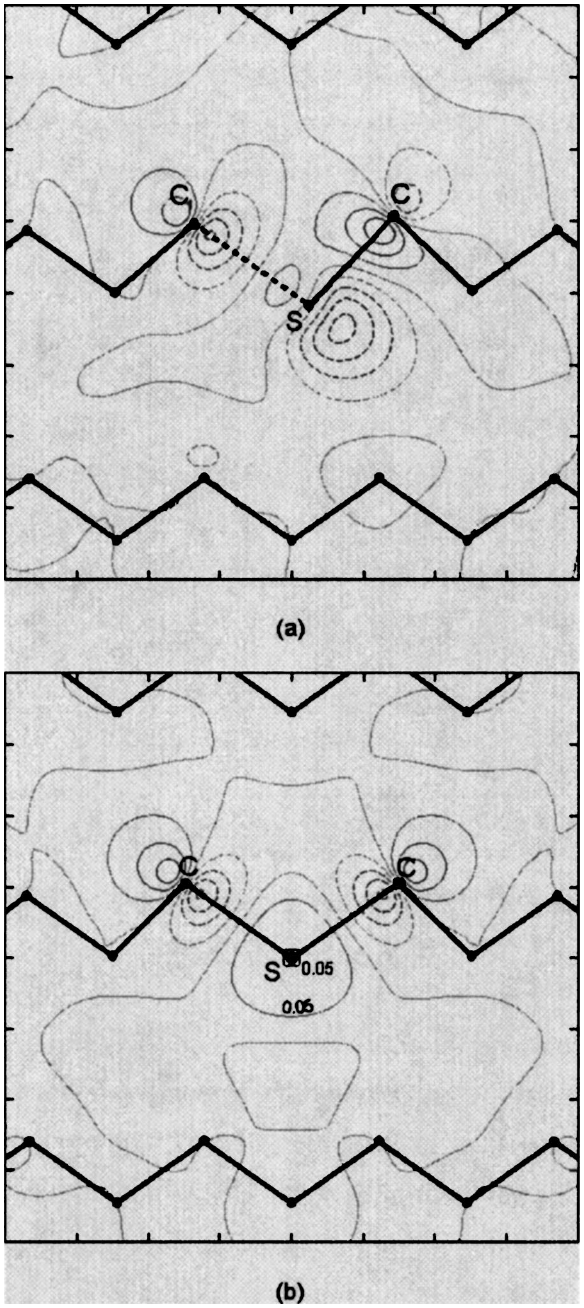

FIG. 3. Contour plots of eigenfunctions associated with the donor levels of sulfur, spin–0 (a) in $C_{3\nu}$ and (b) in T_d symmetry. The spacing between contours is 0.05 (in units which would express the charge density as $e\,.\,\mathrm{a.u.}^{-3}$). Contours corresponding to negative amplitudes are indicated with dashed lines. The first solid contour corresponds to zero amplitude. All plots are parallel to a [110] plane.

creasing by 22%. A fully occupied, nondegenerate one-electron level is induced at $E_c - 0.16$ eV [Fig. 1(d)]; the eigenvector corresponding to this level [Fig. 3(b)] has an antibonding nature between S and all its C neighbors. If the initial geometry in the calculation is the C_{2v} structure reported by Miyazaki *et al.*,[47] our calculations also find that this structure is metastable, with an energy slightly higher than that of the T_d structure.

A further metastable state of C_{3v} symmetry was found with spin-1, with an energy 0.28 eV higher than the spin-0 analog. Two nondegenerate, singly occupied one-electron levels were observed in the band gap, at $E_c - 0.17$ eV and $E_c - 0.36$ eV [Fig. 1(e)]. The eigenfunctions corresponding to these levels are illustrated in Fig. 4.

Hence, together with the stable C_{3v} zero spin configuration, sulfur has two additional metastable low-energy states with T_d and C_{2v} symmetries, as well as a spin-1 configuration with C_{3v} symmetry. All metastable states induced one-electron energy levels shallower in the band gap than the corresponding level found for the C_{3v} configuration. This is the first study, to our knowledge, where all these possible configurations of substitutional sulfur have been reported.

2. Ionized sulfur

We find that the C_{3v} symmetry of S^+ has a slightly lower energy than the T_d structure, unlike Wang and Zunger,[38] who only found a T_d symmetry for S^+. For S^+ with a C_{3v} geom-

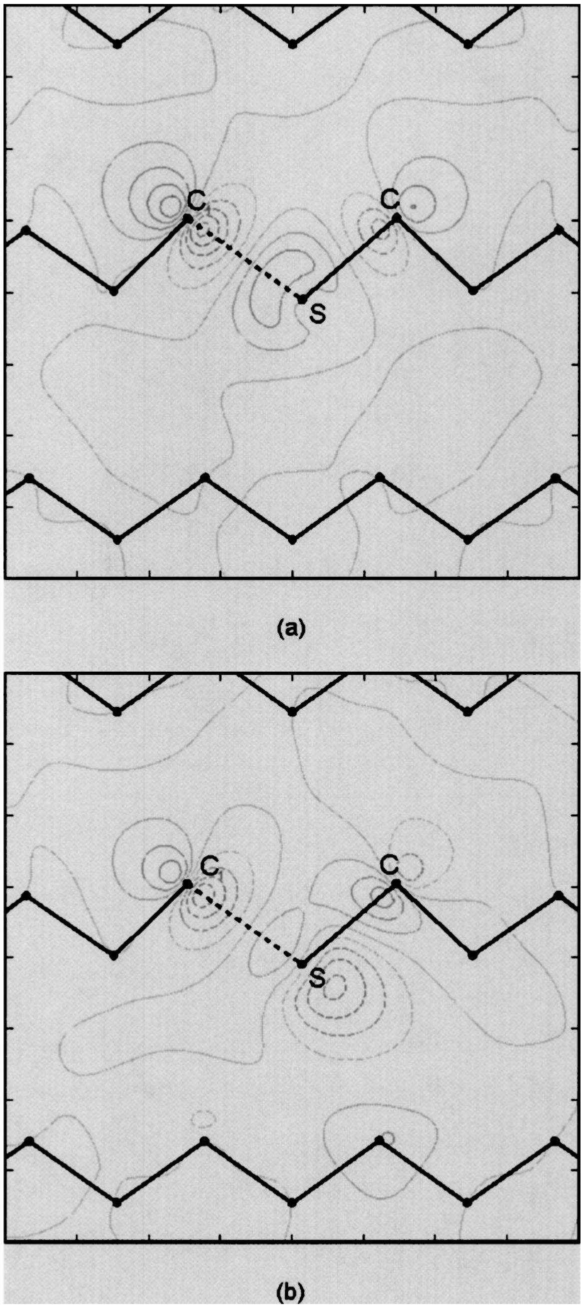

FIG. 4. Contour plots of eigenfunctions associated with (a) the highest and (b) the second highest partially occupied donor levels of sulfur, spin-1, in C_{3v} symmetry. Contours are as in Fig. 3.

etry, we find the S atom and one of its C neighbors (C_1) relax strongly away from each other in a $\langle 111 \rangle$ direction, elongating this S-C_1 bond by 20%. The other C atoms also relax away from S, elongating these S-C bonds by 17%. A one-electron level is induced in the band gap at $E_c - 0.76$ eV, in agreement with the result of Saada *et al.*[48] This level is nondegenerate and singly occupied, as is expected.

Doubly ionized S^{++} has T_d symmetry; the S-C bonds elongate by 19%. S^{++} has no one-electron levels in the band gap, in agreement with Saada *et al.*[48]

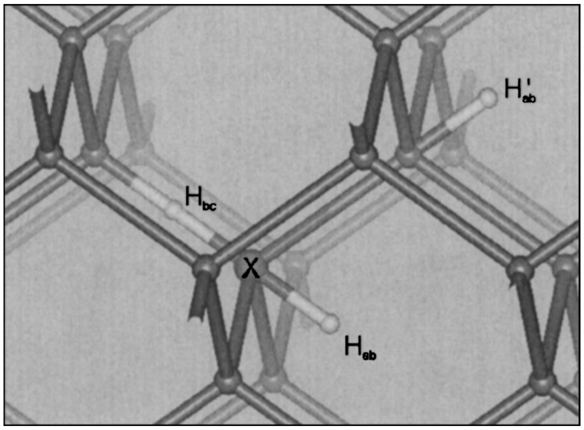

FIG. 5. The alternative positions of hydrogen around a substitutional dopant, *X*, in diamond.

3. Electronic levels of sulfur

We find the sulfur $(0/+)$ donor level at $E_c - 1.1$ eV, which is about 0.3 eV shallower than the corresponding theoretical $(0/+)$ level of single substitutional nitrogen, but considerably deeper than the donor level of phosphorus. This value falls in the center of the range of previous estimates.[10,38,47,48] We find the second ionization $(+/++)$ energy of sulfur at $E_c - 3.7$ eV.

D. Interstitial hydrogen

Hydrogen in bond-centered (H_{bc}) and antibonding (H_{ab}) interstitial sites together with the H_2^* defect (which consists of two hydrogen atoms, one in each site along the same axis) were modeled. Of the two single interstitials, H_{bc} was the more stable, in agreement with previous results;[9,10,24,49] H_{bc} induces a singly occupied nondegenerate one-electron level in the band gap at $E_c - 1.78$ eV. Its carbon neighbors relax outwards, with the carbon-carbon bond length elongating by 47% (similar values to those reported by Refs. 9 and 24). At the antibonding site, H_{ab} induces a singly occupied nondegenerate one-electron level in the band gap at $E_c - 1.89$ eV, and a 34% elongation of the C-C bond on the axis. For the H_2^* defect, an occupied one-electron level was induced at the edge of the valence band. The second hydrogen atom was bound by 1.57 eV.

We find H_{bc} generates a very deep $(0/+)$ donor level at $E_c - 3.0$ eV, together with an acceptor $(-/0)$ level at $E_c - 1.45$ eV, resulting in a center with a large positive $U = 1.55$ eV. This is between the value predicted by Goss *et al.*[9] and that of Wang and Zunger.[38]

IV. COMPLEXES OF DOPANTS WITH HYDROGEN

For complexes consisting of a single hydrogen trapped at a substitutional dopant (X), we expect the following structures to be possible (see Fig. 5): (i) X-H_{bc} with the H_{bc} at the center of one of the X-C bonds, with an X-H-C axis; (ii) X-H_{ab} with the H_{ab} behind the impurity atom, with a H-X-C axis; (iii) X-H'_{ab} with the H'_{ab} behind a carbon neighbor, with an X-C-H axis. This last case has only rarely been considered for impurities in diamond, despite this being the most stable site of H at P in silicon.[50,51] All these X-H complexes have C_{3v} symmetry with $\langle 111 \rangle$ axes. In our calculations, the hydrogen atom was initially displaced a small distance off-axis to allow the complex to relax to a lower symmetry structure if that had a lower energy.

A. Boron-hydrogen complexes

The B-H_{bc} structure was found to relax to a configuration where the B-C bond is strongly buckled, lying close to a (001) direction from the B atom. The center has a mirror plane in the $\langle 110 \rangle$ axis passing through the B, C, and H atoms. This is illustrated in Fig. 6(a); this is very similar to the structure predicted in Ref. 9. We find that B-H induces a very deep $(-/0)$ acceptor level at $E_c - 1.0$ eV; there are no partially occupied one-electron levels in the diamond band gap and boron is electrically passivated. The B-H_{bc} complex is 3.2 eV more stable than neutral B and H_{bc}, which compares well with the experimental binding enegy energy of 2.5 eV.[28] We find the dissociation energy into charged B^- and ${H_{bc}}^+$ to be larger at 3.8 eV. This is summarized in Table III. The activation energy of diffusion may be estimated by placing the hydrogen atom at a bond centred site at second neighbors from the boron atom, from which we obtain a value of 1.3 eV. This is smaller than has previously been predicted[9] but in close agreement with the experimental value of 1.43 eV observed in highly B-doped diamond with equal boron and hydrogen concentrations introduced from a deuterium microwave plasma.[26]

A similar configuration consisting of a buckled H_{bc} atom rotated 180 ° about the B-C_1 axis, and H slightly closer to this axis, was metastable (0.03 eV higher in energy than the above configuration). Other B-H complexes were unstable or relaxed into the B-H_{bc} structure. B-H in the spin-1 state yields a minimum energy configuration consisting of the H atom on a B-C bond; this spin state is 4.68 eV higher in energy than the spin-0 configuration described above and is therefore unlikely to occur.

The boron and hydrogen atoms were also modeled, placed as far away from each other as is possible in the cluster without either impurity being close to the edge of the cluster. Since the H level is higher in the band gap than the boron's acceptor level, the hydrogen atom's electron is captured by the boron, leaving the boron's acceptor level completely occupied. These levels can be associated with a charge transfer, or compensation of the acceptor:[25]

$$B + H \rightarrow B^- + H^+. \tag{8}$$

In heavily boron-doped diamond with hydrogen introduced from a microwave plasma, it has been found from secondary-ion-mass spectroscopy (SIMS) analysis that the hydrogen (deuterium) concentration matches that of boron throughout the sample depth, due to hydrogen diffusion being governed by the trapping-detrapping of hydrogen at boron.[25,26] However, for the hydrogen concentration to follow the boron concentration as closely as has been found experimentally, it is also necessary that multihydrogen centers should not be

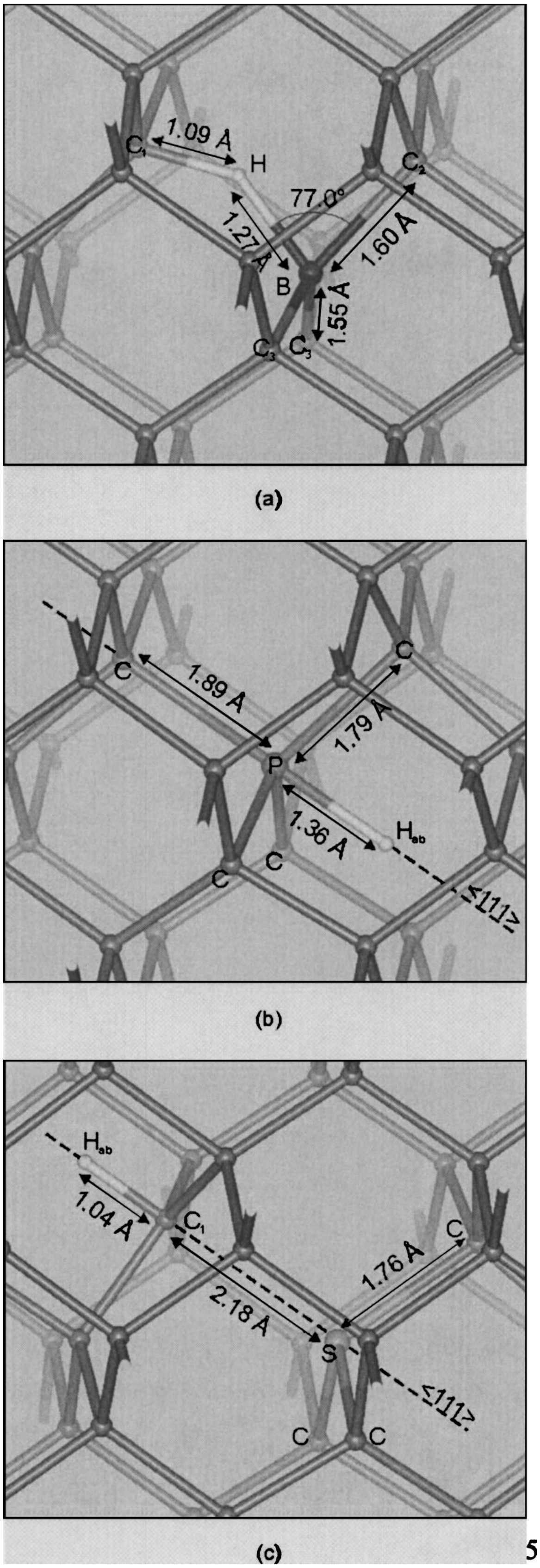

FIG. 6. Relaxed structures of the most stable dopant-H complexes: (a) B-H, (b) P-H, and (c) S-H.

TABLE III. Cohesive energies of impurity-hydrogen complexes in diamond relative to neutral and charged components.

Reaction	u (eV)
$B+H \rightarrow BH$	−3.22
$B^{-}+H^{+} \rightarrow BH$	−3.76
$P+H \rightarrow PH$	−0.25
$P^{+}+H^{-} \rightarrow PH$	−1.76
$S+H \rightarrow SH$	−1.57
$S^{+}+H^{-} \rightarrow SH$	−3.63
$SH+H \rightarrow S\text{-}H_2$	−1.49
$SH^{+}+H^{-} \rightarrow S\text{-}H_2$	−3.08

present in significant concentrations. In this regard, we find that it is energetically favorable (by 4.9 eV) for H_2^* complexes to break up in the presence of single boron atoms, forming B-H defects.

B. Phosphorus-hydrogen complexes

All of the P-H complexes described in Sec. IV were stable or metastable, but the lowest energy structure had the antibonded hydrogen atom behind the phosphorus atom with C_{3v} symmetry [P-H_{ab}, see Fig. 6(b)], in agreement with what has been found previously[9,10] for diamond, but in contrast with what has been found in silicon.[50,51] The energy gain was 0.25 eV relative to dissociation into neutral components. The dissociation energy relative to charged P^+ and H^- was larger, at 1.76 eV. The P-H complex has a deep $(0/+)$ level at $E_c - 2.86$ eV, the most stable complex inducing the deepest level. The Kohn-Sham one-electron level was filled and dropped deeper in the band gap. We find that when the P and H were separated as far as possible in the cluster, the hydrogen compensated the phosphorus. Hence hydrogen passivates both donor and acceptors in diamond, with the donor transferring its electron to hydrogen in *n*-type doped diamond, forming P^+ and H^-, while in *p*-type diamond, hydrogen transfers an electron to the boron acceptor, forming B^- and H^+.

C. Sulfur-hydrogen complexes

S with a single hydrogen atom has previously been modeled,[11,52] although the configuration of H at an antibonding site behind a C neighbor of S has not been considered. We find that precisely this S-H'_{ab} configuration is the most stable form of the S-H complex in diamond, illustrated in Fig. 6(c). All other sulfur-hydrogen complexes described in Sec. IV were metastable. The sulfur-hydrogen $(0/+)$ donor level is now at $E_c - 0.61$ eV—shallower than the bare sulfur donor level and very close to the P donor level. The eigenfunction associated with the donor level of S-H'_{ab} is very delocalized, indicating shallow donorlike behavior. The recently observed sulfur-related activation energy of 0.5 −0.75 eV in sulfur-doped CVD diamond[19] may possibly be related to this S-H'_{ab} complex. The symmetry of the S-H'_{ab} center is C_{3v}, with a S-C-H_{ab} axis, where the S-C bond is 39% longer than the normal diamond C-C bond. The energy gain when this complex forms from an isolated sulfur donor and a hydrogen interstitial H_{bc} atom is 1.57 eV, relative to neutral sulfur and hydrogen.

Other metastable S-H complexes also had donor levels shallower than the substitutional sulfur, with the shallowest level corresponding to the most stable geometry, described above.

V. COMPLEXES OF DOPANTS WITH TWO HYDROGEN ATOMS

Where two hydrogen interstitial atoms are trapped at the dopant, far more combinations are possible than for a single H, but they can be described, broadly, in terms of combinations of the possible sites for single H atoms. Impurities with two hydrogen atoms were modeled with the H atoms initially near the above sites, both in axial and nonaxial configurations. The calculations are not restricted to these structures or symmetries, since in the initial geometry, the hydrogen atoms are displaced a small distance off-site in a random direction, which allows them to relax to more stable structures if these exist.

A. Complexes of boron with two hydrogen atoms

The lowest energy configuration proved to have the second hydrogen on a bond center between the second and third neighbors of the B-H_{bc} complex. Though the complex is stable with regard to dissociation into B with two distant H_{bc} atoms, it is energetically favorable for the complex to dissociate into a B-H_{bc} pair and a distant H_{bc} interstitial, by 0.4 eV. Other B-H_2 configurations were metastable, with higher energy, and would dissociate into a B-H complex with a distant H_{bc} atom. We note that under conditions of excess hydrogen, it is energetically favorable for these surplus H_{bc} atoms to form H_2^* complexes, though B-H complexes remain the most stable form of H in B doped diamond.

All the B-H_2 complexes induced deep donor levels in the band gap of diamond, with $(0/+)$ levels between $E_c - 1.84$ eV and $E_c - 2.88$ eV. Wave functions corresponding to the partially occupied levels in the band gap were localized. Due to the deep nature of the electronic levels found for all B-H_2 complexes studied here together with their instability, we conclude that the experimental findings of shallow *n*-type conductivity[5] in deuterated B-doped diamond are unlikely to arise from a B-H_2 complex. Our calculations conflict with a recent report of models of B-H_2 complexes with shallow (Kohn-Sham) donor levels,[53] but this report did not state if the complexes were stable against dissociation, and their finite clusters contained only 35 carbon atoms.

B. Complexes of phosphorus with two hydrogen atoms

Of the combinations of P-H_2 initially modeled,[54] none were bound with respect to dissociation into isolated P-H_{ab} and H_{bc}. We find that only the more complex structure illustrated in Fig. 7 had a lower energy than the separated P-H_{ab} and H_{bc} defects, by only 0.07 eV. This configuration induces a $(0/+)$ level slightly deeper in the band gap than

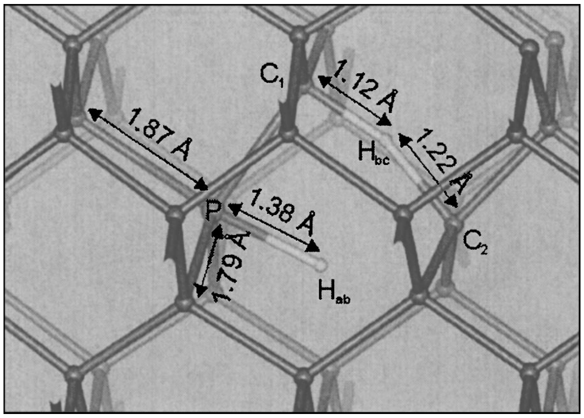

FIG. 7. Relaxed structure of the most stable configuration of P with two H atoms [slightly rotated from a (110) plane].

the phosphorus donor level, at $E_c - 0.62$ eV. The very small energy gain makes it unlikely that this complex is a common one.

Despite the cohesive energy of a second H at P being relatively small, it is energetically very favorable for a H_2^* defect to be nucleated at a phosphorus donor:

$$\mathrm{P}-\mathrm{H}_{\mathrm{ab}}+\mathrm{H}_{\mathrm{bc}} \rightarrow \mathrm{P}+\mathrm{H}_2^{*}, \qquad (9)$$

which is exothermic with an energy gain of 1.32 eV. It is also favorable for existing P-H pairs to break up, forming substitutional P atoms with H_2^*,

$$2(\mathrm{P}-\mathrm{H}_{\mathrm{ab}}) \rightarrow 2\mathrm{P}+\mathrm{H}_2^{*}, \qquad (10)$$

which is exothermic with an energy gain of 1.08 eV. Further, P-H_2 will break up spontaneously, forming substitutional P with H_2^*, with an energy gain of 1.25 eV.

Hence in P-doped diamond, H would predominantly be present in the form of H_2^* defects. Since H_2^* complexes will be immobile in diamond[9] at temperatures below 1000 °C and have an activation energy of diffusion greater than that of H^-, we predict that the diffusion of H will be suppressed by the trapping of H as immobile H_2^* complexes. We suggest that hydrogen diffusion in *n*-type diamond is limited by the immobility of H^- and the formation of immobile H_2^* complexes.

Therefore in *n*-type P-doped diamond, the formation of immobile H_2^* complexes and the diffusion of hydrogen in the negative charge state will inhibit diffusion. This contrasts with the situation in *p*-type B-doped diamond, where H_2^* dissociates in the presence of boron forming B-H complexes and the hydrogen diffuses in the more mobile positive charge state. Thus the diffusion of hydrogen is governed by the trapping and detrapping of H at B, as is observed experimentally.[16,25,30]

C. Complexes of sulfur with two hydrogen atoms

It is energetically very favorable for a further hydrogen atom to be trapped at an existing S-H'_{ab} complex. The most stable structure consists of two antibonding hydrogen atoms, bound to different carbon neighbors of the sulfur (S-H'_{ab}-H'_{ab}) with C_{2v} symmetry. The binding energy of the second H atom is 1.49 eV, which is similar to that for H_2^* in diamond, indicating that it is a very stable center. For this structure, both C-S bonds were seen to break, elongating by 38%. This is illustrated in Fig. 8(a). S-H'_{ab}-H'_{ab} induces a deep $(0/+)$ level at $E_c - 3.30$ eV; therefore the two hydrogen atoms have passivated the sulfur donor. There are two occupied one-electron levels at $E_v + 2.34$ eV and $E_v + 1.32$ eV; the eigenfunction corresponding to the highest occupied orbital is illustrated in Fig. 8(b). From this it is seen that the *s* orbitals of the H atoms overlap with the lobes of the antibonding *p* orbitals associated with S and its C neighbors, leading to a very stable structure. The antibonding nature of

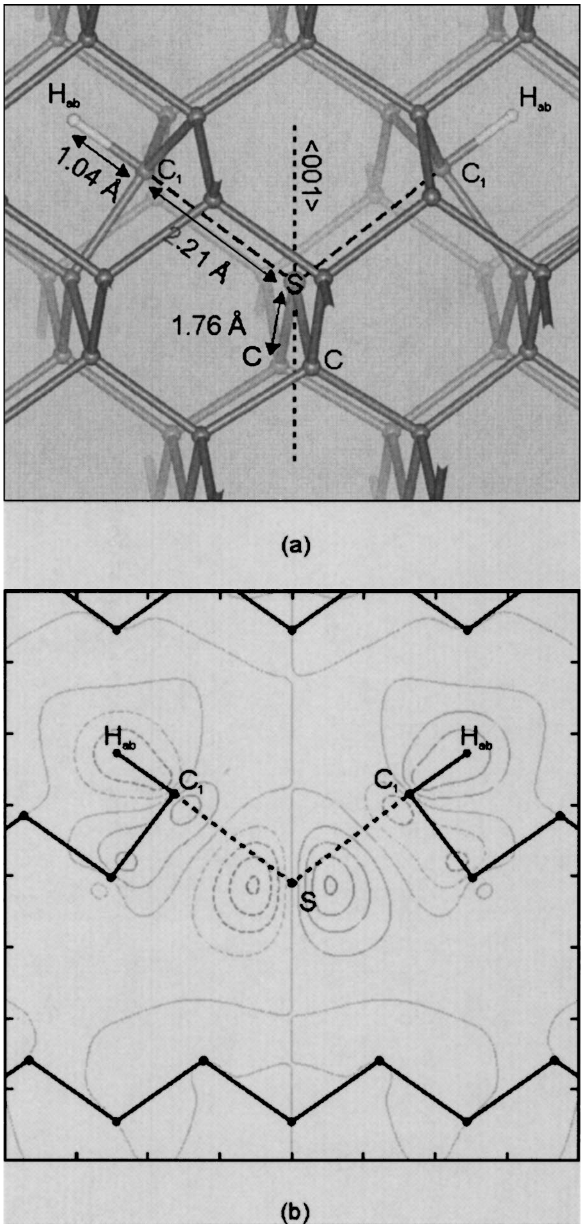

FIG. 8. (a) Relaxed structure of the most stable configuration of S with two H atoms [slightly rotated from a (110) plane], with (b) the eigenfunction corresponding to the highest occupied Kohn-Sham level of this geometry. Contours are as in Fig. 3.

the eigenfunction between the S and the unique C neighbors leads to the breakage of these bonds.

Other configurations of S-H_2 were also bound and electrically inactive, but less stable than the S-H'_{ab}-H'_{ab} structure. Several configurations of S-H_2 were bound with regard to dissociation into S-H with a distant H_{bc} atom. These included (a) S-H_{bc} with H'_{ab} behind a different C neighbor, (b) S-H_{bc} with an additional H_{bc} at a second neighbor of S, (c) H_{ab}-S⋯C-H'_{ab} with C_{3v} symmetry, and (d) S with two H_{bc} atoms at different BC sites at S.

We suggest that since the S-H'_{ab} complex is a shallower donor than isolated sulfur, it may be worth trying to produce this complex to dope diamond. The binding energy of the second hydrogen (−1.49 eV) is smaller than that of the first (−1.57 eV), so one would expect that in equilibrium conditions of limited hydrogen availability, the S-H complex would form in preference to S-H_2. However, CVD growth is very far from an equilibrium situation, and it may prove very difficult to achieve or control S-H codoping.

Nevertheless, under conditions of limited hydrogen availability, H_2^* will break up in the presence of substitutional S atoms forming either S-H'_{ab} pairs (energy gain of 1.57 eV) or S-H_2 with a gain of 1.49 eV. S-H_2 complexes will also break up in the presence of substitutional S, forming two S-H pairs with an energy gain of 0.08 eV. Hence under conditions of limited hydrogen availability ($[H]<[S]$) S-H pairs would form in preference to S-H_2 or H_2^* complexes. With higher H concentrations ($[H]<[S]$), H_2^* will break up in the presence of S-H pairs, forming S-H_2 complexes with an energy gain of 1.41 eV. Hence S-H_2 is the most stable form of H in S-doped diamond with an excess of hydrogen, while S-H is the most stable in S-doped diamond with limited hydrogen availability.

We predict that diffusion of hydrogen in *n*-type S-doped diamond will occur in the less mobile negative charge state, similar to the case in *p*-type diamond. However, since H_2^* is not nucleated in S-doped diamond, we expect that the diffusion would be governed by the trapping and detrapping of hydrogen by the sulfur. Both S-H and S-H_2 complexes would be formed, and a dynamic equilibrium between the complexes would be established at temperatures where the H^- was mobile.

VI. CONCLUSIONS

It is energetically favorable for hydrogen to bind to boron, phosphorus, and sulfur dopants in diamond; hydrogen is seen to passivate boron and phosphorus, while two hydrogen atoms are required to achieve passivation of sulfur. Several metastable S-H complexes have shallow, delocalized energy levels in the band gap, the shallowest level corresponding to the most stable configuration. Further, we show that this complex is stable under conditions of limited H availability. We therefore suggest that it may be worth trying to produce this previously unconsidered complex to dope diamond.

In hydrogenated P-doped diamond, it is energetically favorable for both P-H and P-H_2 to dissociate, forming H_2^*. H diffusion in *n*-type P-doped diamond will be inhibited by this formation of immobile H_2^*. This is in contrast to B-doped diamond, where we have shown that H_2^* will dissociate in the presence of substitutional B atoms, forming B-H complexes. H will be predominantly present in the form of B-H pairs and diffuse in the mobile H^+ charge state, this diffusion being governed by the experimentally observed[25,26,30] trapping-detrapping of H at B. Multihydrogen complexes are unlikely to be present in heavily boron-doped diamond, these complexes dissociating in the presence of single B atoms, forming B-H pairs. This explains why the SIMS profile of hydrogen in deuterated heavily B-doped diamond follows the profile of boron very closely throughout the sample depth.[25,26]

We have shown that the recently observed shallow *n*-type conductivity in deuterated boron–doped films[5] is unlikely to originate at B-H_2 complexes, first because these complexes would dissociate into B-H and H defects and second because there are no shallow donor levels associated with them. Another suggestion that the shallow donor is a metastable state of the B-H complex[55] is not supported by these calculations, which indicate that all conceivable B-H complexes which we considered are unstable, or have an inaccessibly high energy, with respect to the equilibrium B-H complex. There is at present no model for the shallow donor.

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