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Ab initio study of boron-hydrogen complexes in diamond and their effect on electronic properties

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The atomic and electronic structures of neutral and charged (+ and −) boron-hydrogen complexes in diamond are studied by means of density-functional theory calculations. The stability of the different configurations is discussed and used to derive ionization energies. For neutral B-H complex, H in puckered position along B-C axis is energetically more favorable. No density of states is then found within the diamond band gap but this configuration gives rise to an acceptor level at $E_v+4.44$ eV. B-H_2 most stable structure gives a donor level at $E_c-2.80$ eV. Other geometries are also investigated to explain the discrepancy observed between recent electronic structure calculations.

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I. INTRODUCTION

Diamond has always been a very attractive material because of its exceptional physical properties and potential applications to electronics.[1–3] However applications require to master both n- and p-type dopings and then to find shallow donors and acceptors with a sufficiently high solubility in the diamond matrix. Although p-type doping is achieved easily, n-type doping with shallow donor remains to be a difficult task.[4,5] Boron is known as the most attractive single electron acceptor impurity for diamond ($E_i \approx 0.37$ eV) and a gradual change from a semiconductor to a metal and eventually to a superconductor is observed as the boron doping level increases above 5×10^{20} cm^{-3}.[6,7] Concerning n-type dopant, substitutional nitrogen acts as a very deep donor with an observed ionization energy at around 1.7 eV, which makes N doped diamond insulating at room temperature.[4,8] The most successful n-type dopant to date is substitutional phosphorus but its high ionization energy ($E_i \approx 0.57$ eV) induces a weak concentration of free electrons at room temperature.[9] Multispecies doping (codoping) has also received tremendous attention, especially to search for n-type conductivity with shallow donor levels.[4,5,10] The codoping concept suggests that the solubility of desirable doping atoms can be enhanced through the Coulomb coupling of the donor-acceptor pairs and that the defect levels concentration can be reduced through the donors and acceptors level repulsion.[5,10]

The experimental report of high n-type conductivity with a low ionization energy of about 0.23 eV of deuterated B-doped diamond was one of the most surprising recent discoveries in the field of wide band gap semiconductors.[11,12] Whereas boron leads to a shallow acceptor level, a first exposure to deuterium passivates the defects as revealed by capacitance-voltage measurements,[13] Hall measurements,[14,15] Fourier transform infrared,[16] and cathodoluminescence measurements.[17] Further deuteration seems to induce n-type doping. The authors of Refs. 11 and 12 proposed that n-type conductivity was due to boron-hydrogen complexes formation. It results in the formation of a shallow donor with an activation energy ≈ 0.23 eV below the conduction band. Later, they report a more accurate value of the ionization energy of the shallow donors: 0.34 eV (Refs. 12 and 18) and 0.37 eV (Ref. 19) instead of 0.23 eV.

From an experimental point of view, the switch from p- to n-type doping upon deuteration is neither controlled nor understood but it is observed that $[\mathrm{D}]\approx 2[\mathrm{B}]$. One can then assume that B-D_2 complexes play a crucial role. Many *ab initio* calculations have been devoted to the study of B-H_n complexes atomic and electronic structures. D is replaced by H to enable the *ab initio* calculations, which seems to be a reasonable assumption. The results are rather divergent and two reasons can explain this: first, some of the calculations are performed using very small cells—and then high complex concentration—but moreover, in some cases, ionization energies and Kohn Sham levels have been calculated from atomic structures that do not correspond to the lowest-energy configuration.

Recently, a mechanism was proposed to explain p to n switch.[20] It is based on the existence of an impurity band related to the B-H defect. Doped by an additional hydrogen, this would give a transition energy level 0.3 eV below the unoccupied impurity-band edge. This model appears interesting at least for two reasons. First it does not need donor level close to the conduction band which appears difficult with the band structure and low dielectric constant of diamond. Then it exhibits a two-step approach when the reported n-type conductivity also seem to appear from two steps.[11,12] Finally, through the effect of the concentration of the B-H complexes on the formation and width of the impurity band, the concentration of boron has important effects on the value of the n-type conductivity as found experimentally.[11,12] However, there is no general agreement on the existence of such an impurity band in the literature. Furthermore, the geometry used by Yan *et al.*[20] for B-H complex and the procedure applied to the density of states (DOS) to scale the gap to the experimental value is not clear. Another point against this model is that switch has been observed experimentally for boron concentration as low as 10^{17} cm^{-3}.[12,18] In this case, localized levels are expected, not a band. Metallic n conductivity by doping of the localized state would then reveal to be impossible. Furthermore carrier concentration in this model would be smaller or in the best case equal to half the boron concentration, which is not observed experimentally.[11]

The understanding of the switch mechanism is far from being achieved. Doing so will require a comprehensive view of B-H and B-H_2 complexes properties. The aim of this paper is to present *ab initio* calculations of the total energy,

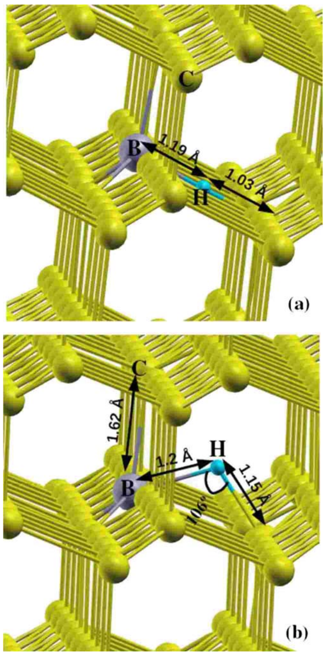

FIG. 1. (Color online) The relaxed structures of B-H complex, (a) hydrogen along the B-C axis and (b) hydrogen at puckered position.

structure optimization, and densities of states for the two complexes in different charge states. Ionization energies are then deduced. Calculation is done with a supercell technique. The use of a large cell and a large set of *k* points limits the possible errors due to calculation parameters. Calculation details are given in Sec. II, B-H results are described in Sec. III and B-H_2 in Sec. IV. Ionization energies are then discussed in Sec. V.

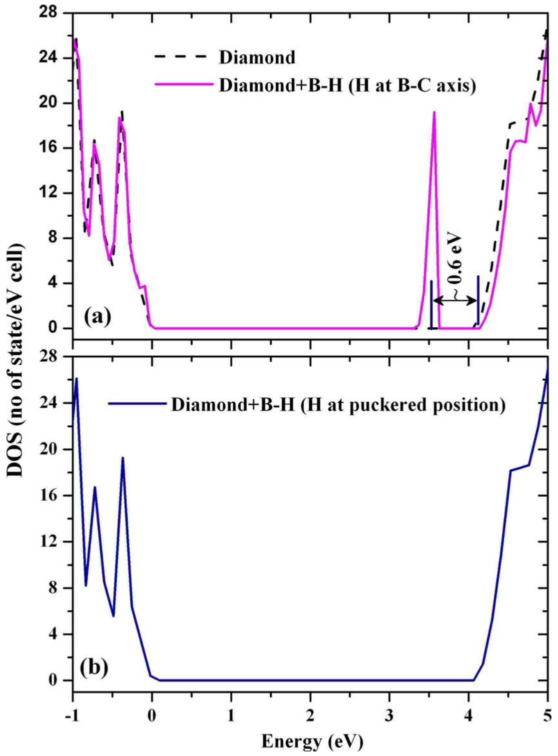

FIG. 2. (Color online) Density of states of B-H complexes in a diamond matrix, (a) hydrogen at bond center along B-C axis, and (b) puckered positions.

II. CALCULATION DETAILS

The structure and electronic properties of boron-hydrogen complexes were investigated using the Vienna Ab-initio Simulation Package (VASP) code.[21] It is based on density-functional theory (DFT) within the generalized gradient

TABLE I. Summary and comparison of theoretical work on B-H complexes in diamond matrix.

Reference	Method	KS levels	Density of complex (cm^{-3})	Relative total energy (eV)
	H at puckered position			
Present work	GGA-VASP,	No level in gap	7.8×10^{20}	0
	216 and 512 C atom unit cell		3×10^{20}	
30 and 39	LDA-AIMPRO,	No level in gap	2.6×10^{21}	
	64 and 216 C atom cubic unit cell		7.8×10^{20}	
37	LDA-AIMPRO,	No level in gap	1.4×10^{21}	
	123 and 165 C atom clusters			
38	DFT cluster,	No passivation		
	35 C atom cluster	(B level in gap)	5×10^{21}	
	H at bond-center position along B-C axis			
Present work	GGA-VASP,	$E_c-0.6$ eV	7.8×10^{20}	0.3
	216 and 512 C atom unit cell		3×10^{20}	
20	GGA-VASP,	$E_c-1.0$ eV		
	64 C atom unit cell		2.6×10^{21}	

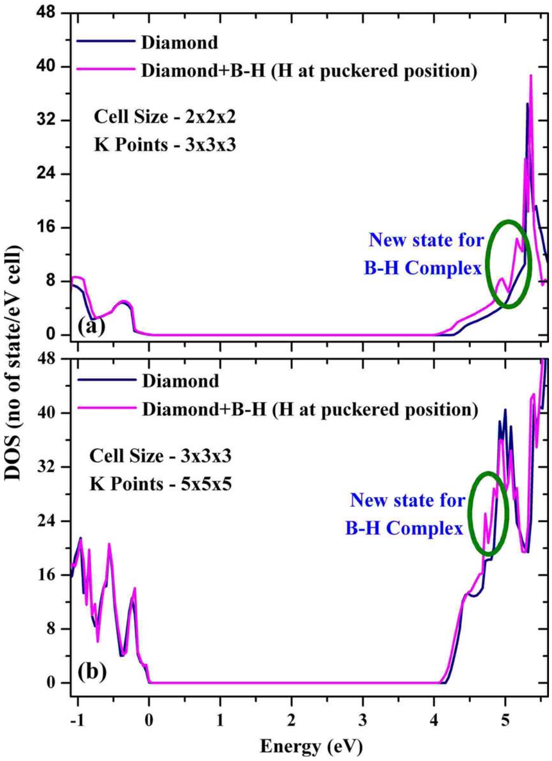

FIG. 3. (Color online) Density of states of B-H complexes in a diamond matrix, hydrogen at puckered positions, for different (a) cell size: 2×2×2, and (b) cell size: 3×3×3.

approximation.[22] Projector augmented wave is used with a basis cutoff equal to 318.6 eV.[23] The Monkhorst-Pack scheme[24] with a set of k-points from $3\times3\times3$ to $5\times5\times5$ has been used for integration in the Brillouin zone. The error of total-energy convergence is smaller than 10^{-4} eV. The densities of states are calculated using the tetrahedron method with Bloechl corrections. The calculation of the energy band gap for pure diamond (E_g=4.2 eV) is in good agreement with other theoretical calculations.[25–27]

Non-neutral charged states were modeled by adding or subtracting one electron to the system. A uniform background is then automatically added by VASP to keep a neutral system and avoid problems related to coulomb energy of ordered interacting charged defects. The error associated to this procedure is reduced for large cells such as the one used here −512 atoms in a $4\times4\times4$ cubic cell.

Calculation of ionization energies is not straightforward because of the well-known drawbacks of the DFT approach: it does not lead to a good value of the gap width[28] and the Kohn Sham levels—eigenvalues obtained by the *ab initio* calculation—have no clear physical meaning and should not be used as the quasiparticle energies. Furthermore, there is no absolute energy reference in *ab initio* calculations that involve different atomic concentration so no way to fix the conduction-band minimum. As we are dealing with point defects, the geometry and then the related electronic level of the defect can change with its state of charge. So that the most stable configuration has to be searched for each charge state to evaluate the ionization energy. There are several methods for calculating the electrical energy levels of defects, none of them has become universally accepted. The formation energy method involves comparison of the calculated formation energies of defects in different charge states.[29] Recently, marker method has been successfully used for electrical energy-level calculations, in the case of boron-hydrogen complex in diamond, chalcogen defects in diamond and silicon.[5,30–32] This method eliminates some of the errors in DFT calculations, such as an underestimate of the band gap, which may influence the position of the defect levels and systematic errors coming from the compensating background for charged defects.[31,33] In present study, the marker method is employed to investigate ionization energies. It scales the searched ionization energy using another known defect, the marker, for which this value is well known as follows:

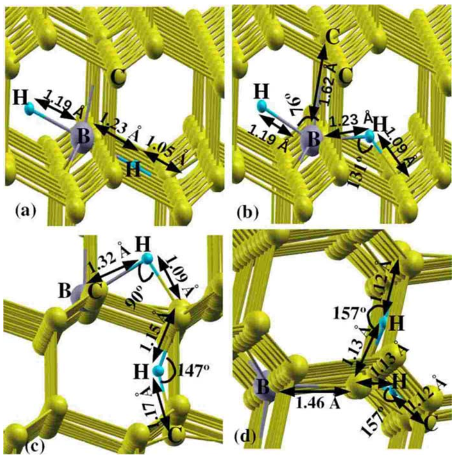

FIG. 4. (Color online) The relaxed structures of B-H_2 complexes, (a) B-H_2^*, one H atom at the B-C bond center and another H atom at antibonding site behind the B atom, along B-C axis, (b) B-H_{2P}^*, one H atom at the B-C bond-centered puckered position and another H atom at antibonding site behind the B atom in puckered position, (c) B-H_{2BC}, one H atom at the B-C bond-centered puckered position and the other H atom at puckered position of a C-C bond first neighbor of the B atom, (d) B-H_{2CC}, two H atoms at the puckered bond-center positions of two C-C bonds first neighbors of the B atom.

For acceptor level

$$\epsilon(-/0,X) = \epsilon(-/0,Y) + \{[E(X,-) - E(X,0)] - [E(Y,-) - E(Y,0)]\}. \tag{1}$$

For donor level

$$\epsilon(0/+,X) = \epsilon(0/+,Y) + \{[E(X,0) - E(X,+)] - [E(Y,0) - E(Y,+)]\}, \tag{2}$$

$\epsilon(-/0,X)$ is the ionization of the studied defect X, $\epsilon(0/-,Y)$ is the “known” ionization energy of the marker defect, E are the total energies for the defects X or Y in the charge state 0, +, or −. In the present paper, experimentally observed ionization energy of B (E_v+0.37 eV) as an acceptor[34] and P (E_c−0.6 eV) as a donor[35] is used for $\epsilon(-/0,Y)$ and $\epsilon(0/+,Y)$, respectively.

TABLE II. Summary and comparison of theoretical work on B-H_2 complexes in diamond matrix. The zero of total energy is taken to be the lowest energy structure in present study. KS denote the Kohn-Sham levels.

Reference	Method	KS level	Density of complex (cm^{-3})	Relative total energy (eV)
		(B-H_{2BC})		
Present work	GGA-VASP, 216 and 512 C atom unit cell	$E_v+1.29$ eV	7.8×10^{20} 3×10^{20}	0
40	LDA-AIMPRO, 64 and 216 C atom unit cell	$E_v+1.2-1.3$ eV	2.6×10^{21} 7.8×10^{20}	
		(B-H_{2P}^*)		
Present work	GGA-VASP, 216 and 512 C atom unit cell	$E_v+1.3$ eV	7.8×10^{20} 3×10^{20}	0.77
20	GGA-VASP, 64 C atom unit cell	Not shown	2.6×10^{21}	
		(B-H_2^*)		
Present work	GGA-VASP, 216 and 512 C atom unit cell	$E_v+0.87$ eV	7.8×10^{20} 3×10^{20}	0.88
		(B-H_{2CC})		
Present work	GGA-VASP, 216 and 512 C atom unit cell	$E_v+1.52$ and $E_v+2.04$ eV	7.8×10^{20} 3×10^{20}	1.95
38	DFT cluster, 35 C atom cluster	*n*-type conductivity	5×10^{21}	

III. B-H COMPLEX

Some theoretical calculations found that H at the bond-center site along the B-C axis on bond geometry, Fig. 1(a) was the position of lowest energy.[20,36] Some deviations from the bond-center site-puckered position, Fig. 1(b) were also reported.[30,37] In the present calculations, we have used these two different structures to investigate the stability and electronic properties of boron-hydrogen complexes. The corresponding relaxed structures are depicted in Fig. 1 for the neutral defect. To generate a puckered position, the hydrogen atom was initially displaced by a small distance off axis and the whole cell was allowed to relax. We want to point out that hydrogen at the bond-center site is only a saddle point, while the puckered bond-center position leads to the lowest energy of the complex (0.3 eV lower). In the puckered position, hydrogen is off the bond-center B-C axis and makes a 106.0° angle (<BHC) as shown in Fig. 1(b). In both relaxed configuration, we found that hydrogen induces a backward relaxation of adjacent boron and carbon atoms. The distance between B and H (1.19 Å for bond center and 1.20 Å for puckered) is larger than the H-C distance (1.03 Å for bond center and 1.15 Å for puckered), but their difference is reduced in puckered position. These values agree with those found earlier from the density-functional theory calculations of hydrogen in diamond.[37,38] In the present study, the bond lengths and bond angles are mentioned within the error bar of ±0.01 Å and ±0.1°, respectively. With supercells as well as cluster approaches, most of the previous work[30,37–39] concluded to a higher stability of the hydrogen in the puckered position. This position allows to relax the stress on the B-H and H-C bonds. The shift of H toward C (with respect to B) has to be related to the fourfold (threefold) coordination of C (B).

The density of states of B-H complexes corresponding to H at bond-center and puckered positions are shown in Fig. 2. Hydrogen at bond-center position gives an energy level [Kohn-Sham (KS) level] in the band gap $\approx E_c-0.6$ eV below the conduction band whereas no state is found in the gap for the puckered position. This later result is consistent with earlier DFT calculations.[30] The energy level ($E_c-0.6$ eV) for the on bond configuration appears as an independent band and not connected to conduction band as in earlier report[20] because of the large supercell used here. The summary of the lowest energy sites and the corresponding positions of the energy levels in the gap from previous studies are given in Table I.

Figure 3 compares the DOS for the puckered B-H complex to the diamond one for two different sizes of cell: $2\times2\times2$ [64 atoms, Fig. 3(a)] and $3\times3\times3$ [216 atoms,

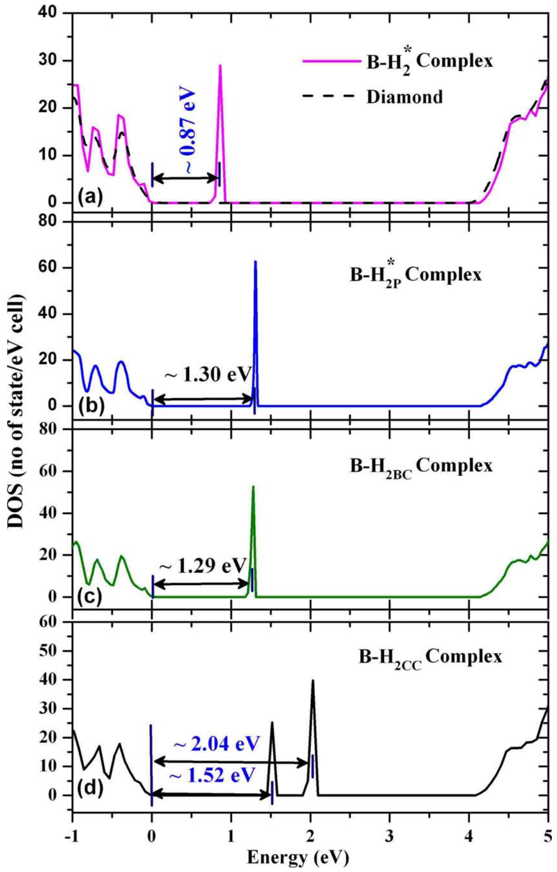

FIG. 5. (Color online) Density of states of B-H$_2$ complexes in a diamond matrix for (a) B-H$_2^*$, (b) B-H$_{2P}^*$, (c)B-H$_{2BC}$, and (d) B-H$_{2CC}$.

Fig. 3(b)]. A state related to B-H is found in the bottom of the conduction band. A shift of the conduction-band minimum to reproduce the experimental value of the gap would leave this state within the gap. Reference 20 reported the existence of a level in the band gap located at E_c-1 eV, but the origin of this level cannot be clearly established since the procedure used to build the DOS in this reference is not clearly described. A first possibility is that the author used the bond-center position of hydrogen, which is not the stable one, or they shift the conduction-band minimum without shifting the Kohn-Sham level. This later way of doing is highly questionable and the possible existence of a localized state within the gap would deserve a complete beyond DFT calculation even if this kind of approach would be really heavy because of the size of the cell.

IV. B-H$_2$ COMPLEX

The different configurations calculated are described in Fig. 4 for neutral B-H$_2$ complex. They correspond to the lowest energy atomic structures determined previously in other *ab initio* calculations.[30,37–39] In the first case, B-H$_2^*$ [Fig. 4(a)], one H atom is at the B-C bond center and the second one H is at the antibonding site behind the B atom along B-C axis. These positions correspond to the one found in silicon for the H$_2^*$ defect. The bond-center H site is almost similar to its position in B-H complex in [Fig. 1(a)]. The second case, B-H$_{2P}^*$ (Fig. 4(b)) is similar to the first one but the H atoms are on bonding and antibonding puckered positions. B-H$_{2BC}$, [Fig. 4(c)] corresponds to one H atom at the B-C bond-centered puckered position and the other one at the puckered position of one of the C-C bond first neighbor of the B atom. B-H$_{2CC}$, [Fig. 4(d)] has two H atoms at the puckered bond-center positions of two C-C bonds first neighbor of the B atom. The bond lengths and angles are given in Fig. 4. The geometry obtained for the B-H$_{2P}^*$ is in good agreement with earlier DFT calculations.[30,37] We find that the B-H$_{2BC}$ is the lowest energy structure for the neutral B-H$_2$ complex in agreement with Ref. 30 but in opposition to Refs. 20 and 38. Yan *et al.*[20] used the B-H$_2^*$ structure to deduce the ionization energy, and Dai *et al.*[38] found B-H$_{2CC}$ to be the most stable structure. The use of much smaller cells in these two calculations can explain the discrepancy between the results, see Table II for a summary.

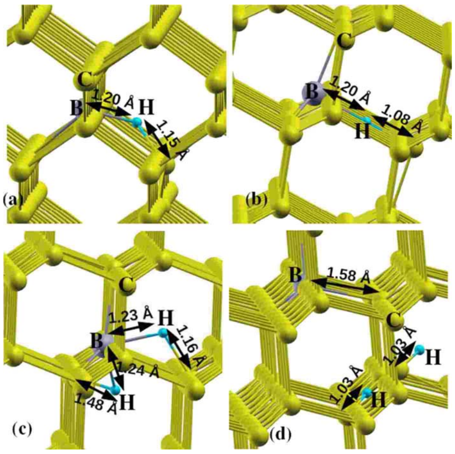

FIG. 6. (Color online) The most stable relaxed structures of B-H and B-H$_2$ complexes with positive and negative charged states. (a) B-H complex with positive charged state, (b) B-H complex with negative charged state, (c) B-H$_2$ complex with positive charged state, and (d) B-H$_2$ complex with negative charge state.

Figure 5 shows the density of states of the relaxed B-H$_2$ complexes for (a) B-H$_2^*$, (b) B-H$_{2P}^*$, (c) B-H$_{2BC}$, and (d) B-H$_{2CC}$. The positions of (KS) levels and the relative total energy are given in Table II and compared to previously reported results. B-H$_2^*$ leads to a KS level ≈ 0.87 eV above the valence band. DOS calculations for B-H$_{2P}^*$ and B-H$_{2BC}$ complexes are rather similar, they lead to the formation of KS levels at ≈ 1.3 and ≈ 1.29 eV above the valence band, respectively. For B-H$_{2CC}$ complex, there are two well separated KS levels at ≈ 1.52 and ≈ 2.04 eV above the valence band. The Kohn-Sham levels or density of states observed in the band gap for the most stable structure is consistent with the energy level observed in band-structure calculations for neutral B-H$_2$ complex.[40] The zero of total energy is taken to be the lowest energy structure (B-H$_{2BC}$) in Table II.

V. IONIZATION ENERGIES

We have searched for the most stable structures for B-H and B-H$_2$ complexes for positive and negative charged states

TABLE III. Total energies for B-H and $B\text{-}H_2$ complexes in neutral, positive, and negative charged states in diamond matrix.

Charge State	Total energy (present work)	Summary and comparison
	B-H complex	
0	−1959.5500	Acceptor level at $E_v+4.44$ eV [Present work]
+	−1970.3491	Donor level at $E_c-4.84$ eV [Present work]
−	−1944.5955	Acceptor level at $E_v+4.49$ eV (Ref. 37)
	$B\text{-}H_2$ complex	
0	−1958.2050	Acceptor level at $E_v+1.14$ eV [Present work]
+	−1971.0462	Donor level at $E_c-2.80$ eV [Present work]
−	−1946.5561	Acceptor level at $E_v+1.6-1.9$ eV (Refs. 30 and 40)
		Donor level at $E_v+2.6$ or $E_c-2.9$ eV (Refs. 30 and 40)
	Phosphorus	
0	−1948.0026	Experimentally observed,
+	−1963.0436	donor level at $E_c-0.6$
−	−1932.7676	(Ref. 35)
	Boron	
0	−1957.6452	Experimentally observed,
+	−1968.3544	acceptor level at $E_v+0.37$
−	−1946.7673	(Ref. 34)

to investigate the ionization energy [charge transition level $(0/+)$ or $(-/0)$] of complex. They are shown in Fig. 6. For B-H complex, the puckered position remains the most stable configuration for positive charged state, while bond-center H position is more stable for negative charged complex. The B-H and H-C bond lengths for B-H complex with negative charged state are slightly larger compared to the neutral charge as depicted in Fig. 1(a). For $B\text{-}H_2$ complex, the two H atoms bond to B in puckered position for the positive charged state configuration while in negative charged state, they bond to carbon atoms next-nearest neighbor to boron. The most stable structures for $B\text{-}H_2$ complex with positive and negative charged states are consistent with previously reported stable geometry.[30,40] This most stable configuration for each charge is used to determine ionization energy of complex.

Table III gathers the total energies and the ionization energies of the most stable structures obtained for B-H and $B\text{-}H_2$ complexes in the 0, +, and − charged states. The total energies values for boron and phosphorus with different charge states are also given. The ionization energies for acceptor and donor levels are determined using Eq. (1) and (2) based on marker method, respectively. These calculations yield an acceptor level at $E_v+4.44$ eV for B-H complex and a donor level at $E_c-2.80$ eV for $B\text{-}H_2$ complex. The calculated acceptor or donor levels for boron-hydrogen complexes are compared with earlier reported levels in literature in Table III. These investigations suggest that the B atoms are passivated when associated to one H atom and the $B\text{-}H_2$ complex for most stable structure does not create a shallow donor level as experimentally observed. It supports the previous findings that $B\text{-}H_2$ does not show an associated shallow donor level in any of the calculated structures.[30,37] The small size of the cell used by Dai *et al.*[38] could explain why they obtain an *n*-type conductivity. In their calculation, the defect concentration is huge (5×10^{21} cm^{-3}) and induces an artificial defect-defect interaction.

VI. CONCLUSION

The present paper reports the structure and the electronic properties of B-H and $B\text{-}H_2$ complexes in diamond. The results obtained here compare well with some of the previously reported studies and show that cells large enough are required to determine the lowest energy structures used to calculate the ionization energies. B-H complex leads to an acceptor level at $E_v+4.44$ eV and $B\text{-}H_2$ to a donor level at $E_c-2.80$ eV. There is no satisfactory theoretical model to explain the shallow *n*-type conductivity in deuterated boron-doped diamond. The *p* to *n* switch upon deuteration remains unexplained, different complex geometries in different charge states have to be investigated but also different mechanism should be considered.

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