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Surprising stability of neutral interstitial hydrogen in diamond and cubic BN

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In virtually all semiconductors and insulators, hydrogen interstitials (H_i) act as negative- U centers, implying that hydrogen is never stable in the neutral charge state. Using hybrid density functional calculations, we find a different behavior for H_i in diamond and cubic BN. In diamond, H_i is a very strong positive- U center, and the H_i^0 charge state is stable over a Fermi-level range of more than 2 eV. In cubic BN, a III-V compound similar to diamond, we also find positive- U behavior, though over a much smaller Fermi-level range. These results highlight the unique behavior of H_i in these covalent wide-band-gap semiconductors.

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I. INTRODUCTION

In semiconductors and insulators, interstitial hydrogen (H_i) impurities show remarkably consistent electrical behavior, with H_i^- being the most stable charge state under n -type conditions and H_i^+ the most stable charge state under p -type conditions [1]. H_i then acts to compensate majority carriers by passivating donors in n -type material and acceptors in p -type material. In the majority of cases, H_i^0 is never the most stable charge state at any Fermi level (E_F). This is referred to as H_i exhibiting “negative- U ” character [2]. The position of the (+/-) transition level shows universal behavior across many different materials, when aligned on an absolute energy scale, and can serve as a reference for estimating band alignments [2].

One exception to this almost universal behavior has been identified: based on density functional theory (DFT) calculations, H_i in diamond was found to exhibit positive- U behavior [3, 4]. However, those calculations were performed within the local density approximation (LDA) [3] or generalized gradient approximation (GGA) [4], both of which underestimate semiconductor band gaps and do not quantitatively predict defect transition levels [5]. The shortcomings are illustrated by the inconsistency between these two studies, which aside from the exchange-correlation functional use the same techniques: Ref. [3] reports $U=+0.5$ eV, while Ref. [4] reports $U=+1.7$ eV.

With a small lattice constant, large band gap, and negative electronic affinity [6], diamond has many properties that make it a promising electronic material. It also is the host for the nitrogen-vacancy (NV) center, which has been thoroughly investigated for applications in quantum computation, spintronics, and metrology [7]. Hydrogen is a common unintentional impurity, and is definitely expected to be present in artificial diamond grown with chemical vapor deposition (CVD) [8, 9]. Hydrogen has

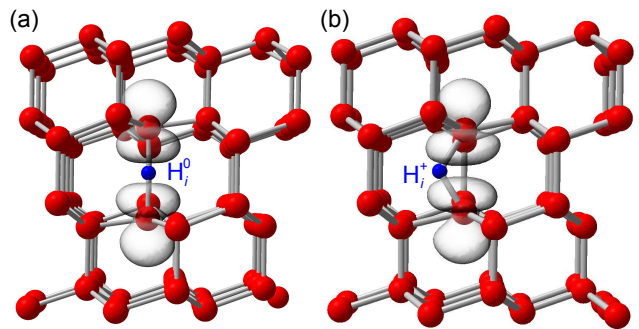


FIG. 1. (color online) (a) Atomic configuration and spin density for H_i^0 in the BC position in diamond. The atomic configuration for H_i^- is very similar. (b) Atomic configuration and wavefunction of the unoccupied defect state of H_i^+ in diamond in the puckered BC position. Isosurfaces are set to 5% of the maximum, C atoms are shown in red and the H impurity is in blue.

been implicated in influencing the charge state of the NV center [10] and in enhancing the optical emission in high-temperature-annealed diamond [9].

Cubic BN (c-BN) is a wide-band-gap semiconductor with electronic properties and a lattice constant very similar to diamond. It is a superhard material, making it useful in wear protection and coating applications [11]. BN is also being explored as a member of the group-III-nitride family of wide-band-gap semiconductors, for instance in the form of high-band-gap BAlN alloys [12] that could serve as barrier layers for deep-UV light emitters or in high-power transistors. c-BN can also be grown by CVD, again making H a likely unintentional impurity [13]. Less is known about H_i in c-BN compared to diamond, though earlier work investigated its ability to passivate nitrogen vacancies [14] and a recent study indicated that H_i is more stable than H_2 molecules in c-BN for all growth conditions [15]. However, those calculations were based on the LDA, and charge states of H_i other than the neutral state were not explored, motivating a more detailed investigation with more advanced techniques.

In this work we employ state-of-the-art DFT calcula-

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tions based on a hybrid functional to explore the behavior of H_i in diamond. In each material we examine a number of different atomic configurations for the hydrogen interstitial, including bond-centered (BC) [Fig. 1a], puckered BC [Fig. 1b], antibonding (AB), and tetrahedral interstitial. We also systematically calculate the three possible charge states (+, 0, and -). We find that H_i exhibits stronger positive- U behavior in diamond than previously predicted, and that H_i^0 is stable in the neutral charge state over a range of 2 eV. The behavior of H_i in diamond is thus very different from that in other materials, where H_i exhibits negative- U behavior, and physical reasons for this difference will be explored. In c-BN, we find that H_i exhibits only weak positive- U behavior, despite having a similar crystal structure, band gap, and covalency to diamond.

II. METHODS

Our calculations are performed using the generalized Kohn-Sham scheme [16] and the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [17, 18] together with projector-augmented-wave potentials [19] as implemented in the *Vienna Ab Initio Simulation Program* VASP [20, 21]. The screened hybrid functional provides excellent structural properties, corrects the band-gap problem and lack of localization inherent to DFT, and provides more quantitative and reliable results for impurities in semiconductors [5]. A 400 eV cutoff, 216-atom supercell, and a 2x2x2 special k-point mesh are used for calculations of H_i . Both the HSE mixing parameter (0.25) and the screening length (0.2 \AA^{-1}) are set to the default values for both diamond and c-BN.

The formation energy of H_i in charge state q in diamond is given by [5]:

$$E^f(H_i^q) = E_{\text{tot}}(H_i^q) - E_{\text{tot}}(\text{diamond}) - \mu_H + qE_F + \Delta^q, \quad (1)$$

where $E_{\text{tot}}(H_i^q)$ is the total energy of the supercell containing one H_i in charge state q , and $E_{\text{tot}}(\text{diamond})$ is the total energy of a perfect bulk supercell. The H atom that is removed from the crystal is placed in a reservoir of energy μ_H , referenced to the energy of one-half the H_2 dimer. Other choices for the chemical potential reference of H are plausible and would change the absolute value of the formation energies presented below. However, we note that this choice does not affect the position of the thermodynamic transition levels of H_i , which are the main focus of this work. E_F is the Fermi level, which will be referenced to the valence-band maximum (VBM). Finite-size supercell corrections for charged states (represented by the Δ^q term) are calculated using the scheme of Refs. 22 and 23. For each charge state, we tested a number of different atomic configurations, which were all consistently relaxed with the hybrid functional. Spin-polarization was included for H_i^0 .

III. RESULTS

A. Hydrogen in diamond

1. Atomic and electronic structure

The bulk properties of diamond calculated with HSE are in close agreement with published results. The calculated lattice constant is 3.54 \AA , compared to the experimental value of 3.57 \AA . We calculate the fundamental band gap, which is indirect, to be 5.35 eV, close to the experimental value of 5.47 eV [25] and the G_0W_0 -calculated value of 5.33 eV based on the LDA [26], though slightly smaller than the G_0W_0 -calculated value of 5.60 eV based on the LDA and using project-augmented wave pseudopotentials [27]. The HSE-calculated direct band gap at Γ is 7.06 eV, compared to the experimentally determined direct band gap of 7.02 eV [25] and the GW -calculated gap of 7.26 eV [26]. The VBM occurs at Γ and the conduction-band minimum (CBM) at one-third of the distance along the Γ - X path, in agreement with previous calculations [28].

As in previous work [3], we find that in the 0 and - charge states H_i adopts a bond-centered (BC) configuration, in which the impurity is situated between two C atoms accompanied by a significant outward relaxation of the C atoms. In the BC configuration for H_i^0 shown in Fig. 1(a) the distance between H and its C neighbors is 1.12 \AA . H_i^0 can also be placed at a tetrahedral interstitial site, but the energy of this metastable configuration is 1.20 eV higher than the BC configuration. For H_i^- at the BC site the distance between H and the nearest-neighbor C atoms is slightly larger, at 1.16 \AA . The C-C distance for the bond in which H_i^- is inserted thus expands to 2.32 \AA , an increase of over 50% relative to the bulk diamond bond length (1.53 \AA). H_i^- strongly prefers the BC configuration; the tetrahedral interstitial position is 1.84 eV higher in energy.

The atomic configuration for H_i^+ is somewhat different: it prefers a puckered BC configuration in which H_i moves away from the BC position, in a direction perpendicular to the C-C bond, with a C-H-C angle of 110° , as shown in Fig. 1(b). In this configuration (which is 0.2 eV lower in energy than the BC configuration), the H-C bond lengths are 1.14 \AA . The energy of the configuration is almost independent of the direction in which the H is displaced within the plane bisecting the C-C bond. The C-C distance is now 1.95 \AA , significantly smaller than in the “straight” BC configuration; this smaller relaxation of C obviously plays a role in the stabilization of the puckered-BC configuration. A similar misaligned BC configuration was identified for H_i in Mg-H complexes in GaN [29].

These atomic configurations for the various charge states of H_i in diamond are distinctly different from those in other semiconductors. In most materials, H_i^- prefers the AB position [2], yet in diamond H_i^- strongly prefers a BC configuration. As discussed above, this leads to

sizeable relaxations of the C atoms neighboring H, causing them to become nearly coplanar with their three C neighbors (see Fig. 1). The adoption of this rare H_i^- configuration is likely linked to the ability of C to adopt planar sp^2 bonding configurations in addition to the sp^3 bonding present in the diamond structure. We note also the similarity with C-H bonding in molecules. The C-H bond lengths discussed above ranged from 1.12 to 1.16 Å in length; C(sp^3)-H bonds are commonly ~ 1.10 Å in length [30].

One might also wonder why H_i^0 and H_i^- prefer the “straight” BC configuration, while H_i^+ adopts the puckered BC configuration (which lowers the elastic energy cost of C displacement). This can be understood based on the electronic structure of the three-center bond that hydrogen forms when located at the BC site (see Fig. 2). In a tight-binding or molecular-orbital picture, H $1s$ orbital combines with the bonding orbital of the C-C bond, leading to a low-energy C-H bonding orbital, always occupied with 2 electrons, and a C-H antibonding orbital, which is always high in energy and always empty. A C-C antibonding orbital (which is nonbonding from the three-center-bond perspective) moves down from the conduction band into the band gap due to the outward relaxation of the C atoms (the charge density of this state for H_i^0 is depicted in Fig. 2). For H_i^+ , this orbital is empty, but for H_i^0 , it is occupied with one electron, and for H_i^- , this orbital is occupied with two electrons. Increasing the C-C distance lowers the energy of this orbital, explaining why putting H at the exact BC site (which maximizes the C-C distance) is favored for H_i^0 , resp. H_i^- . The elastic energy that could be gained by reducing the relaxation of the C atoms apparently does not outweigh the cost of raising of the occupied antibonding orbital.

2. Formation energies and charge-state transition levels

The formation energies versus Fermi level for the three charge states of H_i in diamond are shown in Fig. 3(a). The (+/0) transition level of H_i^+ occurs at 1.76 eV above the VBM and the (0/-) level at 3.79 eV. Thus, H_i exhibits strong positive- U behavior. The value of U , which is defined as the difference in energy between the H_i^0/H_i^- transition level and the H_i^+/H_i^0 transition level, is thus $U = 2.03$ eV, implying that H_i^0 is stable over a range of Fermi-level positions spanning 2.03 eV. We also calculate a large exchange splitting of 2.52 eV (taken as the difference in energy between the spin-up and spin-down eigenvalues at Γ) for H_i^0 .

While the positive- U behavior of H_i calculated here is in qualitative agreement with previous work, the transition levels and U value are markedly different. Previous calculations using the LDA [3] found that the (+/0) level occurred at 2.60 eV above the VBM, and the (0/-) level at 3.10 eV, resulting in a U value of 0.5 eV. Calculations based on GGA [4], in contrast, found a (+/0) level at 1.30 eV and a (0/-) level at 3.00 eV above the VBM, and thus

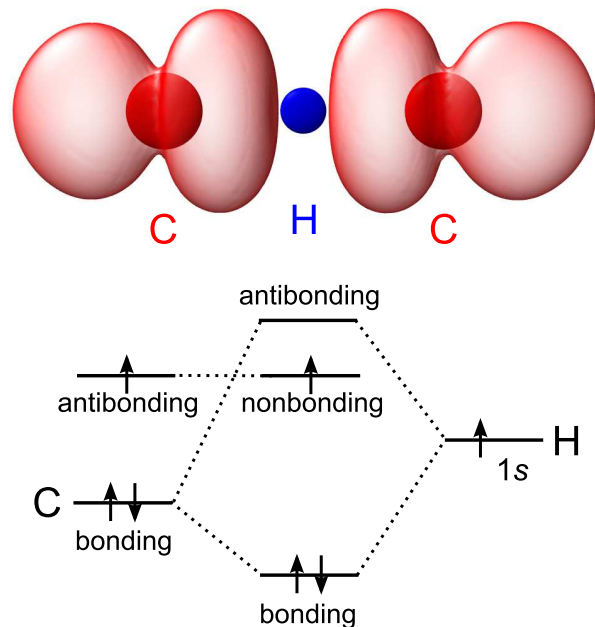


FIG. 2. Schematic of the three-center bond for the configuration of H_i^0 and H_i^- in diamond. For H_i^0 the non-bonding state will be occupied by a single electron (as shown below), whereas for H_i^- this state will be doubly occupied. Above, the charge density associated with the occupied non-bonding state of H_i^0 is plotted, with isosurface set to 5% of the maximum.

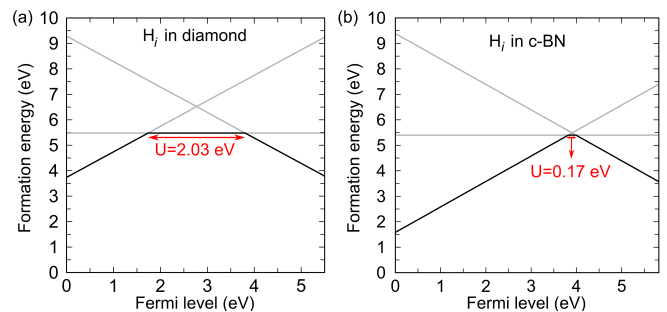


FIG. 3. Formation energy versus Fermi level of H_i in (a) diamond and (b) c-BN. The most stable charge state at each Fermi level is indicated with the bold line.

$U=1.70$ eV. A major part of the difference between the GGA and HSE transition levels can be attributed to the fact that HSE tends to shift down the VBM on an absolute energy scale [31, 32]. In addition, exchange splittings tend to be larger in HSE, which leads to a lowering of the occupied Kohn-Sham state and hence a lowering of the formation energy in the case of H_i^0 . This increases the range of stability of this charge state, resulting in a larger U value.

The unique behavior of H_i in diamond is also evident from the position of the H_i (+/-) transition level, which occurs at 2.78 eV above the VBM. The absolute position of the H_i (+/-) level has been shown to be consistent across a wide range of materials, and thus can be used

as a reference to align the band-edge positions [2]. In most materials, the $(+/-)$ level lies close to -4.5 eV, if the vacuum level is set to zero [2]. If the H_i $(+/-)$ level in diamond would be placed at -4.5 eV, the absolute position of the VBM would then be at -7.28 eV. However, measurements of electron affinity for unhydrogenated (100) surfaces have indicated that the VBM in diamond lies close to 6.5 eV below the vacuum level [33] (it would be even higher on a hydrogenated surface). The position of the $(+/-)$ level with respect to the VBM is therefore higher than it should be to be consistent with the “universal alignment”.

We attribute the discrepancy to the fact that the formation energy of H_i^- is uncharacteristically high in diamond (at least, when compared to H_i^+), probably due to its small lattice constant. Hydrogen at the tetrahedral interstitial site is high in energy due to repulsion with the electron cloud of the surrounding C atoms. So high, in fact, that it is more favorable for H_i^- to adopt the BC site, highly unusual for a negative interstitial. But this position is still high in energy, due to the occupation of C-C antibonding states [34]. Overall, due to its strong interaction with the lattice, interstitial H in diamond does not fulfill the conditions required to allow the $(+/-)$ level to exhibit the “universal alignment” [2].

These new insights in the behavior of hydrogen in diamond may impact important technological problems, such as the formation of the NV center as a result of implantation and annealing. Currently, only a very small fraction of NV centers that could potentially form (based on the concentrations of nitrogen and vacancy centers in the crystal) actually act as addressable single-spin centers with the desired characteristics. The diamond host crystals are grown by CVD [9], a process which incorporates hydrogen. The interaction of H with NV centers was considered by Deák *et al.* [35] in their comprehensive study of the formation and migration of vacancies and their interaction with N in diamond, but only through a calculation of the NVH complex. A full analysis should include a study of formation and dissociation of this complex with respect to isolated H, as well as a study of NH and VH complexes. The fact that interstitial hydrogen displays a $(0/-)$ transition within the energy range of the charge-state transition levels of the NV center and its constituents will affect the kinetics of formation. Given that hydrogen effectively renders the NV center inactive, a fuller understanding of these issues, building on the new insights provided here, will be fruitful.

B. Hydrogen in cubic BN and comparison with diamond

1. Atomic and electronic structure

We now examine the properties of H_i in c-BN. The band structure and structural properties of c-BN, calculated with HSE, were previously reported in Ref. 36. The

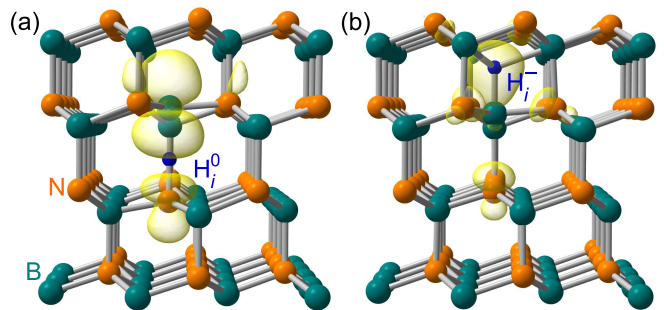


FIG. 4. (color online) (a) Atomic configuration and spin density of H_i^0 in c-BN in the BC position. The atomic configuration for H_i^+ is very similar. (b) Atomic configuration and wavefunction of the occupied defect state of H_i^- in a cation-antibonding state. Isosurfaces are set to 5% of the maximum, B atoms are shown in green, N atoms in orange, and the H impurity is in blue.

calculated lattice parameter is 3.58 Å, in close agreement with experiment, and the indirect band gap is 5.84 eV, within the range of experimentally reported gaps [36]. Both the lattice parameter and band gap of c-BN are very similar to diamond.

The atomic configurations of H_i in various charge states in c-BN are shown in Fig. 4. As in diamond, H_i^0 in c-BN prefers to occupy the BC site, as shown in Fig. 4(a). H_i^0 breaks a B-N bond, and sits 1.06 Å from the nearest N and 1.29 Å from the nearest B atom. The distance between the B and the N atoms expands to 2.35 Å, an increase of more than 50% of the bulk c-BN bond length. The BC site is more stable than the anion-antibonding site by 0.13 eV.

The lowest energy configuration for H_i^+ is also the BC position [which only has small differences from what is shown in Fig. 4(a)]. The hydrogen forms a 0.97 Å bond with an N atom, and causes an increase in the B-N distance by 0.78 Å (or by 50% relative to the bulk BN bond length). This BC configuration is favored over the anion-antibonding configuration by 0.09 eV.

The atomic configuration for H_i^- is shown in Fig. 4(b). H_i^- in c-BN occupies a cation-antibonding configuration, situated 1.18 Å from one B atom, and at a distance of 1.57 Å from three other B atoms. The B atom to which the hydrogen bonds most strongly is pulled 0.36 Å off of its lattice site (and away from a N atom). Because of these relaxations, the H atom ends up approximately at the tetrahedral interstitial site surrounded by B atoms. For H_i^- , this configuration is more stable than the BC configuration by 1.21 eV.

The most striking difference in the behavior of H_i between c-BN and diamond thus occurs for the negative charge state: in diamond H_i^- occupies the BC site, whereas in c-BN it occupies a cation-antibonding site. We attribute this difference to the more electropositive character of B compared to C, which favors incorporation of H_i^- close to a B atom in the interstitial void; at the

same time, the ionic character of BN increases the energy of the BC configuration due to the cost of occupying the antibonding orbital associated with a B-N bond. Overall, the atomic configurations for interstitial H in c-BN are in line with what has been observed in many other semiconductors [2]: a BC position (with H closest to the anion) for H_i^+ , and an antibonding position, bonded to the cation and close to the tetrahedral site, for H_i^- .

2. Formation energies and charge-state transition levels

The formation energy as a function of Fermi level for H_i in c-BN is plotted in Fig. 3(b). We find that the (+/0) transition level occurs at 3.82 eV above the VBM and the (0/-) at 3.99 eV above the VBM, resulting in a (+/-) level at 3.91 eV. Thus, H_i exhibits weak positive- U behavior, with $U = 0.17$ eV, and H_i^0 is stable for Fermi-level positions that span only 0.17 eV. Although U is much smaller in c-BN relative to diamond, the positive- U behavior of H_i in c-BN is still far different from other wide-band-gap semiconductors (such as GaN and AlN), where U is invariably negative and large in magnitude [1, 37].

Interestingly, despite the much smaller U , the exchange splitting in c-BN (calculated to be 2.34 eV) is close to that of diamond (2.52 eV), indicating that H_i^0 exhibits very similar properties in the two materials. This is also evident from the similarity in formation energies of H_i^0 in Figs. 3(a) and (b). The large difference in U values can be attributed in part to the more ionic nature of c-BN relative to diamond: H_i^+ exhibits stronger bonding to N than to C, while H_i^- binds more strongly to B than to C. This lowers the formation energies of the charged species in BN and leads to a smaller value of U . To explain the decrease in U on this basis, a lowering in formation energy of the charged species by $(2.03-0.17)/2=0.93$ eV is required.

Our calculated formation energies allow an assessment of how much hydrogen will be incorporated into c-BN grown by CVD [13] under various growth conditions. c-BN intrinsically has a high thermal conductivity, but for use as a superhard material low thermal conductivity is desirable [11]. Incorporation of impurities such as hydrogen can have a distinct impact on thermal conductivity.

We can again relate the behavior of H_i to other materials by noting the position of the (+/-) transition level. First, we use the alignment of (+/-) levels to obtain a band alignment between diamond and c-BN. Since in diamond the (+/-) level is at 2.78 eV and in c-BN at 3.91 eV, the valence-band offset would be 1.13 eV, with the VBM in diamond lying at higher energy than in c-BN.

We can compare this value to a valence-band offset of 1.41 eV reported in Ref. 28 based on explicit interface calculations. Our value is almost 0.3 eV smaller than the previous value, which may again be due to the fact that the VBM of diamond, predicted from the (+/-) alignment, lies too low on an absolute energy scale. Assuming that the (+/-) level would lie at the universal position of -4.5 eV [2], the predicted position of the VBM of c-BN would be at $4.5 \text{ eV} + 3.91 \text{ eV} = 8.41 \text{ eV}$ below the vacuum level. We have not been able to find any experimental information regarding this alignment.

Finally, we note that we can combine our arguments about band alignment and effects of ionicity to produce a consistent picture for the formation energies of all charge states of H_i in diamond and BN. We have already noted that the formation energies of H_i^0 are almost identical. The formation energy of H_i^+ at the VBM in BN is $(3.75-1.58)=2.17$ eV lower in BN than in diamond. Above, we attributed 0.93 eV of this difference to the larger ionicity of BN. The remaining amount, 1.24 eV, is consistent with the fact that the VBM in BN lies $\sim(1.1-1.4)$ eV below the VBM in diamond, according to the band alignment discussed above. Similar arguments apply to H_i^- .

IV. CONCLUSIONS

Using hybrid density functional calculations we have investigated the unique positive- U behavior of H_i impurities in diamond and c-BN. Our calculations indicate that H_i is a strong positive- U center in diamond, with the neutral charge state H_i^0 stable over a Fermi-level range of 2.03 eV. In BN, H_i also exhibits positive- U behavior, but with a smaller value of U , with H_i^0 being stable over a range of Fermi levels of 0.17 eV. This behavior of hydrogen is very different from other semiconductors where H_i is a strong negative- U center. We attribute the unique behavior of H_i in c-BN and diamond to their small lattice constants which destabilize the H_i^- configuration.

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