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Equilibrium structures of neutral interstitial hydrogen in zinc-blende BN and BP

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We present the first calculations of the equilibrium configurations, potential-energy surfaces (PES), and electronic structures of an impurity (neutral interstitial hydrogen) in zinc-blende BN and BP. The host crystals are described by clusters and the calculations are done at an approximate *ab initio* Hartree-Fock level with the method of partial retention of diatomic differential overlap. The PES for H^0 has three minima in each host: near the center of a covalent bond (with H primarily bound to the group-III atom) and at the two tetrahedral interstitial sites. The three sites are energetically comparable in BP but quite different in BN. The chemical structure of bond-centered H^0 in III-V compounds is quite different from that in group-IV hosts. The properties of H^0 in BN and BP are discussed in terms of the difference of ionicity between the two hosts. The characteristics of muon-spin relaxation (μSR) spectra are predicted and qualitatively compared to the experimental data in GaP and GaAs.

I. INTRODUCTION

The study of properties of defects and impurities, in particular hydrogen, in exotic semiconductors such as cubic (zinc-blende) BN and BP (denoted *c*-BN and *c*-BP) is motivated by a number of considerations. First, there is a growing interest in these materials for special applications such as high-temperature devices (the first *p*-*n* junction diode of *c*-BN has recently been built[1]). Second, all-electron, parameter-free, self-consistent studies of electronically simple compounds ("simple" in the sense that they are well described with *s* and *p* orbitals only) allow the development of methodologies which subsequently can be applied to heavier compounds, such as GaP or GaAs. Third, the properties of interstitial H in *c*-BN and *c*-BP can be compared to those obtained in diamond[2-7] and Si.[4,5,8-15] This provides a deeper insight into the various factors influencing the relative stability of different sites. Finally, hydrogen plays crucial roles in many semiconductors (for recent reviews, see Refs. 16-18).

Even though *c*-BN and *c*-BP have similar electronic structures, their properties are quite different. The first single crystals of *c*-BN ("borazon") were prepared[19] in 1957 at high temperatures and under high pressures (1200-2000 °C and 45-75 kbar). The typical size of the crystals obtained was 0.7 mm, but 3 mm sizes were recently[20] achieved. The material has many properties similar to those of diamond. It is very hard (it scratches, and is scratched by diamond[19]). Its index of refraction[19,20] is about 2.1 to 2.2 (diamond: 2.4), static dielectric constant[21] 7.1 (diamond: 5.7), Debye temperature[21] 1700 K (diamond: 2340 K), and melting point 3300 K (diamond: 3850 K). The thermal conductivity[22] of *c*-BN is very high (13 W/cm K at room temperature, as compared to 20 for diamond and 4.3 for silver). The measured[23,24] (indirect) band gap is the largest of all group-IV elemental and III-V compound semiconductors: 6.0-6.4 eV, with a valence-band width[24] of about 22 eV (diamond: 5.4, 24.2 eV). The lattice constant[19] (3.615 Å) and density[19] (3.45 g/cm^3) also are close to the diamond values (3.567 Å, 3.51 g/cm^3). However, *c*-BN is one of the most ionic of all III-V compounds (an inspection of Pauling's electronegativities[25] shows that only AlN would be more ionic), while diamond is of course 100% covalent. The Pauling ionic character[25] of *c*-BN is 22%, a value consistent with the large effective charge obtained from measurements[21] of the dielectric constant and with a variety of theoretical estimates.[26-29] Cubic BN can be doped[1,19] both *p* type (e.g., with Be) and *n* type (e.g., with S or Si). The ground-state properties of bulk *c*-BN have been calculated by a number of groups.[26-30] The predicted band structures show indirect (Γ-X) band gaps of 4.2-14 eV (the predicted direct gaps are about 2 eV larger), valence-band widths of 18-20 eV, and lattice constants rather close to the experimental one: 3.606-3.652 Å.

On the other hand, crystals of *c*-BP can be obtained[31] at much lower pressures (2 atm) even though high temperatures still are required (1100 °C). The hardness is comparable[32] to that of β-SiC. The thermal conductivity[22] is much smaller than that of *c*-BN (3.6 W/cm K), and the index of refraction[32] is very high (3-3.5). The lattice constant[33] is 4.538 Å. The (indirect) band gap[33,34] is "only" 2.0-2.2 eV, and the valence-band width[35] less than 17.0 eV. Like *c*-BN, it can be doped[32] *p* and *n* type. Unlike *c*-BN, it is almost completely covalent,[21,33] with a Pauling ionic character[25] of only 2.5%. Theoretical studies of *c*-BP have been reported by several groups.[27,29] An excellent review of the calculated properties of *c*-BN and *c*-BP can be found in Ref. 29.

In the present contribution, we report the first calculations of equilibrium geometries, potential-energy surfaces (PES) and electronic structures of a simple interstitial (H^0) in *c*-BN and *c*-BP. In Sec. II, we describe the clusters used to represent the hosts, the theoretical method, and some bulk properties of *c*-BN and *c*-BP calculated using clusters. In Sec. III, the equilibrium structures of H^0 in both hosts are discussed and compared to the results obtained earlier at the same theoretical level in diamond[6,7] and silicon.[11] Finally, in Sec. IV, we summarize the key results, discuss the influence of the ionicity of the host on the microscopic properties of interstitial H^0, and qualitatively compare the predicted muon-spin relaxation (μSR) spectra in *c*-BN and *c*-BP to the experimental data in GaP and GaAs.

II. THEORETICAL DESCRIPTION

The host crystals are represented by clusters. In contrast to group-IV semiconductors where the only restrictions to cluster size and center are associated with the problem of correctly saturating[36,37] the surface dangling bonds, clusters of III-V compound semiconductors must have the same number of group-III and group-V atoms. If not, the average number of valence electrons per (host atom) site is not exactly 4, i.e., there are holes in the valence band or electrons in the conduction band. This restricts the possible centers of these clusters to two sites: the bond-centered (BC) and the hexagonal interstitial (*H*) sites. Around the BC site, the smallest clusters that can be saturated contain 4 or 22 group-III and group-V atoms, and around the *H* site, the smallest usable cluster has 19 atoms of each species. The clusters used for *c*-BN in the present calculations are $B_4N_4H_{18}$, $B_{19}N_{19}H_{44}$, and $B_{22}N_{22}H_{42}$, and the corresponding ones for the *c*-BP. The surface dangling bonds are saturated[36,37] with H atoms located at optimized B—H and N—H (or P—H) bond lengths. All the host atoms in the clusters (including those on the surface) are tetrahedrally coordinated at equilibrium. We have considered various alternatives to this procedure: threefold-coordinated surface atoms (which results in distortions in the bulk region of the clusters), or different saturators, such as F, OH, CH_3, or even OCH_3. We found that the use of H atoms is the best choice, resulting in the most uniform Mulliken charge distributions in the bulk, the smallest overlap between saturators and bulk host atoms, and the fastest convergence of the calculations. In *c*-BN, the optimized B—H and N—H bond lengths are 1.147 and 1.023 Å, respectively, and in *c*-BP, $d_{\text{B—H}} = 1.138$ Å and $d_{\text{P—H}} = 1.362$ Å. The small difference in B—H bond lengths in *c*-BN and *c*-BP is associated with the difference in covalent character between the neighboring B—N and B—P bonds.

Our calculations were done with the approximate *ab initio* method of partial retention of diatomic differential overlap (PRDDO).[38-41] It is a parameter-free, all-electron, self-consistent Hartree-Fock (HF) technique which consistently reproduces the results of *ab initio* (minimal basis-set) HF calculations at a fraction of the cost. The reliability of the method at predicting the correct minimum-energy configurations, accurate geometries, and a number of other equilibrium properties has been established by extensive testing against *ab initio* (restricted and unrestricted) HF calculations and against experiment for a large number of molecules and molecular ions[38-41] as well as impurities in semiconductors.[6,7,11,36,37] Unlike *ab initio* HF methods, PRDDO uses Slater orbitals (rather than linear combinations of Gaussians) and is highly vectorizable. A typical $B_{22}P_{22}H_{42}$ calculation with an interstitial H atom in C_1 symmetry reaches full convergence in 8 to 10 iterations and requires some 15 minutes of CPU time on a Cray X-MP computer.

Using the largest of our clusters, we obtain $d_{\text{B—N}} = 1.565$ Å and $d_{\text{B—P}} = 1.906$ Å, which corresponds to the lattice constants 3.614 Å for *c*-BN and 4.402 Å for *c*-BP [measured values: 3.615 Å (Ref. 19) and 4.538 Å (Ref. 33), respectively]. Our valence-band widths are 24.8 eV for *c*-BN (experimental: 22 eV, Ref. 34) and 22.4 eV for *c*-BP (experimental: 17 eV Ref. 35). As discussed in Ref. 37, our calculated valence-band widths are larger than the experimental ones because of the use of a minimal basis set to describe the host: Five Slater orbitals for B and N ($1s,2s,2p$), nine for P ($1s,2s,2p,3s,3p$). The better agreement with experiment in the case of *c*-BN than *c*-BP reflects the fact that the inclusion of a set of vacant *d* orbitals is more important for P than for B or N: A similar situation occurs in diamond[6] (23.9 versus 24.2 eV) and silicon (15.8 versus 12.4 eV).

In contrast to diamond or silicon which are 100% covalent, III-V compounds are partly ionic. This results in a small net charge on each atom, i.e., a long-ranged Coulomb interaction. It is well known that the resulting Madelung energy may contribute significantly to the total energy of the system. However, in the present calculations, we are only interested in *total energy differences* for various positions of an *electrically neutral* (or almost neutral) impurity, i.e., the corrections to the PES of H^0 due to the Madelung energy are extremely small. Since all the electrostatic interactions within the clusters are included, only the part of the Madelung energy from *outside* the clusters is neglected. Were this correction significant, cluster size effects would be large. In the present calculations, these effects are small (e.g., from $B_4P_4H_{18}$ to $B_{22}P_{22}H_{42}$), comparable in magnitude to those obtained for H in diamond[6,7] and silicon.[11] Therefore, the inclusion of the Madelung energy is not necessary in the present work. However, the presence of an effective charge on each host atom affects the impurity wave function. This localized effect of the ionicity of the host is important (see Sec. IV). Despite the existence of an effective charge on each host atom, the covalent character clearly dominates. It can be estimated via the *degree of bonding*.[42] It is 0.00 if there is no covalent character (purely ionic case), 1.00 for a purely covalent two-electron bond, 2.00 for a four-electron bond, etc. The degrees of bonding are 0.88 in *c*-BN and 0.95 in *c*-BP, which reflects the fact that *c*-BP is much more covalent than *c*-BN.

III. H^0 IN *c*-BN AND *c*-BP

We found three minima of the PES for neutral interstitial hydrogen in each host. Two of them correspond to a

TABLE I. Total energy differences (in eV) between the various minima of the potential-energy surface for neutral interstitial H in *c*-BN, *c*-BP, diamond (Refs. 6 and 7), and silicon (Ref. 11). The zero of the energy corresponds to H^0 at the BC site with first and second NN relaxed (in C_{3v} symmetry). The host atoms around the *T* sites are not relaxed. The last column gives the energy of the perfect cluster with H^0 far outside relative to that of H^0 at the BC site. All the results correspond to PRDDO calculations in the clusters $HB_{22}N_{22}H_{42}$, $HB_{22}P_{22}H_{42}$, $HC_{44}H_{42}$, and $HSi_{44}H_{42}$, respectively.

Host	BC	T_B	T_N or T_P	$H=\infty$
c-BN	0	1.24	2.81	−4.56
c-BP	0	0.45	0.68	−3.70
	BC	T		$H=\infty$
Diamond	0	2.70		−5.10
Silicon	0	0.89		−0.81

nonbonded configuration, with H^0 at either one of the two inequivalent tetrahedral interstitial sites: T_B, surrounded by four boron nearest neighbors (NN) and T_N or T_P, surrounded by four nitrogen or phosphorus NN. The third minimum corresponds to a bonded configuration, with H^0 near the center of a relaxed B—N or B—P bond (BC site). The total energy differences between the BC site (with first and second NN relaxed in C_{3v} symmetry), the *T* sites (unrelaxed[43]), and the perfect cluster with H^0 far outside, are given in Table I. Note that the latter energy always is negative (i.e., H^0 is more stable outside the cluster). However, this number is not proportional to the solubility of H^0, since the BC site for a single H^0 is not necessarily the lowest-energy configuration for hydrogen in a real crystal.

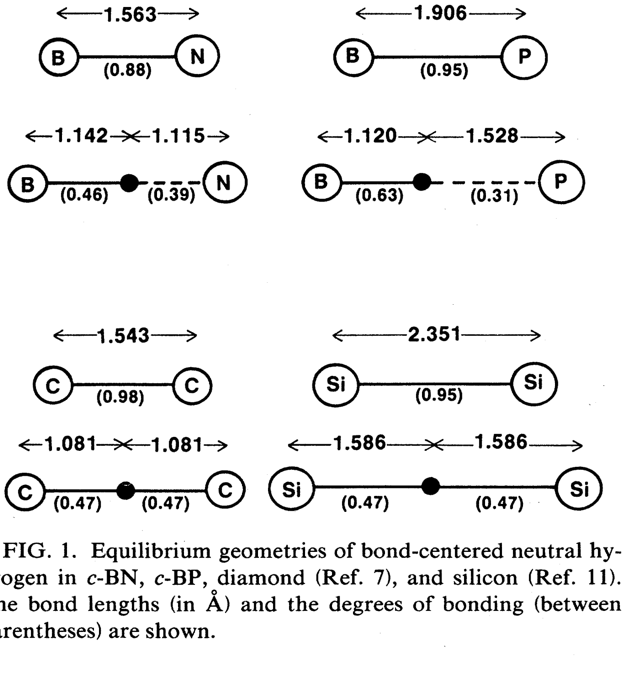

FIG. 1. Equilibrium geometries of bond-centered neutral hydrogen in *c*-BN, *c*-BP, diamond (Ref. 7), and silicon (Ref. 11). The bond lengths (in Å) and the degrees of bonding (between parentheses) are shown.

A. Bonded interstitial hydrogen

The optimized geometries and corresponding degrees of bonding are shown in Fig. 1 for *c*-BN, *c*-BP, diamond, and silicon. A recent modified neglect of diatomic overlap (MNDO) calculation[12] led to the suggestion that in Si, there might be two equivalent positions for the impurity on either side of the middle of a relaxed Si—Si bond, corresponding to H^0 primarily bound to one or the other Si atom. In diamond,[7] silicon,[11] *c*-BN, and *c*-BP, we find only one minimum of the total energy along the bond. It is exactly at the center of the bond in group-IV hosts, and off center in III-V compound semiconductors, with H^0 primarily bound to the group-III atom. Two configurations are *a priori* possible: H^0 bound to B with the odd electron in a nonbonding orbital on P (or N), or vice versa. Which configuration is realized depends on the relative strength of the B—H versus P—H (or N—H) bonds, and on the relative stability of an electron in a nonbonding orbital on P (or N) versus B. In the present case, the B—H, N—H, and P—H bond strengths are quite comparable (3.50, 3.25, and 3.56 eV, respectively), but the nonbonding electron is greatly stabilized by residing dominantly on the more electronegative atom (P or N). Except for the presence of an unpaired electron, the final configuration is reminiscent[44] of that of hydrogen-passivated shallow acceptors in *c*-Si.

The amount of first NN relaxation (43% in *c*-BN, 39% in *c*-BP) is comparable to that in diamond[7] (42%) and silicon[11] (36%). In *c*-BN, B moves by 0.32 Å and N by 0.35 Å, while in *c*-BP, B moves by 0.39 Å and P by 0.35 Å. The second NN relaxations (two types of displacements in C_{3v} symmetry) in *c*-BN (*c*-BP) are of the order of 1 to 2 % (2 to 3 %) and, after readjustment of the first NN positions, lower the total energy by about 0.25 eV (0.65 eV).

The calculated reduced contact spin density at the impurity (relative to that of free atomic hydrogen) is +0.04 in *c*-BN and −0.08 in *c*-BP, i.e., is much smaller than in diamond[7] (−0.19) and silicon[11] (−0.21). The unpaired spin density essentially resides on the two NN, much more on the group-V than on the group-III atom. This indicates a highly localized hyperfine interaction. The calculated contact densities are far too small to predict an average hyperfine frequency for Mu* in *c*-BN and *c*-BP, in particular since the large zero-point motion of the impurity will cause the spin density to be an average over a rather large region surrounding the BC site. The curvature of the energy for displacements of H along the bond is about 5.0 (4.2) times larger than for displacements perpendicular to it in *c*-BN (*c*-BP).

An upper limit to the potential-energy barrier between the BC and the T_B sites has been estimated by displacing linearly all the relaxed atoms from the optimized BC configuration ($\lambda=0$) to the T_B one ($\lambda=1$). The results are shown in Fig. 2. The corresponding barriers for diamond[7] and silicon[11] are 2.4 eV (with $\lambda=0.66$) and 2.0 eV (with $\lambda=0.50$), respectively. In *c*-BN, they are only 1.0 eV ($\lambda=0.50$), and in *c*-BP, 1.50 eV ($\lambda=0.55$). Figure 2 also shows the variation in degrees of bonding as H^0 is moved from the BC to the T_B sites. In both cases, the B—H degree of bonding first slightly increases, and past our "saddle point," rapidly drops as the B—N (or B—P) bond strengthens.

B. Nonbonded interstitial hydrogen

Figure 3 shows the energy profile for H along a ⟨111⟩ direction in *c*-BN, *c*-BP, diamond, and silicon. All the curves correspond to PRDDO calculations with clusters of comparable sizes ($B_{19}N_{19}H_{44}$, $B_{19}P_{19}H_{44}$, $C_{30}H_{40}$, and $Si_{30}H_{40}$). Note that in all cases, the barrier heights are overestimated because of the use of a minimal basis set. The basis-set dependence has been analyzed for diamond[6] and silicon.[11] Because no small clusters are available for *c*-BN and *c*-BP in which large basis-set calculations are computationally tractable, we only show (dotted lines) the large basis-set results obtained for diamond (with a polarized 3-21G* basis set) and silicon (with a 3-21G basis set).

In *c*-BN, we find two minima of the PES along the ⟨111⟩ direction, at the T_B and T_N sites, which are 1.24 and 2.81 eV above the fully relaxed BC site, respectively (see Table I). Only one of them, the T_B site, should be occupied by H, even at low temperatures. The zero-point energy [Fig. 3(a)] relative to the barrier height indicates that a proton as well as a muon are localized. Since the μSR technique can detect metastable states (provided that a muon remains localized for a microsecond or so), it is impossible to predict with certainty whether one or two Mu signals will be observed. Since the height of the potential barrier is overestimated in the present calculations, we believe that only one Mu signal will be seen. However, if both centers coexist at low temperatures, a Mu(T_N)→Mu(T_B) transition should be observed as the temperature is increased. Such transitions have been seen in very ionic hosts such as some cuprous halides.[45] By scaling the calculated (with PRDDO) hyperfine frequencies for Mu in diamond[6] and silicon[11] to the experimental values (tabulated in Ref. 18), we tentatively predict the hyperfine splittings to be about 2150 MHz for Mu(T_B) and 4590 MHz(!) for Mu(T_N). The latter would be the largest hyperfine splitting for Mu in any semiconductor, and indicates a very localized wave function. Also noticeable is the large difference between the two Mu splittings. Since *c*-BN is one of the most ionic of all III-V compounds with N carrying the negative charge, we expect that the electronic wave function on Mu will be repelled (attracted) by the four nitrogen (boron) NN, thus contributing to the localization (delocalization) of the impurity wave function. Thus, at T_N, the impurity has a much larger contact (spin) density than at T_B, leading to a very large difference in hyperfine splittings between the two sites. Further, since such a delocalization of the wave function generally stabilizes the interactions, the large difference in energy between the T_B and T_N sites also is not surprising.

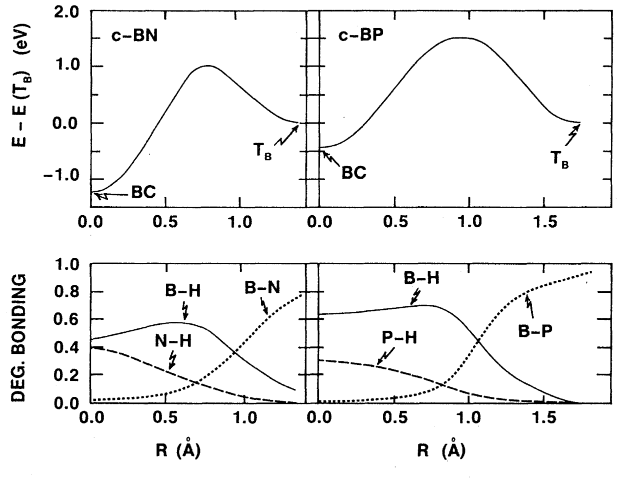

FIG. 2. Upper limit to the BC-T_B potential barrier in *c*-BN (left) and *c*-BP (right). At the BC site, the first and second NN are relaxed. These atoms and H^0 are displaced linearly from the BC site ($\lambda=0$) to the position they occupy at the T_B site ($\lambda=1$). Below the potential barriers, the variations of degrees of bonding (see text) are shown.

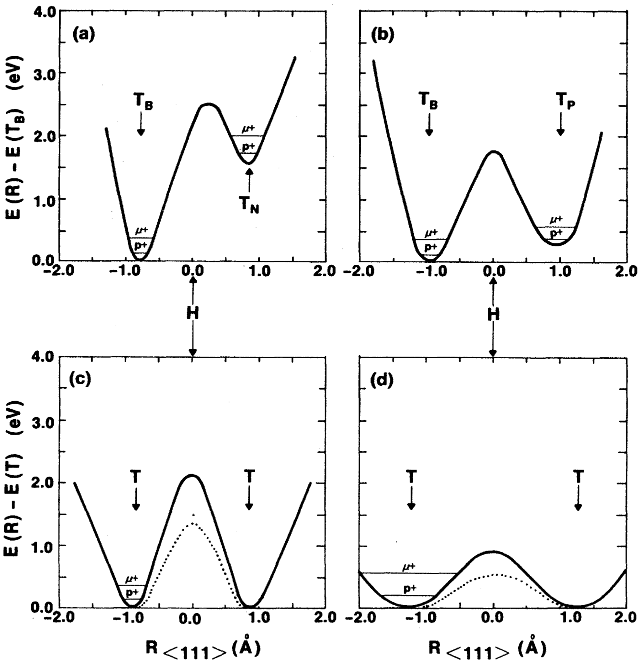

FIG. 3. Energy profiles for neutral interstitial hydrogen along a ⟨111⟩ direction in (a) *c*-BN, (b) *c*-BP, (c) diamond (Ref. 6), and (d) silicon (Ref. 11). The solid lines are PRDDO results obtained with clusters containing at least 4 host atom shells. The dotted curves in (c) and (d) show the reduction in barrier heights obtained with large basis sets (see text). The horizontal lines are the zero-point energies of a proton and a muon in the (harmonic) potentials.

In *c*-BP, the T_P site is higher in energy than the T_B site, but only by 0.23 eV [see Fig. 3(b) and Table I]. The potential barrier between these two minima is overestimated in the present calculations, and H could diffuse at room temperature, via phonon-assisted tunneling along ⟨111⟩ directions. The predicted hyperfine frequencies are about 3030 MHz for Mu(T_B), and 3120 MHz for Mu(T_P). The small difference in energy between the two sites and the similarity between the hyperfine frequencies are consistent with the very low ionicity of *c*-BP as discussed above. At high temperatures, a Mu(T_P) $\rightarrow$Mu(T_B) transition could be observed.

IV. SUMMARY AND DISCUSSION

Energetics. The PES for H^0 in *c*-BN and *c*-BP has three inequivalent minima. The lowest-energy configuration in the perfect bulk crystal is at the (relaxed) BC site, and the second lowest at the T_B site. Upper limits for the BC-T_B barrier heights are 1.0 eV in *c*-BN and 1.5 eV in *c*-BP. These barriers are about 1 eV lower than in diamond[7] and silicon.[11] Since a Mu$\rightarrow$Mu* transition has been observed at high temperatures in diamond[46,47] and in silicon,[48] we anticipate that a similar transition should occur in *c*-BN and (probably) in *c*-BP as well (in *c*-BP, the gain in energy for this transition is low: see Table I). The third minimum of the PES is at the T_N [$E(T_B)+1.57$ eV] or the T_P [$E(T_B)+0.23$ eV] sites. Since the barriers between T sites (Fig. 3) are overestimated in the present calculations, we believe that the T_N site is not significantly populated by H (or Mu), and that a $T_P \rightarrow T_B$ transition should occur at high temperatures. H^0 probably diffuses along T_B-T_P paths, via the saddle point near the hexagonal interstitial site.

Stability. The stability of the T sites correlates with the amount of delocalization of the impurity wave function. Two factors influence this delocalization: the ionicity of the host and, of course, the lattice constant. At T_B, the impurity is surrounded by four positively charged NN. This increases the overlap between the impurity and its host. At T_N or T_P, the NN are negatively charged, which hampers the overlap, distorts and localizes the impurity wave function. Since *c*-BN is much more ionic than *c*-BP, there is a much larger difference in energy and contact spin density between H^0 at T_B and T_N than between H^0 at T_B and T_P.

Electronic structure. The chemical structure of bond-centered H^0 is different in group-IV elemental and in III-V compound hosts. In diamond and silicon, hydrogen bridges a C—C or Si—Si bond in a way somewhat similar to, e.g., diborane or many other stable chemical compounds.[49] In *c*-BN and *c*-BP, H^0 forms a strong bond with the group-III atom (see the degrees of bonding in Fig. 2), and the odd electron is in a nonbonding orbital on the group-V atom. The results of recent calculations[52] of the electronic structure of bond-centered H^0 in GaAs are consistent with the present dicussion. At the T sites, H^0 is roughly atomic, except for the ionicity effects discussed above.

Experimental data in GaP and GaAs. The only experimental information[50,51] in III-V compounds relevant to the present study stems from μSR and level-crossing resonance (LCR) experiments in GaP and GaAs. A single Mu signal is seen in both cases, with frequencies 2914 (GaP) and 2884 (GaAs) MHz. These numbers are within 1% of each other which suggests[50] that Mu is at the T_{Ga} site. Our calculations indicate that in *c*-BN and *c*-BP, the T site surrounded by four group-III NN atoms is the lowest in energy. As mentioned above, it is quite likely that only one Mu center exists in *c*-BN. The lattice constants and ionic characters[25] of GaP and GaAs are very similar (5.451 and 5.653 Å, 11.8 and 9.5 %, respectively). In view of the above discussion, it is not surprising that the hyperfine parameters of Mu are so similar in the two hosts. LCR data[51] show that Mu* is near the BC site, with nearly identical hyperfine tensors in the two hosts, indicating that Ga dominates the interaction. Further, the unpaired spin density primarily resides on P or As, not on Ga. The features are again identical to those we find for bond-centered hydrogen in *c*-BN and *c*-BP. Ongoing work on the structure of hydrogen in AlP and SiC will shed more light on these problems.

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