

## Similarities, differences, and trends in the properties of interstitial H in cubic C, Si, BN, BP, AlP, and SiC

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The potential-energy surfaces (PES's) and electronic structures of neutral interstitial hydrogen in zinc-blende AlP and SiC are calculated and compared with those previously obtained at the same theoretical level in diamond, Si, and zinc-blende BN and BP. The calculations are done in a variety of clusters at the approximate *ab initio* Hartree-Fock level with the method of partial retention of diatomic differential overlap. The PES has three minima in each host: near the bond-centered (BC) site, and at the two inequivalent tetrahedral interstitial (*T*) sites. At the BC site,  $H^0$  always forms a stronger bond with the least electronegative atom. The lowest in energy of the two *T* sites always is the one with the four least electronegative nearest neighbors. In AlP and SiC, the BC site is not the absolute minimum of the PES. Systematic trends in the properties of  $H^0$  with the ionic character of the host are apparent. The diffusion characteristics of H in the various hosts are discussed. The equilibrium structures of  $H^0$  and  $H^+$  are calculated. Our results show that  $\mu^+$  is  $(Mu^*)^+$ . The various transitions involving  $\mu^+$  ( $Mu^* \rightarrow \mu^+$ ,  $Mu \rightarrow \mu^+$ , or  $\mu^+ \rightarrow Mu$ ) observed in Si, Ge, GaAs, or SiC are consistent with our PES's.

### I. INTRODUCTION

Hydrogen is one of the most studied<sup>1-4</sup> impurities in semiconductors, particularly silicon. Hydrogen always is present but has never been observed isolated, except for a recent electron paramagnetic resonance (EPR) spectrum<sup>5</sup> (labeled *AA9*) of bond-centered (BC) hydrogen in silicon. In as-grown silicon crystals, solubilities are low (typically,  $10^{15}$  or less).<sup>1</sup> There are many traps for hydrogen, and only a small fraction of the total hydrogen concentration forms isolated interstitials. The main (known) traps are dangling bonds (e.g., at grain boundaries or vacancies), shallow acceptors and donors, chalcogen impurities,<sup>6</sup> and a variety of other centers, such as transition-metal impurities.<sup>2,3</sup> Hydrogen also activates<sup>7</sup> normally inactive defects, such as substitutional Si in Ge. Further, it has been suggested that hydrogen interstitials interact with each other and form dimers (such as  $H_2$  molecules<sup>8,9</sup> or bond-centered-antibonding pairs<sup>9,10</sup>). Complexes involving many hydrogen atoms (such as platelets<sup>11</sup>) have been observed. There is also evidence<sup>12-15</sup> that hydrogen "clusters" or "precipitates" around already passivated shallow dopants (B or P in Si). Recent experimental studies show that H also plays indirect roles, such as enhancing the formation rate of oxygen-related thermal donors in silicon<sup>16-18</sup> (a microscopic mechanism to explain this role of H has recently been proposed.<sup>19</sup>) At various temperatures, hydrogen is released from specific traps, thus becoming an interstitial for at least some time. It is therefore important to understand the behavior of isolated interstitial hydrogen as well.

In contrast to hydrogen, a considerable amount of experimental information has been obtained about isolated muons in a variety of semiconductors.<sup>20,21</sup> In group IV and III-V hosts, three muonium centers usually are ob-

served at low temperatures for a wide range of dopant concentrations.<sup>20</sup> First, a nonparamagnetic signal is seen at the frequency corresponding to the Larmor frequency of the muon spin in the applied field. This signal, labeled " $\mu^+$ ," usually is associated with the bare positive muon, but could be due to  $Mu^- (= \mu^+ e^- e^-)$  as well. At most, about 10% of incoming muons form this center. Very little else is known about  $\mu^+$ . The other two signals correspond to paramagnetic defects, and are named "normal muonium" ( $Mu = \mu^+ e^-$ ) and "anomalous muonium" ( $Mu^*$ ). At low temperatures, Mu typically accounts for 60% and  $Mu^*$  for 30% of the incoming muons.<sup>20</sup> The muonic atom, Mu, is characterized by an isotropic hyperfine interaction with a somewhat delocalized wave function: the Fermi contact density for Mu in diamond is 83% of the free atom value, but it is only 48% in silicon. In diamond, Mu does not diffuse at low temperatures. Because of the observed isotropy of its hyperfine tensor, it must therefore be localized at the tetrahedral interstitial (*T*) site. In Si and Ge, Mu rapidly diffuses even at low temperatures. On the other hand,  $Mu^*$  always has a highly anisotropic hyperfine tensor, implying a localized defect. Most of the unpaired spin density resides on two nearest-neighbor (NN) host atoms. There is experimental evidence<sup>22-24</sup> that  $Mu^*$  is a bond-centered interstitial in Si and GaAs. In diamond<sup>25</sup> and in irradiated<sup>26</sup> Si, a  $Mu \rightarrow Mu^*$  transition has been observed at higher temperatures, demonstrating the metastability of the paramagnetic species. Models for Mu and  $Mu^*$  in various hosts have been proposed<sup>27</sup> by Symons, and Cox and Symons, on the basis of molecular orbital arguments. Several other transitions have been observed.<sup>20</sup> They involve a change in the charge state:  $Mu \rightarrow \mu^+$  in Si and Ge,  $Mu^* \rightarrow \mu^+$  in Si, Ge, and GaAs, and  $\mu^+ \rightarrow Mu$  in cubic SiC.

Theoretical work on hydrogen in semiconductors has recently been reviewed.<sup>28,29</sup> We will therefore restrict ourselves to a brief overview.

(a) In diamond, the lowest-energy site for  $H^0$  is the relaxed BC site.<sup>30–35</sup> The experimental contact and dipolar hyperfine parameters have been rather well reproduced. The metastable configuration<sup>31–33</sup> with  $H^0$  at the  $T$  site is about 2 eV higher than the BC site, and is a deep minimum of the potential-energy surface (PES).<sup>36,37</sup> The barrier between adjacent  $T$  sites is high enough ( $\sim 1.3$  eV) to localize a muon.<sup>37</sup> The large barrier between the  $T$  and the BC configurations indicates<sup>32</sup> that the  $T$  site should be occupied even though it is much higher in energy than the BC site.

(b) The PES in Si is much flatter than it is in diamond, and the various theoretical predictions differ on many points. Most authors agree that  $H^0$  is metastable in Si, and that the stable configuration is at the relaxed BC site.<sup>31,38–41</sup> Approximate *ab initio* and *ab initio* Hartree-Fock (HF) calculations in clusters<sup>31,38</sup> predict that the  $T$  site is metastable, about 0.9 eV above the BC site, with a low barrier for diffusion between adjacent  $T$  sites ( $\sim 0.5$  eV). Semiempirical modified intermediate neglect of differential overlap calculations<sup>39,40</sup> find the metastable site to be at an antibonding (AB) location, with a low AB-to-AB barrier height, and a high BC-to-BC diffusion barrier. Using density-functional theory in periodic supercells, Chang and Chadi<sup>9</sup> find the  $T$  site to be stable and the BC site metastable, but only 0.25 eV above the  $T$  site. Finally, using a similar approach, Van de Walle *et al.*,<sup>8</sup> predict the BC site to be a minimum of the PES but find no metastable configuration. Their barrier for diffusion between adjacent BC sites is very small (0.2 eV). Both density-functional supercell approaches find that  $H^0$  has weakly negative- $U$  properties, i.e., that the reaction  $2H^0 \rightarrow H^+ + H^-$  is slightly exothermic. The hyperfine structure of bond-centered hydrogen or muonium has been calculated,<sup>31,34,38</sup> but no clear picture has yet emerged for the metastable species. At the  $T$  site, HF-based calculations<sup>38</sup> find an atomic-like impurity (irrespective of basis set or cluster size) while the experimental data show that the wave function is about 50% delocalized. The experimental value of the contact spin density has been reproduced<sup>42,43</sup> for  $H^0$  at the  $T$  site. However, this site is found to be a maximum<sup>8</sup> of the PES at the theoretical level used in these calculations. The dynamic model for Mu proposed by Symons, and Cox and Symons,<sup>27</sup> currently is under investigation.<sup>44</sup>

(c) In Ge, only a few calculations have been performed. The results<sup>34,45</sup> indicate that H in Ge behaves in a manner very similar to H in Si. The BC site probably is the lowest in energy. The  $T$  site has been predicted to be metastable,<sup>34</sup> with an activation energy of 0.49 eV.

(d) As concerning compound semiconductors, a study of the PES's and electronic structures of  $H^0$  in zinc-blende BN and BP has been published.<sup>46</sup> The calculations, performed with the approximate *ab initio* HF method of partial retention of diatomic differential overlap (PRDDO),<sup>47,48</sup> show that the PES has three minima: near the BC site and at the two inequivalent  $T$  sites. Bond-centered hydrogen forms a stronger bond with the

least electronegative (LE) atom (boron in the present case) while the odd electron resides in a nonbonding orbital primarily located on the most electronegative (ME) atom (nitrogen or phosphorus). A similar conclusion was drawn from an *ab initio* HF study<sup>49</sup> of bond-centered  $H^0$  in GaAs. The  $T$  site surrounded by four LE NN ( $T_{LE}$ ) always is lower in energy than the one surrounded by four ME NN ( $T_{ME}$ ). Cluster calculations at the density-functional level found<sup>50</sup> the same to be true in the case of  $H^0$  in GaAs. All of these results are consistent with the interpretation of experimental data<sup>23,24</sup> for muons in GaP and GaAs.

In order to get a broader understanding of the factors influencing the relative stability of  $H^0$  at the various minima of the PES in semiconductors, we report here the results of calculations in zinc-blende AlP and SiC. These new results and the ones obtained at the same theoretical level in diamond,<sup>31,32,37</sup> silicon,<sup>31,38</sup> and zinc-blende BN and BP (Ref. 47) show definite trends. In Sec. II the theoretical method, hosts, and some calculated properties of the perfect clusters are discussed. The results for  $H^0$  in AlP and SiC are contained in Sec. III. The common features, differences, and trends for  $H^0$  in diamond, Si, BP, AlP, SiC, and BN are discussed in Sec. IV. We also discuss the diffusion characteristics and compare the equilibrium structures of  $H^0$  and  $H^+$  at the BC site in the various hosts. We propose that  $\mu^+$  is  $(Mu^*)^+$  and discuss the various observed<sup>20</sup> transitions involving  $\mu^+$  using our calculated PES's. Section V concludes with a brief summary of the main results.

## II. DESCRIPTION OF THE HOSTS AND THEORETICAL METHODS

The host crystals are represented by clusters terminated with hydrogen saturators.<sup>51,52</sup> As discussed in Ref. 46, all the host atoms are four-fold coordinated. For each crystal the lattice constant and host-saturator bond lengths were cyclicly optimized in various clusters to obtain the lowest-energy geometry. Each cluster must contain the same number of atoms of each species to ensure that the average number of valence electrons at each (host atom) site is exactly 4. This restricts the possible centers of the cluster to two sites: the BC and the hexagonal interstitial (H) sites. To test cluster size and center effects, we used five clusters for each host:  $A_4B_4H_{18}$ ,  $A_{13}B_{13}H_{30}$ ,  $A_{22}B_{22}H_{42}$  (built around the BC site), and  $A_7B_7H_{20}$ ,  $A_{19}B_{19}H_{44}$  (built around the H site). Our calculations include all the electrostatic interactions within the clusters, but neglect the long-ranged Madelung potential arising from the electrostatic interactions outside our clusters which would be present for an infinite crystal. This appears reasonable in view of the fact that the ionic character of the compounds under study is low and that the impurity ( $H^0$ ) is electrically neutral. However, we did notice the cluster size effects to be more important<sup>46</sup> in the most ionic host (BN) than in the less ionic ones. These size effects do not influence qualitatively our results, but may have an effect on quantities such as barrier heights between adjacent sites. However, the fact that cluster size effects seem to increase with increasing ionic

characters of the host indicates that the results obtained with small clusters (on supercells) may be unreliable. We plan on further testing these effects with significantly larger clusters. The results reported below correspond to calculations done in our largest clusters ( $A_{19}B_{19}H_{44}$  and  $A_{22}B_{22}H_{42}$ ) unless specified otherwise. These clusters contain all the interstitial sites, and allow lattice relaxations (first and second NN) around the BC site to be included.

In most calculations, interstitial H is at sites of low or no symmetry. Because of the large number of orbitals involved and of the low symmetry, even single-point calculations at the *ab initio* HF level are computationally prohibitive. We performed all of our calculations using the approximate *ab initio* HF method of PRDDO.<sup>47,48</sup> In contrast to *ab initio* HF, which requires the calculation and subsequent manipulation of some  $N^4$  two-electron integrals (where  $N$  is the total number of orbitals), PRDDO is an  $N^3$  method. The reduction from  $N^4$  and  $N^3$  is done without introducing semiempirical parameters. PRDDO has been extensively tested,<sup>47,48</sup> and predicts equilibrium geometries usually as good as (or better than) the ones obtained at the *ab initio* HF level with large basis sets. Further, relative energies of the various minima of a PES usually are reliable. It is, however, a minimal basis-set technique with no correction for electron correlation, except for the antisymmetry of the wave function. The PRDDO wave functions and densities are more qualitative than those obtained at the *ab initio* HF level. Further, potential barrier heights usually are overestimated. Since transition points usually involve larger (and weaker) bonds, they are only approximately described by minimal basis-set and uncorrelated wave functions. Further, the search for saddle points is very difficult (at least one eigenvalue of the Hessian must remain negative at all times) and costly (because of slow convergence). At least some of these difficulties are inherent to the problem rather than to the method used.

A variety of band-structure studies have been published for zinc-blende BN (Refs. 54–57), BP (Refs. 56 and

TABLE I. The experimental fundamental (indirect) band gap  $E_g$  in eV, the difference  $\Delta X$  of (Pauling) electronegativity between the two-component atoms, Pauling's ionic character  $f = 100[1 - \exp(-\Delta X/4)]$ , and the calculated difference of electron affinity  $\Delta E_A$  between the two-component atoms in eV. The crystals are listed in order of increasing ionic character. On the same scale, the ionic characters of GaAs and GaP are  $f = 9.5$  and 11.8, respectively.

Crystal	$E_g$ (eV)	$\Delta X^a$	$f^a$ (%)	$\Delta E_A^b$ (eV)
BP	2.0 <sup>c</sup>	0.1	2.5	+0.47
AIP	3.0 <sup>d</sup>	0.6	13.9	+0.31
SiC	2.4 <sup>e</sup>	0.7	16.1	-0.12
BN	6.4 <sup>f</sup>	1.0	22.1	-0.35

<sup>a</sup>Reference 66.

<sup>d</sup>Reference 63.

<sup>b</sup>Reference 67.

<sup>e</sup>Reference 64.

<sup>c</sup>Reference 62.

<sup>f</sup>Reference 65.

57), SiC (Refs. 58–60), and AIP (Ref. 61). Several properties of elemental and compound semiconductors relevant to the present work are given in Table I. It contains the experimental (indirect) band gaps<sup>62–65</sup>  $E_g$  for the zinc-blende crystals considered here. We characterize the ionic character of the crystals using Pauling's<sup>66</sup> differences in electronegativity  $\Delta X$  and Pauling's ionic characters  $f$ . Finally, the table contains the calculated<sup>67</sup> differences in electron affinity  $\Delta E_A$  between the two-component atoms.

The choice of Pauling's ionicity scale is not unique. Phillip's scale is (qualitatively) similar, and a "self-consistent" scale based on effective charges obtained from dipole moment calculations (with PRDDO) could be used as well. All of these scales are to some extent empirical. However, this is not of critical importance in the present work since the trends we obtain versus the ionicity are qualitative and, to a large extent, independent of the ionicity scale used. Pauling's scale, based on a chemical rather than solid-state perspective, was chosen since we are using molecular-orbital theory in finite clusters.

TABLE II. Comparison between experimental and calculated bond lengths (in Å) and valence-band widths (in eV). The calculated values were all obtained with PRDDO in clusters containing five or more host atom shells, with surface dangling bonds saturated with H atoms located at an optimized distance from the host atoms.

Crystal	Bond length (Å)		Valence-band widths (eV)	
	Calc.	Expt.	Calc.	Expt.
BP	1.906 <sup>a</sup>	1.965 <sup>b</sup>	22.4 <sup>a</sup>	17 <sup>c</sup>
AIP	2.219 <sup>d</sup>	2.360 <sup>e</sup>	20.5 <sup>d</sup>	$f$
SiC	1.844 <sup>d</sup>	1.888 <sup>g</sup>	20.3 <sup>d</sup>	18.5 <sup>h</sup>
BN	1.563 <sup>a</sup>	1.565 <sup>i</sup>	24.8 <sup>a</sup>	22 <sup>c</sup>
C	1.545 <sup>i</sup>	1.544 <sup>e</sup>	23.9 <sup>j</sup>	24.2 <sup>k</sup>
Si	2.352 <sup>l</sup>	2.352 <sup>e</sup>	15.8 <sup>l</sup>	12.4 <sup>m</sup>

<sup>a</sup>Reference 47.

<sup>h</sup>Reference 72.

<sup>b</sup>Reference 62.

<sup>i</sup>Reference 70.

<sup>c</sup>Reference 71.

<sup>j</sup>Reference 37.

<sup>d</sup>Present work.

<sup>k</sup>Reference 73.

<sup>e</sup>Reference 68.

<sup>l</sup>Reference 52.

<sup>f</sup>We found no experimental data in the literature.

<sup>m</sup>Reference 74.

<sup>g</sup>Reference 69.

A comparison between calculated and experimental bond lengths and valence-band widths is shown in Table II. The average error in the calculated bond length of compound semiconductors (0.06 Å too short relative to experimental values) is somewhat larger than expected<sup>53</sup> from PRDDO calculations. As concerning the valence bands, they are too wide because of the use of a finite cluster and of a minimal basis set (see, e.g., the discussion in Ref. 52).

### III. RESULTS FOR AlP and SiC

We studied the PES and electronic structure of H<sup>0</sup> in zinc-blende AlP and SiC following the same procedures we used for diamond,<sup>31,32,37</sup> Si (Refs. 31 and 38), cubic BN and BP (Ref. 47). The PES has three minima: near the (relaxed) BC site and at the two inequivalent (unrelaxed) *T* sites.

To obtain the equilibrium geometry for BC hydrogen, we first optimized the positions of H and its two NN's in H<sub>4</sub>A<sub>4</sub>B<sub>4</sub>H<sub>18</sub>, and used the result as an input for geometry optimizations in H<sub>4</sub>A<sub>22</sub>B<sub>22</sub>H<sub>42</sub>. In the latter cluster, the first and second NN's were optimized (while preserving trigonal symmetry). In the final configurations, the Al atom moves by 0.40 Å and the P atom by 0.56 Å. The Al-H and H-P separations are 1.429 and 1.753 Å, respectively. However, in AlH<sub>3</sub>,  $d(\text{Al-H})=1.72$  Å (Ref. 75) and in PH<sub>3</sub>,  $d(\text{P-H})=1.415$  Å (Ref. 68). Therefore, in our case, H is much further away from P than it is from Al. In fact, the Al-H distance is shorter than would be expected. The "degree of bondings"<sup>76</sup> is an index defined from the density matrix which takes the values 0.00 for a perfectly ionic bond with no covalent character, 1.00 for a perfectly covalent two-electron bond, etc. In the present case, we get  $d(\text{Al-H})=0.60$  and  $d(\text{P-H})=0.23$ , showing that Al dominates the interaction. Most of the unpaired spin density resides in a nonbonding orbital primarily localized on the P atom. We found no other minimum for H<sup>0</sup> along this bond in a conformation where it would be bound to P rather than Al. Note that the dissociation energies of the P—H and Al—H bonds in the diatomic molecules<sup>66</sup> are comparable (3.1 and 3.0 eV, respectively).

In the case of BC hydrogen in SiC, the situation is qualitatively the same: Si moves by 0.35 Å and C by 0.49 Å. In the final configuration,  $d(\text{Si-H})=1.301$  and  $d(\text{C-H})=1.389$  Å. Si—H and C—H bond lengths<sup>68</sup> in SiH<sub>4</sub> and CH<sub>4</sub> are 1.480 and 1.091 Å, respectively, i.e., the Si—H bond in SiH<sub>4</sub> is longer than it is for H in the BC configuration. Our results show that the Si—H bond largely dominates for BC hydrogen in SiC: the degrees of bonding are  $d(\text{Si-H})=0.74$  and  $d(\text{C-H})=0.19$ . This comes a little as a surprise, since the C—H bond is stronger than the Si—H bond (the bond strengths<sup>68</sup> of the H—CH<sub>3</sub> and H—SiH<sub>3</sub> bonds are 4.5 and 3.9 eV, respectively), and intuition would favor a configuration where the C—H bond dominates. However, as will be discussed in the next section, the bond strength is not the only factor determining the stability of this conformation. The odd electron is again located in a nonbonding orbital primarily on the C atom.

In the unrelaxed lattice, the two inequivalent *T* sites are local minima of the PES, the lowest of the two being the *T* site surrounded by four Al or Si NN's, i.e., by the four LE NN's (*T*<sub>LE</sub> site). For both AlP and SiC, we found the *T*<sub>LE</sub> site to be lower than the BC site (even with first and second NN relaxed and no relaxation around the *T*<sub>LE</sub> site) by 0.36 and 0.09 eV, respectively. Thus, the *T*<sub>LE</sub> site becomes the stable site for H<sup>0</sup> in these two compounds.

### IV. COMPARISONS AND TRENDS

We now collect the data for H<sup>0</sup> in diamond, Si, BN, BP, AlP, and SiC. Most of the results for the first four hosts have been published separately.<sup>31,32,37,38,46,51,52</sup> However, we complemented these results with new calculations wherever some of the needed information was lacking.

#### A. Bond-centered hydrogen

A comparison of the initial (no H, perfect lattice) and final (H at the fully relaxed BC site) configurations is shown in Fig. 1. The bond lengths are shown to scale and the various atoms are represented by circles with radius equal to their covalent radius.<sup>77</sup> The figure clearly shows that there is much more overlap between H and the LE atom than between H and the ME atom. Bond lengths and degrees of bonding<sup>76</sup> for the same configurations are also shown. As an example, Fig. 2 shows the spin distribution for H at the BC site in BP. For all the compound hosts studied, most of the unpaired electron density resides on the ME atom nearest to H. Since PRDDO is a minimal basis-set approximation to *ab initio* HF, its calculated wave functions are less reliable than its energies. Our best estimate of the fraction of the total spin density on H and its two NN's is shown in Table III.

#### B. BC-*T*<sub>LE</sub> barrier

The potential-energy barrier between H at the (fully relaxed) BC site and H at the (unrelaxed) *T*<sub>LE</sub> site have been calculated by linearly displacing all the atoms from the positions they occupy in the BC configuration ( $\lambda=0$ ) to that in the *T*<sub>LE</sub> configuration ( $\lambda=1$ ). This process overestimates the barrier height. At present, PRDDO is not equipped to find true transition-point geometries. However, even if we could guarantee that (at least) one of the eigenvalues of the Hessian is negative during the geometry optimization process, the barrier height would still be overestimated because of the use of a minimal basis set and of the lack of electron correlation. Figure 3 shows the barriers as well as the changes in degrees of bonding between the various atoms as  $\lambda$  varies from 0 to 1. The following should be noted: (a) the BC-*T*<sub>LE</sub> barrier heights are significantly lower for compound than for elemental semiconductors, (b) the (LE atom)—H bonding clearly dominates, while the (ME atom)—H bonding dies out very rapidly as  $\lambda$  increases, and (c) for AlP and SiC, the energy at the *T*<sub>LE</sub> site is lower than that at the BC site.

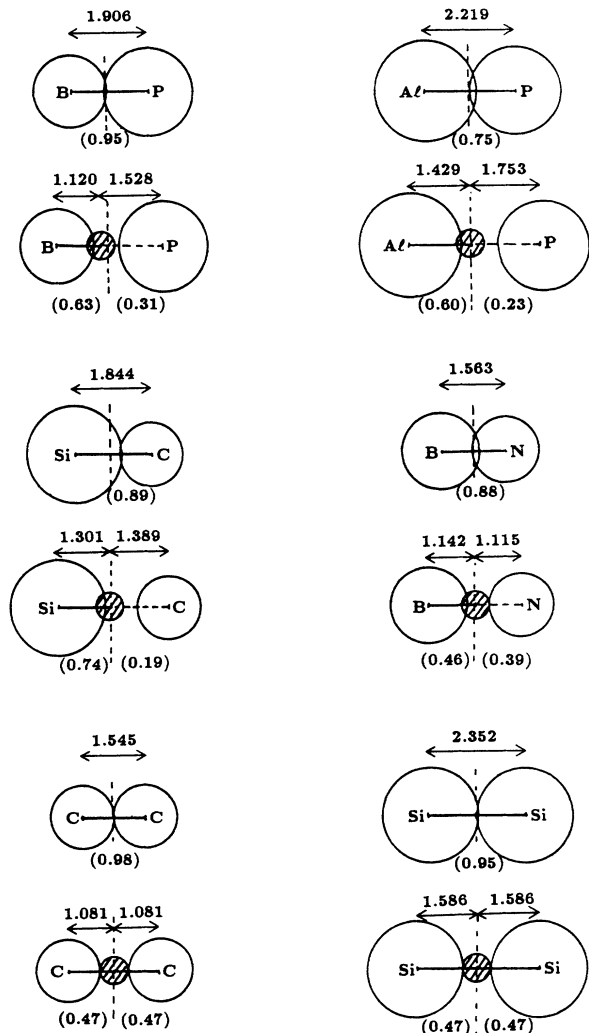


FIG. 1. Comparison of the geometries for the undisturbed bonds and the bonds containing bond-centered hydrogen (shaded circle). The vertical lines show the positions of the (geometrical) centers of the bonds. The bond lengths are drawn to scale using the covalent radii (Ref. 77) of the various atoms. Bond lengths (in Å) and degrees of bonding (Ref. 76) in parentheses are shown.

TABLE III. Fraction (in %) of the unpaired density for  $H^0$  at the BC site, associated with H, its LE NN, and its ME NN. If the spin density of the second NN's to H is added, we account for all of the odd electron, to a good approximation.

Host	Net spin density (in %) associated with		
	H	its LE NN	its ME NN
BP	-6	49	68
AlP	+8	16	75
SiC	-10	20	80
BN	+3	52	48
C	-17	70	70
Si	-16	65	65

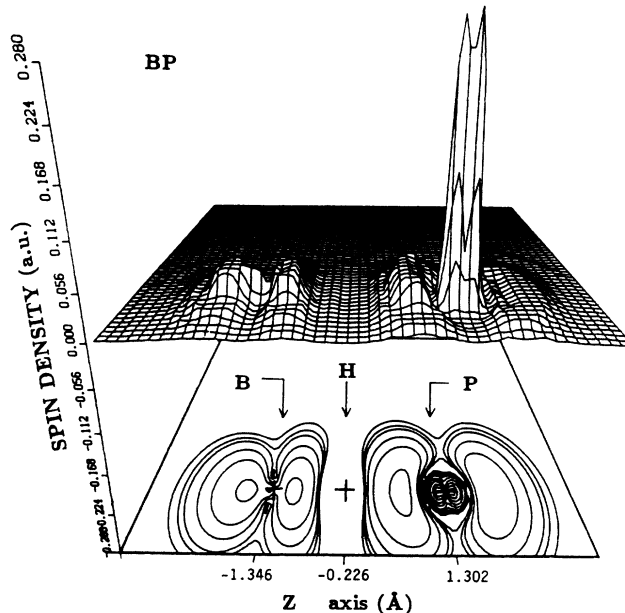


FIG. 2. Spin-density distribution for H at the BC site in BP calculated at the PRDDO level. An estimate of the net spin density associated with the three atoms shown is in Table III.

### C. $T$ sites

For all compound semiconductors, the energy for  $H^0$  at the  $T_{LE}$  site is lower than at the  $T_{ME}$  site. In our notation, the  $T_{LE}$  site is the one with the four LE host atoms (B, Al, Si) as NN, and  $T_{ME}$  refers to the  $T$  site surrounded by four ME host atoms (P, N, C). The PES for  $H^0$  displaced between adjacent  $T$  sites along a  $\langle 111 \rangle$  direction are shown in Fig. 4. As discussed above, the barrier heights are overestimated. A study of the effects of basis-set size on these barriers can be found in Refs. 37 and 38. However, the relative energies of the two  $T$  sites results from a comparison between two *minima* of the PES (rather than between a minimum and a saddle point). Since the methodology is much more reliable at describing minima, the difference in energy between the two  $T$  sites is a quantitative prediction.

We attribute the fact that  $E(T_{LE}) < E(T_{ME})$  to the difference in overlap between the electronic wave function of the impurity and its four NN's. At the  $T_{LE}$  site, the wave function is attracted by its four (positively charged) NN's. This delocalizes the wave function and stabilizes the interactions. At the  $T_{ME}$  site, the wave function of the impurity is repelled by its four (negatively charged) NN's. This repulsion tends to localize the wave function at a cost in energy. The correlation between the stability of the site and the effective charge on the NN's is shown in Fig. 5, where we plot the calculated difference in energy between the  $T_{LE}$  and  $T_{ME}$  sites versus the Pauling ionic character  $f$  (Table I).

### D. Relative energies

Table IV contains the calculated energy differences between  $H^0$  at the BC site with first and second NN's re-

TABLE IV. Energies at various sites for  $H^0$  relative to the energy at the fully relaxed BC site. The last column refers to the energy of the perfect clusters with  $H^0$  far outside. All the energies are in eV.

Host	BC	$T_{LE}$	$T_{ME}$	$\infty$
BP	0.00	+0.45	+0.68	-3.70
AlP	0.00	-0.36	+0.49	-2.03
SiC	0.00	-0.09	+0.97	-3.99
BN	0.00	+1.24	+2.81	-4.56
C	0.00		+2.70	-5.10
Si	0.00		+1.45	-0.25

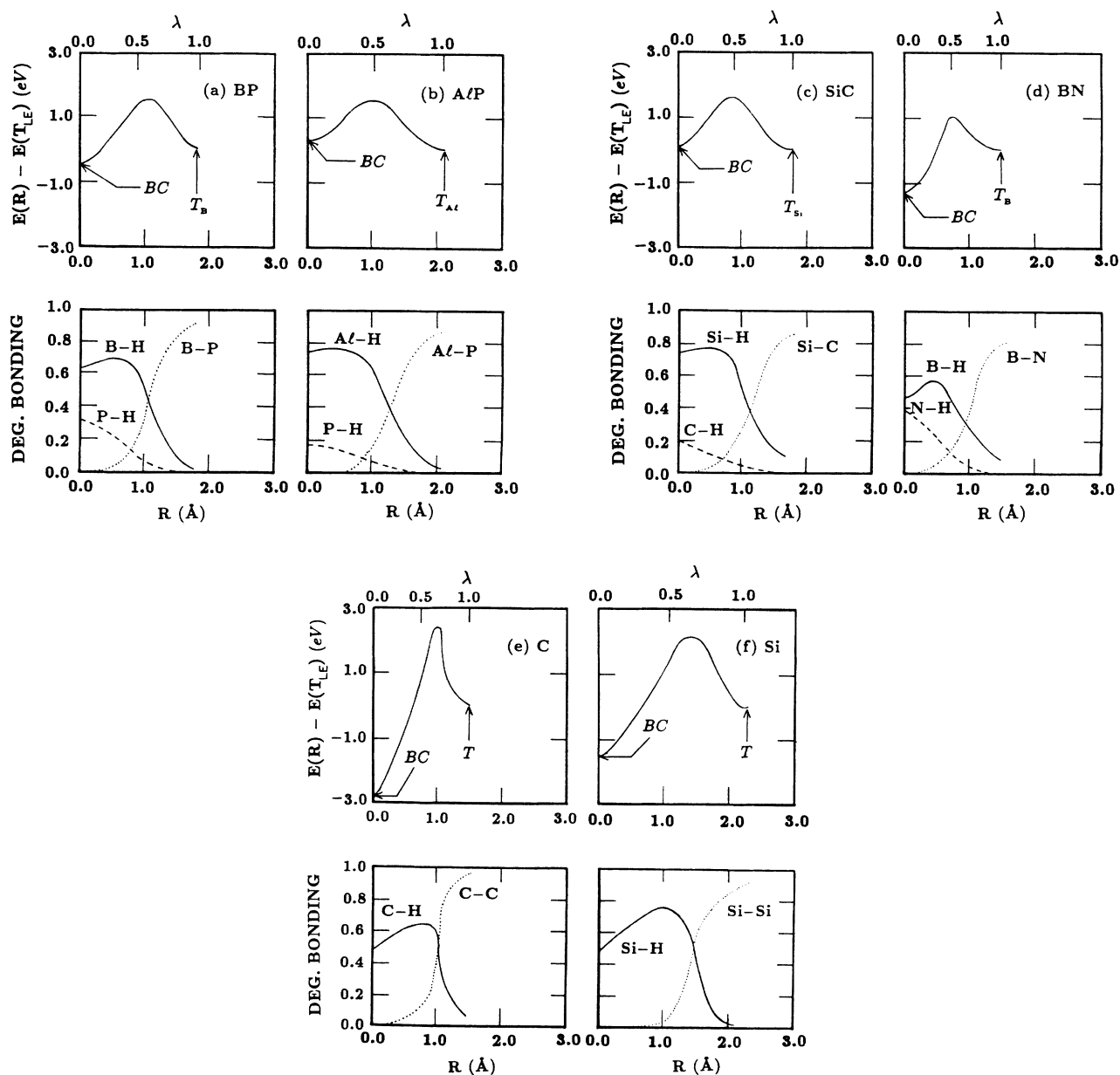


FIG. 3. Estimates (upper limits) of the potential barrier for H between the BC ( $\lambda=0$ ) and the  $T_{LE}$  ( $\lambda=1$ ) sites (see text). The variations of degrees of bonding between the three relevant pairs of atoms are also shown.

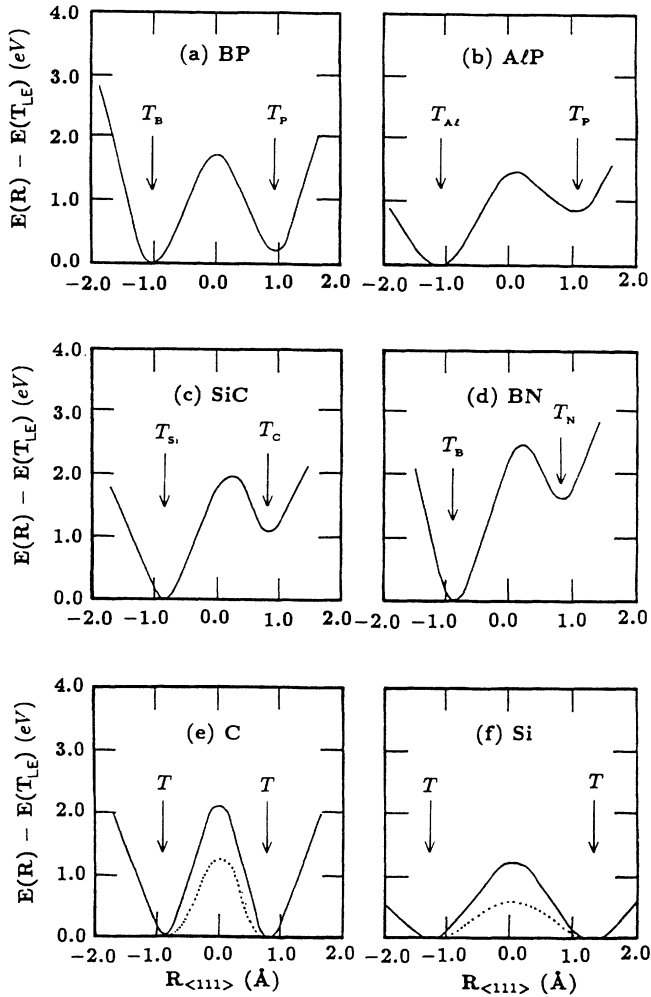


FIG. 4. PES along a  $\langle 111 \rangle$  direction for  $H^0$  displaced between the  $T_{LE}$  and the  $T_{ME}$  sites. The PRDDO (and *ab initio* HF, minimal basis sets) barrier height is overestimated (see text). The dashed curves in (e) and (f) show the barriers calculated with large basis sets at the *ab initio* HF level.

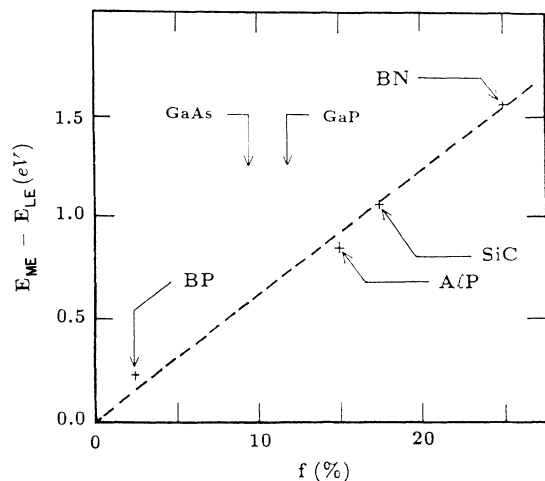


FIG. 5. Difference in energy between the two  $T$  sites vs the Pauling ionic characters  $f$  (Table I). No calculations are available for GaP and GaAs, but arrows point to their locations on the ionicity scale.

laxed ( $E=0$ ) and  $H^0$  at the  $T_{LE}$  and  $T_{ME}$  sites, as well as  $H^0$  far outside the perfect cluster. In the case of Si, a previously published<sup>38</sup> difference in energy between the BC and the  $T$  site was  $-0.89$  eV (in favor of the BC site). This value included only relaxations of the first NN's around the BC site. In the present study, all the energies associated with the BC site correspond to first and second NN's fully relaxed. The following should be noted.

(a) In all cases, we find H to be more stable outside the cluster.

(b) In diamond, Si, BN, and BP, the stable configuration corresponds to  $H^0$  at the BC site. This site is heavily favored over the  $T_{LE}$  site in diamond, Si, and BN, and slightly favored in BP. A  $Mu \rightarrow Mu^*$  transition has been seen in diamond<sup>25</sup> and in silicon.<sup>26</sup>

(c) In AlP and SiC, we find the  $T_{LE}$  site to be the lowest in energy. Because of the large lattice relaxation required to access the metastable state at the BC site, it is unlikely that the latter will be occupied at all. Note that a single Mu species has been observed<sup>78</sup> in cubic SiC, but no  $Mu^*$  has been detected.

### E. Diffusion characteristics

A quantitative description of diffusion properties requires the knowledge<sup>79</sup> of PES's, in particular saddle-point configurations and energies. These quantities always are difficult to calculate, in particular for hydrogen since it is not known how much the (heavy) host atoms relax during the diffusion of the (light) interstitial. Further, tunneling<sup>80</sup> may play a role in some cases. Until high-level molecular-dynamics<sup>81</sup> calculations can be carried out down to low temperatures, the knowledge of the details of hydrogen diffusion will necessarily be based on an approximate static PES. Molecular-dynamics calculations assume PES's and force constants. As discussed above (Sec. I), there are disagreements about the PES of H in Si, ranging from the existence and location of a metastable minimum of the energy to the location and energy of saddle points. Our discussion of the diffusion of H in the hosts considered here is based on the available  $\mu$ SR data (for muons in diamond and silicon), on recent hydrogenation data (in Si), and on our PES's.

(a) *Experimental evidence.* In all the hosts where bond-centered muonium ( $Mu^*$ ) has been observed (C, Si, Ge, GaP, GaAs), the hyperfine tensor is highly anisotropic<sup>20</sup> implying that  $Mu^*$  is localized and does not rapidly diffuse between neighboring BC site (this would average out the anisotropy). The hydrogen analog of  $Mu^*$  (the  $AA_9$  center<sup>5</sup>) also is highly anisotropic. This rules out direct BC-to-BC diffusion, even for an impurity as light as a muon. In diamond, the metastable species, Mu is localized. In Si, Mu is highly mobile even at low temperatures. Recent hydrogenation data<sup>82</sup> show that the activation energy of H in Si is of the order of 0.5 eV, in the range 1200 °C down to room temperature. We find H to be localized at the BC site in diamond and Si, localized at the  $T$  site in diamond [Fig. 4(e)] and mobile along  $\langle 111 \rangle$  directions ( $T$ - $H$ - $T$  paths) in Si with an activation energy

of 0.59 eV [Fig. 4(f)].

(b) *Diffusion of H in Si.* Our calculations for H in Si are consistent with the following picture for H diffusion at low temperatures. Hydrogen self-traps at the BC site where it stays a “long” time. H then jumps to a  $T$  site and rapidly diffuses along  $T$ - $H$ - $T$  paths until the conditions are right (phonons, vicinity of a defect, etc.) for it to self-trap again at a BC site where it stays a long time, etc. The actual motion occurs between  $T$  sites.

(c) *Predictions for compound semiconductors.* As mentioned above, the barrier heights calculated with a minimal basis set (PRDDO or *ab initio* HF) are overestimated. Large basis-set calculations<sup>37,38</sup> show convergence towards the dashed barriers in Figs. 4(e) and 4(f). For compound hosts, similar calculations are much more expensive because there are no acceptable small clusters containing all the desired sites. Therefore, we base our discussion on the barrier heights relative to the ones in diamond (H is localized at the  $T$  site) and silicon (H diffuses along  $T$ - $H$ - $T$  paths).

(i) In cubic BN, H and Mu are localized at the  $T_B$  site and the diffusion of H should be slow even at high temperatures [Fig. 4(d)].  $\mu$ SR data in BN should be similar to those in diamond, with a single Mu species, and a stable  $\text{Mu}^*$  species (see Table IV).

(ii) In cubic SiC, we also expect a single Mu signal, corresponding to the  $T_{LE}$  site, with no metastable state at the  $T_{ME}$  site, but with the possibility of a metastable state at the BC site which is only 0.09 eV higher in energy. Our PES is consistent with H trapped at a  $T_{LE}$  site at a low temperature.

(iii) In AIP, the lowest-energy site is the  $T_{LE}$  site, as in SiC, but the BC site is much higher (0.45 eV). This renders the probability for H to occupy a BC site in AIP very low. Again, we expect only the  $T_{LE}$  site to be occupied. However, the barrier for diffusion between  $T$  sites in AIP is only slightly higher than it is in Si. We therefore anticipate diffusion (but without self-trapping at the BC site).

(iv) In cubic BP, all three minima of the PES (BC,  $T_{LE}$ ,  $T_{ME}$ ) are rather close in energy with the absolute minimum at the BC site and a barrier height between the  $T_{LE}$  and  $T_{ME}$  site intermediate between those in C and Si. We expect one  $\text{Mu}^*$  and two Mu signals in BP, with  $\text{Mu}^I \rightarrow \text{Mu}^{II}$ ,  $\text{Mu}^I \rightarrow \text{Mu}^*$ , and  $\text{Mu}^{II} \rightarrow \text{Mu}^*$  transitions, to be observed.

(v) As a final comment, we note that it is unexpected to find the BC site to be heavily favored in cubic C and in Si, but not in cubic SiC. The fact that we find H primarily bound to Si [see Figs. 1 and 3(c)] while the C—H bond is stronger than the Si—H bond, indicates that there is competition between opposing stabilizing factors. This may render this site less stable.

#### F. $\text{H}^+$ at the BC site

At the BC site, H always forms a three-center two-electron bond. The odd electron is, for the main part, in a nonbonding orbital. Removing this electron results in an  $(A-H \cdots B)^+$  configuration which is essentially as stable (perhaps even slightly more stable<sup>8,9</sup>) than the neutral one. We have reoptimized the geometry at the BC

site after removing the odd electron. In all cases, we can account for most of the change in charge on the H atom, its NN and second-NN atoms. The geometries and electronic structures change very little, and  $\text{H}^+$  remains strongly bound to the LE atom. The bond length between H and its NN changes on the average only by 0.12 Å with no apparent trend with the ionic character of the host. In the positive charge state, bond-centered hydrogen tends to move towards the host atom with which its bond strength is the largest (e.g., towards C in SiC). However, when an electron is removed from a cluster while H is at a  $T$  site, the charge does not come off hydrogen or its immediate neighborhood, but off the many host-saturator bonds at the surface of the clusters. This is independent of cluster size. Therefore, removing an electron when H is at the  $T$  site is not a stabilizing factor (this was noted<sup>8</sup> by Van de Walle *et al.*). At the  $T$  site, H remains atomic even in  $p$ -type material.

This implies that the observed  $\mu^+$  signal can only correspond to a bond-centered muon with no odd electron in a nonbonding orbital, i.e., that  $\mu^+$  is in fact  $(\text{Mu}^*)^+$ . The  $\text{Mu} \rightarrow \mu^+$  transition observed in Si and Ge would therefore correspond to a  $T \rightarrow \text{BC}$  transition with a change of charge state.<sup>20</sup> In these hosts, the BC site is lower in energy. The  $\text{Mu}^* \rightarrow \mu^+$  transitions seen in Si, Ge, and GaAs, simply corresponds to a change in the charge state (loss of an electron or capture of a hole) with no significant change in the local geometry. This is consistent with the fact that  $\text{Mu}^* \rightarrow \mu^+$  transitions occur at lower temperatures than the  $\text{Mu} \rightarrow \mu^+$  transitions.

Finally, the  $\mu^+ \rightarrow \text{Mu}$  transition seen<sup>78</sup> in SiC is the transition from the BC site (in the positive charge state) to the  $T$  site (with capture of an electron). The latter is lower in energy according to our calculations.

Note that in the cases where a  $\text{Mu}^* \rightarrow \mu^+$  transition is observed (Si, Ge, GaAs), different relative amplitudes of the  $\mu^+$  and  $\text{Mu}^*$  signals should be seen in the dark or under illumination with light. This is consistent with the fact that the only successful observation of paramagnetic hydrogen in a semiconductor (the  $A A 9$  center in Si) was performed under illumination.<sup>5</sup> Light releases electrons which, captured by the  $p^+$  or  $\mu^+$  defect, form the paramagnetic center  $A A 9$  or  $\text{Mu}^*$ .

## V. CONCLUSION

We have calculated the properties of interstitial hydrogen in cubic AIP and SiC, and compared the results to earlier ones obtained at the same theoretical level in C, Si, BN, and BP. The key results can be summarized as follows.

(1) At the BC site, H forms a strong bond with its LE NN. Only two electrons participate in the  $A-H \cdots B$  three-center bond, and the odd electron resides in a nonbonding orbital primarily located on the ME atom. Since this odd electron does not participate in the bonding, the defect is easily ionized. The equilibrium geometry of the  $(A-H \cdots B)^+$  configuration is very similar to that of  $(A-H \cdots B)^0$ .

(2) Of the two inequivalent  $T$  sites in zinc-blende compound semiconductors, the  $T_{LE}$  site for H always is lower energy than the  $T_{ME}$  site. The difference in energy for H



at those two sites varies linearly with the (Pauling) ionic character of the hosts. Removing an electron from the cluster with H at a  $T$  site results in the charge coming off as far away as possible from the impurity (in our case: the surface of the cluster). The electron (essentially  $1s$ ) is strongly bound to the proton and the  $T$  site species (Mu) remains electrically neutral even in  $p$ -type material.

(3) An analysis of the various neutral and positively charged configurations leads us to conclude that the  $\mu^+$  center is in fact  $(\text{Mu}^*)^+$ , i.e., the BC species with no odd electron in the nonbonding orbital. The various observed transitions between muon states are therefore (a)  $\text{Mu} \rightarrow \text{Mu}^*$  (in C and Si): transition from the metastable ( $T$ ) to the stable (BC) sites of the neutral interstitial; (b)  $\text{Mu}^* \rightarrow \mu^+$  (in Si, Ge, GaAs): ionization of bond-centered muonium; (c)  $\text{Mu} \rightarrow \mu^+$  (in Si and Ge): same as (a) with loss of an electron (capture of a hole); (d)  $\mu^+ \rightarrow \text{Mu}$  (in cu-

bic SiC): transition from the positively charged BC state (metastable) to the neutral  $T$  site (stable).

*Note added in proof.* At room temperature, the  $\mu\text{SR}$  intensities of the Mu and  $\text{Mu}^*$  signals are too small to be observed,<sup>20</sup> and the spectrum consists entirely of the diamagnetic signal, labeled  $\mu^+$ . Recent channeling data<sup>83</sup> at room temperature indicate that this center is at the BC site, in agreement with the conclusions of the present work.

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