Hydrogen and hydrogen dimers in c-C, Si, Ge, and α-Sn

S.K. Estreicher and M.A. Roberson
Physics Department, Texas Tech University, Lubbock, Texas 79409-1051

Dj. M. Maric
Swiss Center for Scientific Computing, 6928 Manno, Switzerland
(Received 17 June 1994)

The relative stabilities of hydrogen at (or near) the tetrahedral interstitial and bond-centered sites as well as that of hydrogen dimers in the molecular and bond-centered–antibonding configurations are calculated at the *ab initio* level in molecular clusters for c-C, Si, Ge, and α-Sn. The trends show that the lowest-energy configurations change as one goes down the Periodic Table. The relative stability of the possible equilibrium sites affects which charge states of H are likely to be realized in a given host. This in turn affects the diffusion properties of H and its interactions with dopants and other defect centers. The trends in equilibrium geometries and relative stabilities show that silicon is a particular case among group IV hosts in which both isolated interstitials and both dimer states are close to each other in energy. We also examine some properties of two charge states of molecular hydrogen in Si in order to determine the key features of their electron paramagnetic resonance spectra.

I. INTRODUCTION

A. Hydrogen in semiconductors

Interest in the properties of hydrogen in semiconductors is due to its ability to interact with a wide range of defects and impurities, which profoundly affects the electrical and optical properties of the crystal.[1,2] Hydrogen activates[3] normally inactive impurities, passivates shallow acceptors[4] and donors,[5] removes from the gap the deep levels associated with dangling bonds[6,7] and some transition metal impurities,[8] and even catalyzes the diffusion[9] of (at least) interstitial O in Si. Similar properties of hydrogen are observed in a number of elemental and compound semiconductors.

The efficiency of the reactions also depends on the diffusivity of H and the capture radius of H by a given defect center. The diffusivity of H is a function of temperature, but not simply via the usual e^{-E_a/k_BT} term (where E_a is an activation energy). Indeed, the trapping of H at a variety of sites may occur at lower temperatures, resulting in trap-limited diffusion. The diffusivity also depends on the *state* of hydrogen present in the sample: Its lowest-energy site and charge state if it is isolated, or the type of dimer (or larger aggregate) it forms in the particular crystal at hand. The capture radius of H by a defect center varies from very large ($r_c \simeq 50$ Å) if the defect and hydrogen are oppositely charged, to quite small ($r_c \leq 5$ Å) when one or both are neutral. Again, the charge state of the defect and of H is a function of temperature, and/or band-gap light illumination. All these factors make it very difficult to measure the diffusivity of hydrogen in Si, except at very high temperatures when trapping does not occur and Fermi level effects become unimportant.

As will be discussed below, in defect- and impurity-free elemental semiconductors, hydrogen can be found in at least four configurations. Isolated, it is at a relaxed bond-centered (BC) site or at (or near) a tetrahedral interstitial (T) site. Paired, it forms a molecule at (or near) a T site or a "bond-centered–antibonding" complex. These centers are labeled H_{BC}, H_T, H_2^T, and H_2^*, respectively. The isolated BC species exists in the 0 and +1 charge states, and interstitial H at the T site is neutral or negatively charged. The configurations are shown in Fig. 1. We do not consider here larger aggregates.

B. Experimental information

For many years, experimental information about isolated H in 1c-C, Si, and Ge was only available from studies of muonium, a light pseudoisotope of hydrogen with mass $m_\mu \simeq m_p/9$. Early muon spin rotation (μSR) studies[10] have shown that, in general, two paramagnetic and at least one nonparamagnetic center form in elemental semiconductors. These defect centers are (i) Normal muonium or Mu_T^0, which has an isotropic hyperfine (hf) tensor, and corresponds to atomiclike muonium either at the T site or rapidly diffusing among sites of lower symmetry in a way that averages out the interactions to T_d symmetry; (ii) Anomalous muonium or Mu_{BC}^0, which has a highly anisotropic hf tensor (with trigonal symmetry), and corresponds to muonium forming a bridged bond at a BC site. This is a three-center two-electron bond similar to the hydrogen bridged bonds in diborane. The odd electron does *not* participate in the bonding. It resides in a nonbonding orbital primarily localized on the two nearest neighbors (NN's) to the muon. Finally, (iii) non-

 ©1994 The American Physical Society

paramagnetic muonium has been originally labeled "μ^+" and, more recently, "diamagnetic muonium." A number of centers can contribute to this signal. The most important ones are Mu_{BC}^+ and Mu_T^-. The latter should not be denoted μ^+ and neither is diamagnetic because Mu_{BC}^+ has no electron and Mu_T^- has presumably two electrons in an s state and is at best very weakly diamagnetic. We will therefore use the "nonparamagnetic" label or specify explicitly which center is being discussed. At low temperatures and in high-resistivity material, the overwhelming majority of muons form a paramagnetic center. In diamond, less than 8% of the incoming muons contribute to the nonparamagnetic signal at low temperatures, and almost none at high temperature (up to 1000 K).

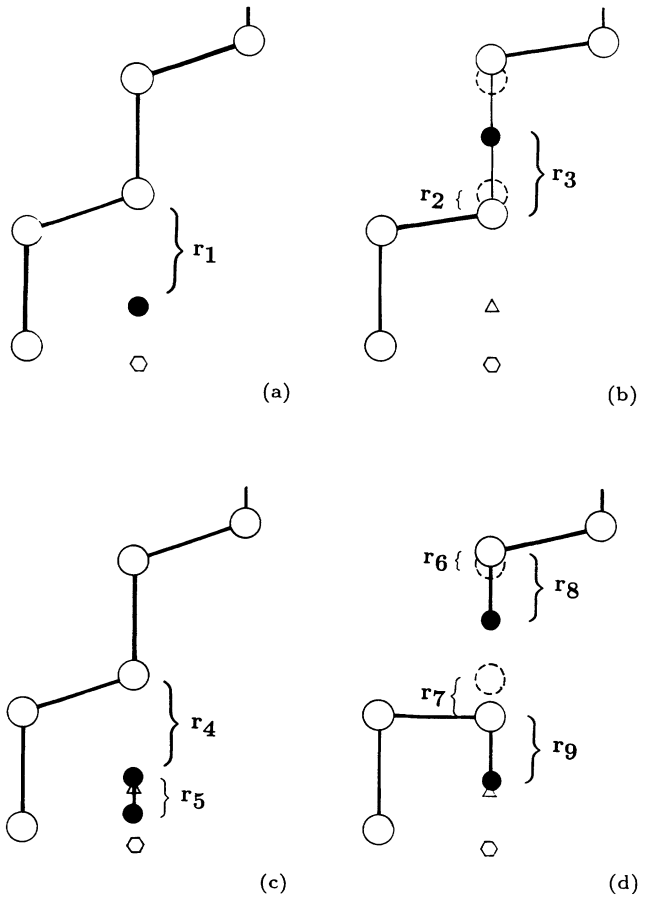

FIG. 1. The four possible H-related centers in defect- and impurity-free elemental semiconductors are (a) hydrogen at (or near) the T site (H_T), (b) hydrogen at the relaxed BC site (H_{BC}), (c) the hydrogen molecule near the T site (H_2^T), and (d) the bond-centered–antibonding pair (H_2^*). The host atoms (open circles) are shown in the {110} plane. The dashed circles are perfect lattice sites and the small full circles are the H atoms. The center of the small triangle (hexagon) is the tetrahedral (hexagonal) site. The relaxations of the NN's to the defect center and the bond lengths are quantitatively correct in the case of Si, and at least qualitatively correct for the other hosts considered here. The distances r_i, $i = 1, \ldots, 9$ have been optimized at the *ab initio* level and are given in Sec. II for the four hosts.

Recent IR absorption, electron paramagnetic resonance (EPR), and new μSR studies have clarified the picture by providing information on the possible states of hydrogen in various hosts under various conditions. These studies look at H itself rather than, indirectly, at a consequence of the presence of hydrogen such as a change in the electrical activity of a specific impurity. The IR absorption study[11] is the identification of the H_2^* defect in high-resistivity (n-type) Si. This defect, shown in Fig. 1(d), has been elusive since its existence was first postulated in diamond[12] and silicon.[13,14] However, the two stretching and two wagging modes have now been clearly identified and calculated,[11] including the various possible D substitutions. Uniaxial stress measurements confirm the C_{3v} symmetry of the defect, and all four IR lines anneal out together around 200 °C.

The EPR studies include two hydrogen-related defects, both in Si. The first, the identification of H_{BC}^0, was first reported[15] in 1987 (the AA9 center) and has now been confirmed.[16] The defect appears at low temperatures in illuminated samples, and anneals out around 200 K. The muonium analog (Mu_{BC}^0) has been observed[10] in c-C, Si, and Ge. Once scaled by the ratio of the muon to proton magnetic moments, the hf tensors of AA9 and Mu_{BC}^0 match very well. The (0/+) level for H_{BC}^0 obtained by deep-level transient spectroscopy (DLTS) is 0.164(11) eV below the conduction band, which is consistent with the annealing behavior of the corresponding EPR center.

Second is the reported EPR observation[17] of what could be a charge state of H_2^T, in Si as well. The charge state is assumed to be -1 and the symmetry axis is $\langle 111 \rangle$. However, as noted by the authors, the spectrum is more complicated than would be expected from an isolated H_2^- molecule in the perfect lattice, and there is a good possibility that the defect observed is part of a larger complex.

The most recent μSR studies are measurements of the total fraction of the nonparamagnetic species in Si as a function of the temperature and dopant concentration [rf-μSR (Ref. 18)]. A preliminary interpretation of the data was published recently.[19] A more complete data analysis will soon be published.[20] The results can be summarized as follows. In high-resistivity Si, the nonparamagnetic fraction is almost zero at low temperatures, but abruptly increases around 140 K. This jump is too sharp to be described by a change of site, and must be assigned to a purely electronic process. It is caused by the ionization of Mu_{BC}^0. Modeling of this process places the Mu_{BC} (+/0) level at 0.22 eV below the conduction band. Note that this ionization energy is similar to that obtained from the DLTS and EPR data discussed above. At higher temperatures (starting around 260 K), a slower but steady increase in the intensity of the nonparamagnetic signal is assigned to the $Mu_T^0 \rightarrow Mu_{BC}^0$ transition, immediately followed by the ionization of the latter. The intensity of the nonparamagnetic signal peaks around 380 K, after which it rapidly drops to zero. This drop is interpreted as follows. At higher temperatures, the BC site becomes unstable, Mu_{BC}^+ is kicked out by phonons, jumps to the T site where it must capture one electron, and becomes Mu_T^0 (or captures two electrons and becomes Mu_T^-). Above 400 K, rapid site change and charge ex-

change processes take place on a submicrosecond time scale, making it difficult to obtain a rf signal. However, longitudinal-field μSR experiments[21] above 450 K clearly show that the rapidly relaxing species is Mu^0_T, not Mu^0_{BC}.

C. Theoretical predictions

Over the past 20 years, theoretical studies of hydrogen and hydrogen dimers in elemental semiconductors have been performed by several groups, at various levels of theory. The major breakthrough occurred with the proposal,[22] followed by the theoretical confirmation by two independent groups, that the most stable site for interstitial hydrogen in diamond[23,24] and silicon[24,25] is the relaxed BC site. Prior to that, only the T-site species was known to exist and except for Mu^0_T, the μSR centers were not properly identified. Together with their charge states, the T and BC species can most likely account for all the observations of hydrogenlike interstitials in semiconductors.

In diamond, the relaxed BC site is substantially lower in energy (about 2 eV) than the T site.[23,24,26–29] The activation energy[29,30] for T-site to T-site hopping (over the hexagonal interstitial site) is high ($\simeq$ 2.5 eV in Ref. 29), suggesting that H_T does not diffuse along this path, except at very high temperatures. A high barrier also needs to be overcome for the T-site species to reach the more stable BC site,[29] a result consistent with the observed thermally induced $Mu^0_T \rightarrow Mu^0_{BC}$ transition near 400 K.[10] A recent semiempirical[31] study of neutral H in diamond finds only the BC site to be stable, and a diffusion mechanism involving direct BC-to-BC diffusion is proposed. At the transition point, the three host atoms involved in two adjacent BC sites are substantially displaced, and their NN's relax as well. The calculated activation energy for this process is 1.9 eV, a number lower than that for the direct T-to-T site diffusion, but still high enough to be consistent with the observed anisotropy of the Mu^0_{BC} hf tensor in diamond. Note that the effective mass for the direct BC-to-BC site diffusion process is large since, in addition to the motion of hydrogen (or muonium), several host atoms must be substantially displaced.

The μSR data[10] in diamond show that, at low temperatures, about 70% of the muons form the Mu^0_T center, 23% the Mu^0_{BC} center, and the rest contributes to the nonparamagnetic signal. As the temperature is increased (data were taken up to 1000 K), a transition from the T to the BC site is observed, but the hf tensor of Mu^0_{BC} remains strongly anisotropic. This indicates that Mu^0_{BC} does not diffuse up to at least 1000 K (this would reduce the anisotropy of the hf tensor). Further, the fact that virtually all the incoming muons form paramagnetic centers implies that no charge states of interstitial hydrogen form in diamond, i.e., that the ionization energy of Mu^0_{BC} is quite large. However, since no data are available in p-type diamond, the existence of a species such as Mu^+_{BC}, resulting from hole capture, cannot be ruled out.

In silicon, the potential energy surface for neutral interstitial H is much more flat than it is in diamond. As a result, the total energy differences are small and the calculated results are sensitive to the details of the approximations involved. Many theorists agree[24,25,32–35] that neutral interstitial H is more stable as H^0_{BC}, and that H^0_T is metastable. However, the T site is found to be stable and the BC site metastable in Ref. 13, and no metastability is found in Refs. 36 and 37. The latter result may be related to the fact that all the atoms in the supercell used were allowed to relax completely for all positions of H, thus eliminating the T-to-BC barrier. A full spin-density-functional (DF) calculation[38] in the same supercell but without lattice relaxation predicts the correct spin distribution when compared to the μSR measurements for Mu^0_T. On the other hand, HF calculations always predict a higher Fermi contact density than experimentally observed. The $Mu^0_T \rightarrow Mu^0_{BC}$ transition observed[10,20] in Si indicates that neutral muonium is metastable and that the stable site is the BC site. The diffusion of H^0_T is predicted[25,29] to occur along a T-to-T site path, with activation energy smaller than 0.59 eV. An alternative mechanism, proposed in Ref. 36, involves direct BC-to-BC diffusion via the mechanism described above in the case of c-C. The small barrier found for this diffusion (less than 0.2 eV) is inconsistent with the large anisotropy of the hyperfine tensors of the AA9 and M^0_{BC} centers, which is possible only if H^0_{BC} is not mobile. Note that the linewidth of Mu^0_T implies a rapidly diffusing ($\simeq 10^{11}\,s^{-1}$) impurity even at low temperatures.

As concerning the charge states of H in Si, there is general consensus that H^+ exists as H^+_{BC} in p-type Si and, above its ionization temperature, in high-resistivity Si. This state was first identified by positron channeling[39] and the site is consistent with the rf-μSR data.[19,20] There is no consensus, however, regarding the abundance and stability of H^- which is H^-_T although there remains little doubt about its existence. It was predicted[13,36] that H is a (weak) negative-U center in Si, i.e., that the reaction $H^0+H^0 \rightarrow H^+ + H^-$ is weakly exothermic. Direct experimental evidence for H^- is lacking, although there is indirect evidence[40] for H^- in n-type material.

Finally, there is consensus among theorists that both the H^T_2 and H^*_2 dimers are stable in Si. However, it is not clear which is the preferred state, even in high-resistivity material. Some authors[13,41] find that H^T_2 is lower in energy than H^*_2, but the opposite is predicted by others.[42,43] There is also disagreement regarding the bond length and orientation of H^T_2, as well as the diffusion properties of H^*_2. If H primarily exists in a charge state in a given sample, for example, H^+_{BC} in p-type Si, one would expect a low probability of dimer formation, as equally charged interstitials would remain far away from each other. We also note that charged states of H^T_2 or H^*_2 are very unlikely. The +1 charge state would have a very weak H–H or Si–H bond, as would the −1 charge state, since the extra electron would have to populate an antibonding orbital.

In germanium, there are fewer experimental data and fewer theoretical predictions. A semiempirical calculation[44] was performed in a large molecular cluster at the CNDO level (CNDO denotes complete neglect of diatomic overlap). Since CNDO is heavily approxi-

mated, the results should be considered qualitative. Further, this study did not include the BC site as a possible configuration. The results show that H^0 is rapidly diffusing along ⟨111⟩ directions with an activation energy of 0.17 eV. The lowest-energy site is off the T site, in an antibonding (AB) configuration. A configuration for H^+ is found off the T site along a ⟨001⟩ direction. Molecule formation at the T site is preferred by 2.5 eV per atom over isolated H^0. The predicted H−H bond length of H_2^T is 0.73 Å and its barrier for diffusion is 0.73 eV.

Two recent and higher-level calculations predict very different behaviors for H in Ge. A first-principles DF study[45] in periodic supercells finds that H_{BC}^+ is the only stable state in p-type Ge, while H_T^- is the only stable state in intrinsic and n-type Ge. In contrast, *ab initio* Hartree-Fock (HF) studies with large basis sets in molecular clusters[43,46,47] provide a very different picture. Neutral H is metastable in Ge. However, in contrast to c-C and Si, H_T^0 is slightly *more stable* than H_{BC}^0. This implies that the BC site is much less populated in Ge than in the lighter elemental semiconductors, since reaching the BC site requires substantially stretching a Ge−Ge bond, which creates a barrier between the T and BC sites. The metastability of the BC site implies that H^+ is uncommon in Ge, since it is a BC species. Further, since H_{BC}^0 is a necessary precursor for H_2^* formation, the H_2^T state should dominate.

D. H (or Mu) in c-C vs Si vs Ge

Theoretical predictions are sensitive to the details of the calculations whenever energy differences between various states are small, and various authors may differ as to what "small" means. Thus, although H is difficult to observe directly in semiconductors for a variety of reasons, one must rely on the available data to determine what is really going on. The most important common features and differences in the observed behavior of H in c-C, Si, and Ge are as follows.

(i) μSR data.[10,19,20] In diamond, most of the incoming muons form the paramagnetic centers Mu_T^0 (about 55%) and Mu_{BC}^0 (about 40%), the rest (less than 8%) form the nonparamagnetic species. A thermally induced $Mu_T^0 \rightarrow Mu_{BC}^0$ transition (in the range 350−450 K) shows that the BC site is the more stable. It also shows that there is a barrier between the T and BC sites. At high temperatures (up to 1000 K), only Mu_{BC}^0 is seen. In high-resistivity silicon and at low temperatures, Mu_T^0, Mu_{BC}^0, and a nonparamagnetic signal coexist, the most abundant one (near 50%) being Mu_T^0. A $Mu_T^0 \rightarrow Mu_{BC}^0$ transition has been seen in irradiated samples. Recent rf-μSR data show that Mu_{BC}^0 ionizes to form Mu_{BC}^+ around 140 K, then, in the range $\simeq 200-300$ K, Mu_T^0 hops to the BC site, where it ionizes as well. Just below 400 K, the muon begins to hop rapidly between the Mu_{BC}^+, the Mu_T^0, and possibly the Mu_T^- states. These reactions occur in times shorter than the 2 μs characteristic of μSR studies. In germanium, no $Mu_T^0 \rightarrow Mu_{BC}^0$ transition is seen. Above 200 K, the nonparamagnetic fraction in Ge is substantially *lower* than in Si.

(ii) Passivation of acceptors.[1] In diamond, we are aware of no reports of H passivation of the B acceptor.[48] Theory predicts[49] that {H,B} pair should form, but be oriented along a ⟨100⟩ direction. In silicon, acceptor passivation is extremely efficient and rather easy to achieve, suggesting a long-ranged $H^+ \leftrightarrow B^-$ attraction. In germanium, however, we are aware of only one report[50] of successful passivation of B in Ge, other attempts having shown no passivation. This argues against an abundance of H^+ in p-type Ge.

(iii) Passivation of donors.[1] Diamond cannot be made n type. In silicon, shallow donors can be passivated by H. Again, pair formation is responsible for the passivation, but the process is less efficient than in the case of acceptors, and donor-hydrogen pairs break up at lower temperatures than the acceptor-hydrogen pairs. In germanium, donor passivation has never been accomplished. This could be due to the rarity of negatively charged H in the sample and/or to the instability of a donor-hydrogen pair at room temperature.

(iv) Thermal effusion.[51] After exposing doped Si and Ge samples to a D plasma (temperature T_{pl}) for 20 h, the total incorporated D and its bonding state were characterized by the thermal effusion technique. Among other results related to the thermal stability of various configurations of D in the crystals, the data show that the total amount of D extracted *increases* with T_{pl} in the case of Si but decreases with T_{pl} in the case of Ge.

Thus there are qualitative differences in the behavior of H as one goes down the Periodic Table. Diamond, Si, Ge, and α-Sn crystallize in the diamond lattice, with bond lengths 1.544, 2.352, 2.450, and 2.810 Å, respectively. The hydrogen chemistry of these elements is very similar. The bond strengths with H are 4.54 (for $H-CH_3$), 3.92 (for $H-SiH_3$), 3.60 (for $H-GeH_3$), and 3.20 eV [for $H-Sn(n-C_4H_9)_3$]. Note that although the numbers for Si and Ge are very close to each other in these comparisons (as they are when using many other parameters), there are striking differences in the way H interacts with these crystals and with defects in these crystals.

E. Content of this paper

In the present paper we contribute to this discussion in the following ways. First, we present the results of *ab initio* and approximate *ab initio* calculations on the equilibrium configurations of isolated H and of H dimers in the four group IV elemental semiconductors c-C, Si, Ge, and α-Sn. We pursued our calculations down to Sn, but not because it is an important semiconductor. In fact, its gap is zero and it is better classified as a semimetal. We did so because we want to push the study of trends as far down the Periodic Table as possible, and plot total energy differences vs lattice constant from the smallest to the largest possible values of a_L. Second, we show that a very simple reason may explain the experimentally observed differences in the behavior of H in Si and

Ge: The relative stability of the T and BC sites is different in the two hosts. This change of relative stability as one goes down the Periodic Table affects not only the diffusion properties of H, but more importantly its charge states, hence the range of its interactions with dopants. Third, we correlate our results to experimental findings, predict the configurations of H in elemental semiconductors, and examine the factors which influence its behavior. Section II describes the results, and the discussion is in Sec. III.

Our calculations were performed at the *ab initio* HF level with split-valence basis sets on all the atoms and polarization functions on selected atoms.[52] *Ab initio* pseudopotentials were used to remove the core orbitals from the calculations. In the cases of Ge and α-Sn, the appropriate relativistic corrections were included. We repeated the H calculations in c-C and Si with the method of partial retention of diatomic differential overlap (PRDDO).[53,54] The latter calculations are more approximate, but do provide excellent geometries and allow us to perform systematic calculations in clusters much larger than are tractable at the *ab initio* level. We used open-shell [unrestricted HF(UHF)] wave functions for isolated H and closed-shell [restricted HF(RHF)] wave functions for H dimers. We repeated several of the RHF calculations at the UHF level to verify that the type of wave function does not affect the result. The transformation from RHF to UHF is accomplished by adding free atomic H to the system (far outside the cluster) in order to generate a spin 1/2 total wave function. These techniques and their application to defects in semiconductors have recently been reviewed.[55]

In all the *ab initio* calculations, the host crystals are represented by a molecular cluster containing 14 host atoms and constructed in such a way that both the T and BC sites have two complete host atom shells around them. The PRDDO calculations were done in the same cluster as well as in clusters containing 44 host atoms, in order to monitor possible cluster size effects. Except for second NN relaxations which lower[29] the energies by a few tenths of an eV, these effects are not important in the present calculations, which focus on *total energy differences* between *local minima* of the potential surface. Extensive studies of cluster size effects[56,57] for both isolated H and H-containing complexes have shown that even our smaller cluster describes many properties of the defects quite accurately. The same conclusion was reached by performing PRDDO calculations in the small cluster and comparing the results to those obtained in the 44 host atom cluster.

In the small cluster, only the first NN's to H_{BC} and H_2^* were optimized. This compensates to some extent the neglect of second NN relaxations. In the cases of H_T and H_2^T, no lattice relaxation was included. We know from earlier studies that lattice relaxation around H_2^T (breathing mode) affects the total energy by an amount comparable to second NN contributions in bound structures such as H_2^*. All the *ab initio* geometry optimizations were performed using gradient-based routines, thus guaranteeing convergence only toward true minima of the potential surface.

II. RESULTS

A. Isolated hydrogen

Figure 2 shows the relative energies of H_T^0 and H_{BC}^0 in elemental semiconductors. The figure shows that in diamond, H_{BC}^0 is substantially lower in energy than H_T^0. In fact, some authors[31] find only the BC site to be a minimum, probably because T is so much higher in energy. As discussed above, this ordering of the T and BC sites is implied experimentally from μSR studies. In Si, we find the BC site to be lower in energy than the T site, but only by a small amount. In Ge, the order is reversed, and this trend is confirmed in the case of α-Sn. This reversal has profound consequences, which are discussed in Sec. III.

The calculated geometries (distances r_1, r_2, and r_3 shown in Fig. 1) are given in Table I. The table also contains the energies of the various sites relative to H^{free} outside the cluster. Note that we always find that it *costs* energy to put H^{free} at the T or BC sites in any elemental semiconductors. The exact amount of energy involved depends on the level of the calculation and on the amount of lattice relaxation allowed around a given site. However, this result conflicts with recent prediction obtained at the DF level[58] which finds a gain in energy. This discrepancy is apparently not due to a uniform shift in the energy scale, as the DF result[58] for the binding energy of H at a dangling bond coincides with the value obtained at the HF level.[59]

One can understand the trend in relative energies shown in Fig. 2 as follows. The stability of the T site increases with the lattice constant simply because a larger volume is available. H^{free} is more stable than H in a cage, and the smaller the cage, the higher the energy of the atom, unless it binds to the cage. We always find a node in the wave function of H_T^0 between the proton and its NN's. The stability of the BC site appears to depend essentially on two factors. The first is the amount of lattice relaxation that can be accomplished. In free radicals, bridged bonds involving H have bond lengths somewhat (typically 15%) longer than the corresponding single (two-electron) bonds. As can be seen in Table I, H

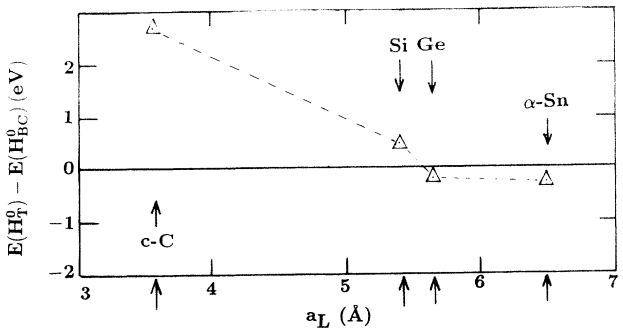

FIG. 2. Energy difference $E(H_T^0)$-$E(H_{BC}^0)$ for c-C, Si, Ge, and α-Sn vs the lattice constant. In diamond and silicon, the BC site is stable and the T site metastable for neutral H. The reverse is true for germanium and tin.

TABLE I. Geometries of the H_T^0 and H_{BC}^0 interstitials in elemental semiconductors. The distances labeled r_1 through r_3, defined in Fig. 1, are in Å. The energy differences are in eV. Note that it costs energy to insert free atomic hydrogen into the various hosts. No lattice relaxation was included for H_T^0, i.e., r_1 is equal to the host-host bond length. Only first NN's were relaxed in the case of H_{BC}^0. These results are from large basis set *ab initio* HF calculations.

	c-C	Si	Ge	α-Sn
r_1	1.545	2.385	2.483	2.829
r_2	0.326	0.383	0.404	0.434
r_3	1.098	1.576	1.645	1.848
$E(H_{BC}^0) - E(H^{free})$	5.10	1.44	1.20	0.78
$E(H_T^0) - E(H_{BC}^0)$	+2.69	+0.45	−0.20	−0.27

can barely squeeze into the BC site in diamond, with a C−H bond length in the bridged bond equal to that of a perfect two-electron bond. The host crystal is too rigid to allow for more relaxation. In Si, Ge, and α-Sn, the softer crystals and longer lattice constants allow virtually optimum relaxation to take place. This accounts for most of the stabilization of the BC site as one goes from diamond to Si and below. The stability of the BC site only moderately increases with the lattice constant from Si to α-Sn and this added stability is partly offset by a decrease in the host-H bond strength. This is the second factor: The bond strengths of group IV elements with H tend to decrease as one goes down the Periodic Table, as noted in Sec. ID, above. Thus the energy of the BC site does not vary much from Si to α-Sn while that of the T site decreases. The two curves cross between Si and Ge.

B. Hydrogen dimers

Figure 3 shows the calculated relative energies of H_2^T and H_2^* in elemental semiconductors. In the case of diamond, the H_2^* complex is clearly favored, as there is simply too little room for a H_2^T molecule in the crystal. As the lattice constant increases, the volume available at the T site increases as well, and molecular hydrogen becomes more favorable. Our calculations predict that

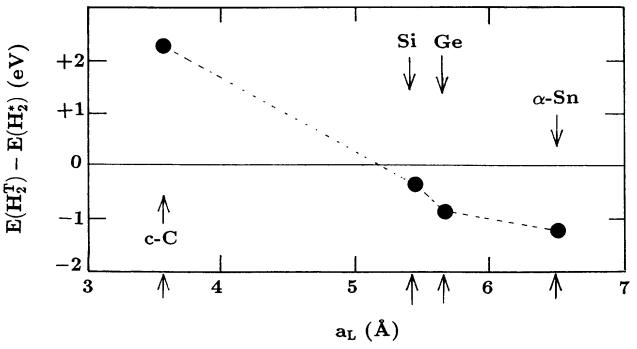

FIG. 3. Energy difference $E(H_2^T) - E(H_2^*)$ for c-C, Si, Ge, and α-Sn vs the lattice constant. In diamond the H_2^* configuration is much more stable than the molecular state. In the other three hosts, the molecule is more stable.

already in Si, H_2^T is slightly more stable than H_2^*, and the trend continues in Ge and α-Sn. We emphasize here that the Si result is too close to call. If second NN relaxations are allowed, the H_2^* configuration will be stabilized more than H_2^T. Thus we believe that both dimers are nearly energetically degenerate in Si. Various authors published contradictory predictions on the relative stability of both configurations in Si, but all find them to be rather close in energy. DF calculations have H_2^T lower than H_2^* by 0.46 eV in Ref. 13, 0.27 eV in Ref. 37, and 0.2 eV in Ref. 41. On the other hand, semiempirical HF favors H_2^* over H_2^T by 0.49 eV in Ref. 14 while PRDDO calculations in much larger clusters favor it by 0.82 eV. Note that the latter calculation includes second NN relaxations which stabilize H_2^* more than H_2^T. As will be discussed in Sec. III, a more important factor in the relative abundance of both species is the availability of the precursor of H_2^*, namely, H_{BC}.

The stability of H_2^T clearly increases with the lattice constant. At first, that of H_2^* increases with a_L as well because the necessary lattice distortion (see Fig. 1) is easier to accomplish. However, as was the case for H_{BC}^0, the host-H bonds get weaker as one goes down the Periodic Table, which ultimately offsets the increased ease with which the lattice can be relaxed.

The calculated geometries (distances r_4 through r_9 in Fig. 1) are given in Table II. The table also contains the energies of the various sites relative to H_2^{free} and the relative energy of H_2^T and H_2^*. Again, it always *costs* energy to force a hydrogen molecule into the crystal. Note that we find the H−H bond length in H_2^T to be *shorter* in the semiconductor than it is for H_2^{free}. This result contrasts with DF predictions[36,41] that this bond length *increases* in Si by about 10% relative to H_2^{free}. As one would expect, our H−H bond length increases with the lattice constant, slowly converging toward the free molecule value.

In silicon, we find that H_2^T is very close to the T site, oriented along the ⟨111⟩ direction (the detailed geometry is shown in Fig. 1 and Table I). However, it is an almost free rotator and other orientations, such as the ⟨100⟩ proposed in Refs. 36 and 41, are less than 0.1 eV higher in

TABLE II. Geometries of the H_2^T and H_2^* dimers in elemental semiconductors. The distances labeled r_4 through r_9, defined in Fig. 1, are in Å. The H−H bond length in H_2^T (parameter r_5) is shorter than that of H_2^{free} (0.731 Å at the present level of theory). The energy differences are in eV. Note that it costs energy to insert a free hydrogen molecule into the various hosts. No lattice relaxation was included for H_2^T, and first NN's were relaxed in the case of H_2^*. These results are from large basis set *ab initio* HF calculations.

	c-C	Si	Ge	α-Sn
r_4	1.296	2.080	2.187	2.535
r_5	0.613	0.704	0.707	0.717
r_6	0.239	0.253	0.236	0.261
r_7	0.503	0.755	0.791	0.833
r_8	0.973	1.441	1.500	1.697
r_9	0.974	1.474	1.558	1.758
$E(H_2^T) - E(H_2^{free})$	12.88	2.39	1.98	1.08
$E(H_2^T) - E(H_2^*)$	+2.23	−0.34	−0.85	−1.22

energy. The calculated barrier for diffusion of H_2^T in Si is 1.74 eV at the *ab initio* level. Such a high activation energy is consistent with the numbers published by other authors: 1.1 eV in Ref. 37, 2.7 eV in Ref. 60, 0.95 eV in Ref. 61. We also calculated the dissociation energy of H_2^* into two H_{BC}^0 interstitials. At the PRDDO level, which tends to overestimate dissociation energies, we obtained 3.8 eV. This number is higher, but not always by much, than the values of other authors: 3.1 eV in Ref. 41, 2 ± 0.5 eV in Ref. 36, and only 1.6 eV in Ref. 13.

We also examined the possibility that H_2^* diffuses as a pair. Instead, we found that it breaks up into $H_T^0+H_{BC}^0$ (or, depending on the type of sample, into a combination such as $H_T^0+H_{BC}^+ + e^-$). Since H_T^0 is highly mobile, the pair then dissociates, and we found no mechanism that would involve the *simultaneous* motion of both H atoms. This does not preclude the subsequent formation of another H_2^* species, involving the same or different H interstitials. This result does not conflict with an earlier examination[13] of the diffusion properties of H_2^*, where only one atom at a time was allowed to move.

Finally, we note that the relative abundance of H_2^T and H_2^* in a given sample depends on both the type and history of the sample, since precursors must be available for dimers to form. In p-type and intrinsic Si, μSR data[19,20] show both H_T^0 and H_{BC}^0 interstitials coexist up to about room temperature. Thus, the reactions $H_T^0+H_{BC}^0 \rightarrow H_2^*$ and $H_T^0+H_T^0 \rightarrow H_2^T$ will result in the formation of both types of dimers. However, if H_{BC}^+ dominates (at higher temperatures or in more heavily doped material), the formation of new dimers is prevented not only by the Coulomb repulsion between positively charged species but also by the lack of the electrons needed to form two-electron bonds. In n-type Si, the BC site appears to be less stable, from both recent μSR evidence[19,20] and theoretical predictions.[13,36] This would prevent the formation of H_2^*. The only type of dimer left is H_2^T, which results from the interaction of two H_T^0 interstitials. If H_T^- dominates, dimer formation becomes less likely not only because of the Coulomb repulsion between H_T^- species, but also because the bond index of $(H_2^T)^-$ is only half that of $(H_2^T)^0$.

C. H_2^+ and H_2^- in Si

Because of the recent report of an EPR signal[17] that could be interpreted as that of a spin 1/2 state of H_2^T in Si, we have investigated the configurations and properties of H_2^{T+} and H_2^{T-} in Si. The EPR results are consistent with H_2^- or H_2^+ oriented along a $\langle 111 \rangle$ direction, but centered at the hexagonal interstitial (H) site. The authors suggested that the signal may not have originated from an isolated molecule, but could be part of some larger defect complex. A puzzling feature of the EPR spectrum is that the g factor of the defect is identical to that of the P_b center. Our calculations rule out the isolated molecule interpretation.

We optimized the geometry of $H_2^{+/0/-}$ at the T and H sites in a small cluster (at the *ab initio* HF level) and in a large cluster (at the PRDDO level). The results can be summarized as follows. (i) At the T site, H_2^+ and H_2^0 are locally identical, i.e., the removal of an electron from H_2^0 does not change significantly the bond length, Mulliken charge, or degree of bonding of the molecule. Much of the electron comes off the Si neighbors to the T site, but the ionization energy of H_2^0 is much too large for the electron to come off the molecule itself. Further, if such a H_2^+ actually occurs in heavily doped p-type material, it should not give an EPR spectrum similar to the one observed. (ii) At the T site, adding an electron to the system results in about 20% of that electron actually going into the antibonding orbital of H_2: The bond length increases by about 10%, and the degree of bonding drops by about the same percentage. In free space, H_2^- would have its degree of bonding decreased by exactly 50% relative to H_2^0. Again, this state would be EPR active, but the spectrum would not have the characteristics observed. (iii) The H site is higher in energy for all three charge states: H_2^+ is 1.13 eV higher than at the T site, and H_2^0 1.74 eV, as mentioned in the preceding section. As for H_2^-, it breaks up at the H site: its bond length more than doubles to 1.5 Å, and its degree of bonding drops from 0.82 (T site) to 0.07 (H site). Although this is a paramagnetic state involving two H atoms, it is not a "molecule" in the usual sense. Further, the energy of this pair is some 0.7 eV higher than that of H_2^- at the T site. Our calculations therefore reinforce the suggestion[17] that the EPR spectrum is not caused by a charge state of an isolated H_2 molecule in Si.

III. DISCUSSION

We have performed *ab initio* HF calculations of the equilibrium geometries, electronic structures, and total energies of interstitial H and H dimers in the bulk of group IV semiconductors. The relative stabilities of H_T and H_{BC} as well as H_2^T and H_2^* change as one goes down the Periodic Table from c-C to α-Sn. Silicon is the element in which the greatest diversity of sites (and therefore of charge states) is possible both for isolated H and for dimers. As a result, the properties of H are far more diverse in silicon than in the other elemental semiconductors. These properties include the possible charge states (which greatly affect the capture radii of H by various impurities and dopants), diffusion properties, and self-trapping mechanisms.

In diamond, H_{BC}^0 is much more stable than H_T^0. However, both species coexist because of the large barrier separating the T and BC sites. There is theoretical (see, e.g., Ref. 29) and experimental[62] evidence for this barrier. μSR studies,[10] have shown that over 92% of incoming muons form either Mu_T^0 or Mu_{BC}^0 at low temperatures, with no "μ^+" fraction at high temperatures (up to 1000 K). This implies that Mu_{BC}^0 does not ionize in that temperature range, i.e., that its (0/+) level is fairly deep below the conduction band. However, since no data were taken in p-type diamond, the existence of a Mu_{BC}^+ species resulting from hole capture cannot be confirmed or ruled out on the basis of the existing experimental evidence.

Two mechanisms for the diffusion of hydrogen have been proposed, and both involve a high activation energy. First, the direct tetrahedral-hexagonal-tetrahedral interstitial path for H_T^0, with $E_a \leq 2$ eV (Ref. 29) and a direct BC-to-BC path for H_{BC}^0 with $E_a \simeq 1.9$ eV (Ref. 31). The latter mechanism involves a substantial relaxation of several host atoms. Since both activation energies are very high, one does not expect to observe substantial diffusion of H^0 in diamond. The μSR evidence is that Mu_T^0 is immobile at low temperatures (then, it converts to Mu_{BC}^0), and that Mu_{BC}^0 is immobile at the μ s time scale up to at least 1000 K, as shown by the persistent anisotropy of its tensor. A species such as H_T^- is unlikely because n-type diamond does not exist.

As concerning dimers, the molecular form H_2^T is very high in energy, and H_2^* is much preferred. However, even it should be uncommon because of the low diffusivity of isolated hydrogen.

The case of silicon is much more complicated. First, both the T and BC sites are occupied, each *a priori* able to accommodate two charge states. This gives four possible states for isolated hydrogen in Si: H_{BC}^0, H_{BC}^+, H_T^0, and H_T^-. Further, both H_2^T and H_2^* can coexist. As is discussed in Ref. 63, the various theorists in the field disagree on many details. However, there is increasingly convincing experimental evidence that, around room temperature, a combination of H_{BC}^0, H_{BC}^+, and H_T^0 coexist in intrinsic and p-type Si, while H_{BC}^0, H_T^0, and H_T^- coexist in n-type Si. Recent μSR data demonstrate[19,20] that the stable state at low temperature is Mu_{BC}^0 (probably Mu_T^- in heavily doped n-type Si).

The diffusion properties of the various states are also the subject of debate. Our view is that direct BC-to-BC diffusion only occurs at very high temperatures. This is supported by the results of molecular dynamics simulations[64,65] and by the observed anisotropy of the hyperfine tensors of Mu_{BC}^0 and of the AA9 center, discussed above. Thermally induced BC-to-BC hopping would reduce the anisotropy of this center, broaden the lines, and end up producing a center with T_d symmetry. Even though around room temperature H may spend most of its time trapped as H_{BC}^+, we believe that it diffuses mostly as H_T^0, which involves T-to-T site hopping with an activation energy[25] of less than 0.5 eV. The presence of an electric field, either external or caused by nearby acceptors, would initially push H_{BC}^+ out of the BC site along field lines, but the actual diffusion involves H_T^0, until it traps again as H_{BC}^+. This process, which involves continuous changes in geometrical configurations and charge states, is also consistent with the most recent interpretation of high-temperature μSR data.[20]

As for the relative stability of the two dimer states, theoretical predictions are author dependent, except for the fact that both states are always predicted to be local minima of the potential energy and are rather close to each other in energy. Our calculations favor (slightly) H_2^T over H_2^*, but the formation probability of the latter depends mostly on the availability of the H_{BC}^0 precursor. Since this state is most likely to dominate at low temperatures in intrinsic and p-type Si, we predict that H_2^* is much more abundant in this material. On the contrary, H_2^T should dominate in n-type material and at higher temperatures. This conclusion agrees with earlier predictions.[13]

In germanium, the T site for isolated hydrogen becomes more stable than the BC site. This reversal relative to Si has major consequences which we discussed in detail in a recent paper.[47] Because H must overcome a barrier to reach the BC site and because this site has a higher energy than the T site, we expect H_{BC} to be much less abundant in Ge than in Si. This means not only that H_{BC}^0 is uncommon, but also that its ionized version H_{BC}^+ is uncommon as well. This prediction provides a simple explanation for the differences observed in the μSR spectra between Si and Ge, and for the differences in the observed efficiency of acceptor passivation. In Si, the very high efficiency of the passivation reaction is believed to be due to the Coulomb attraction between a negatively charged acceptor and H^+. In Ge, there would be no (or very little) H^+, and acceptor passivation is very hard to achieve because the capture radius of H^0 by B^- is small.

Another consequence of the low stability of the BC site in Ge is the low concentration of precursors for H_2^* formation. Further, our calculations show that H_2^T is the more stable dimer. Thus we predict that nearly immobile molecules are the dominant form of H dimers in Ge. As discussed in Ref. 47, this conclusion provides a simple explanation for the differences in the thermal effusion data[51] reported between Si and Ge.

Thus the properties of H are much simpler in Ge than in Si. The dominant isolated species in H_T^0, which rapidly hops from T to T site via the hexagonal interstitial site. It is possible that H_T^- also exists in n-type Ge. The absence of donor passivation could be explained either by a low formation probability or ionization energy of this species, or by the low stability of the resulting hydrogen-acceptor pair.

The case of α-Sn was included here only to pursue the study of trends as far down the Periodic Table as possible. α-Sn crystallizes in the diamond lattice with the longest lattice constant of the elements considered here. It also forms the weakest bond with H, but has otherwise a qualitatively similar chemistry. Our results illustrate that the BC site for interstitial H becomes increasingly unstable as one goes down from diamond to tin, and that both T-site species (H_T and H_2^T) are the only ones to be expected. However, because of its metallic characteristics, the formation of paramagnetic muonium (or hydrogen) is prevented by overscreening by the free electrons present.[66]

ACKNOWLEDGMENTS

The work of S.K.E. has been supported by Grant No. D-1126 from the Robert A. Welch Foundation and Contract No. XAI-4-14195-01 from the National Renewable Energy Laboratory. We are grateful to the Swiss Center for Scientific Computing for providing some of the computer resources.

[1] S.J. Pearton, J.W. Corbett, and M.J. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992).
[2] *Hydrogen in Compound Semiconductors*, edited by S.J. Pearton [Mater. Sci. Forum **148-149** (1994)].
[3] R.N. Hall, IEEE Trans. Nucl. Sci. **NS-21**, 260 (1974); in *Proceedings of the International Conference on Lattice Defects in Semiconductors, Freiburg, Germany, 1974*, IOP Conf. Proc. No. 23 (Institute of Physics and Physical Society, London, 1975), p. 190; J.M. Kahn, R.E. McMurray, Jr., E.E. Haller, and L.M. Falicov, Phys. Rev. B **36**, 8001 (1987).
[4] The first reports of acceptor passivation were published by C.T. Sah, J.Y.C. Sun, and J.J.T. Tzou, Appl. Phys. Lett. **43**, 204 (1983); J.I. Pankove, D.E. Carlson, J.E. Berkeyheiser, and R.O. Wance, Phys. Rev. Lett. **51**, 2224 (1983). See also Refs. 1 and 2.
[5] The first reports of donor passivation were published by N.M. Johnson, C. Herring, and D.J. Chadi, Phys. Rev. Lett. **56**, 769 (1986); N.M. Johnson and S.K. Hahn, Appl. Phys. Lett. **48**, 709 (1986). See also Refs. 1 and 2.
[6] This is documented by the rich IR spectrum of hydrogenated Si due to Si–H stretching and wagging modes. The first study was published by H.J. Stein, J. Electron. Mater. **4**, 159 (1975). See also Refs. 1 and 2.
[7] The most extreme case is that of hydrogenated amorphous Si. See, e.g., R.A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, New York, 1991).
[8] S.J. Pearton and A.J. Tavendale, Phys. Rev. B **26**, 7105 (1982).
[9] The first experimental reports were by A.R. Brown, M. Claybourn, R. Murray, P.S. Nandhra, R.C. Newman, and J.H. Tucker, Semicond. Sci. Technol. **3**, 591 (1988); H.J. Stein and S.K. Hahn, Appl. Phys. Lett. **50**, 63 (1990). A theoretical model for this process was proposed by S.K. Estreicher, Phys. Rev. B **41**, 9887 (1990).
[10] B.D Patterson, Rev. Mod. Phys. **60**, 69 (1988).
[11] J.D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).
[12] P. Briddon, R. Jones, and G.M.S. Lister, J. Phys. C **21**, L1027 (1988).
[13] K.J. Chang and D.J. Chadi, Phys. Rev. Lett. **62**, 937 (1989); Phys. Rev. B **40**, 11 644 (1989).
[14] P. Deák and L.C. Snyder, Radiat. Eff. Defects Solids **111-112**, 77 (1989).
[15] Yu.V. Gorelkinskii and N.N. Nevinnyi, Pis'ma Zh. Tekh. Fiz. **13**, 105 (1987) [Sov. Tech. Phys. Lett. **13**, 45 (1987)].
[16] B. Bech Nielsen, K. Bonde Nielsen, and J.R. Byberg, Mater. Sci. Forum **143-147**, 909 (1994).
[17] P. Stallinga, T. Gregorkiewicz, C.A.J. Ammerlaan, and Yu.V. Gorelkinskii, Phys. Rev. Lett. **71**, 117 (1993); Mater. Sci. Forum **143-147**, 853 (1994).
[18] S.R. Kreitzman, Hyperfine Interact. **63-65**, 1055 (1990).
[19] R.L. Lichti, K.H. Chow, T.L. Estle, B. Hitti, R.F. Kiefl, S.R. Kreitzman, and J.W. Schneider, Mater. Sci. Forum **143-147**, 915 (1994).
[20] S.R. Kreitzman, B. Hitti, R.L. Lichti, T.L. Estle, and K. H. Chow (unpublished).
[21] K.H. Chow, R.F. Kiefl, J.W. Schneider, B. Hitti, T.L. Estle, R.L. Lichti, C. Schwab, R.C. DuVarney, S.R. Kreitzman, W.A. MacFarlane, and M. Senba, Phys. Rev. B **47**, 16 004 (1993).
[22] M.C.R. Symons, Hyperfine Interact. **17-19**, 771 (1984); S.F.J. Cox and M.C.R. Symons, Chem. Phys. Lett. **126**, 516 (1986).
[23] T.A. Claxton, A. Evans, and M.C.R. Symons, J. Chem. Soc. Faraday Trans. **82**, 2031 (1986).
[24] T.L. Estle, S.K. Estreicher, and D.S. Marynick, Hyperfine Interact. **32**, 637 (1986); Phys. Rev. Lett. **58**, 1547 (1987).
[25] S.K. Estreicher, Phys. Rev. B **36**, 9122 (1987).
[26] P. Briddon, R. Jones, and G.M.S. Lister, J. Phys. C **21**, L1027 (1988).
[27] S. Vogel, M. Celio, Dj.M. Maric, and P.F. Meier, J. Phys. C **22**, 4729 (1989).
[28] T. Hoshino, T. Asada, and A. Terakura, Phys. Rev. B **39**, 5468 (1989).
[29] C.H. Chu and S.K. Estreicher, Phys. Rev. B **42**, 9486 (1990).
[30] S.K. Estreicher, J.L. Fry, A.K. Ray, and D.S. Marynick, Phys. Rev. B **34**, 6071 (1986).
[31] S.P Mehandru, A.B. Anderson, and J.C. Angus, J. Mater. Res. **7**, 689 (1992).
[32] P. Deák, L.C. Snyder, and J.W. Corbett, Phys. Rev. B **37**, 6887 (1988); P. Deák, L.C. Snyder, J.L. Lindström, J.W. Corbett, S.J. Pearton, and A.J. Tavendale, Phys. Lett. A **126**, 427 (1988).
[33] A. Amore-Bonapasta, A. Lapiccirella, N. Tomassini, and M. Capizzi, Phys. Rev. B **39**, 12 630 (1989).
[34] S. Vogel, M. Celio, Dj.M. Maric, and P.F. Meier, J. Phys. C **1**, 4729 (1989).
[35] G.G. DeLeo and W.B. Fowler, Phys. Rev. B **38**, 7520 (1988).
[36] C.G. Van de Walle, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988); C.G. Van de Walle, P.J.H. Denteneer, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).
[37] C.G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).
[38] C.G. Van de Walle, Phys. Rev. Lett. **64**, 669 (1990); C.G. Van de Walle and P.E. Blöchl, Phys. Rev. B **47**, 4244 (1993).
[39] H. Simmler, P. Eschle, H. Keller, W. Kündig, W. Odermatt, B.D. Patterson, I.M. Savić, J.W. Schneider, B. Stäuble-Pümpin, U. Straumann, and P. Truöl, Mater. Sci. Forum **83-87**, 1121 (1992).
[40] A.J. Tavendale, S.J. Pearton, and A.A. Williams, Appl. Phys. Lett. **56**, 949 (1990).
[41] R. Jones, Physica B **170**, 181 (1991).
[42] P. Deák, M. Heinrich, L.C. Snyder, and J.W. Corbett, Mater. Sci. Eng. **4**, 57 (1989).
[43] Dj.M. Maric, M.A. Roberson, and S.K. Estreicher, Mater. Sci. Forum **143-147**, 1245 (1994).
[44] G.S. Khoo and C.K. Ong, J. Phys. C **20**, 1385 (1987).
[45] P.J.H. Denteneer, C.G. Van de Walle, and S.T. Pantelides, Phys. Rev. Lett. **62**, 1884 (1989).
[46] Dj.M. Maric, P.F. Meier, and S.K. Estreicher, Mater. Sci. Forum **83-87**, 119 (1992).
[47] S.K. Estreicher and Dj.M. Maric, Phys. Rev. Lett. **70**, 3963 (1993).
[48] The passivation by H of electron-hole recombination centers has been reported by M.I. Landstrass and K.V. Rau, Appl. Phys. Lett. **55**, 1391 (1989).
[49] S.J. Breuer and P.R. Briddon, Phys. Rev. B **49**, 10 332 (1994).
[50] K. Kohler, J.W. Coburn, D.E. Horne, E. Kay, and J.H. Keller, J. Appl. Phys. **57**, 59 (1985).
[51] M. Stutzmann, J.-B. Chevrier, C.P. Herrero, and A. Breitschwerdt, Appl. Phys. A **43**, 47 (1991).
[52] We use the GAMESS implementation of *ab initio* HF:

M.W. Schmidt, K.K. Baldridge, J.A. Boatz, J.H. Jentsen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus, and S.T. Elbert, QCPE Bull. **10**, 52 (1990).

[53] T.A. Halgren and W.N. Lipscomb, J. Chem. Phys. **58**, 1569 (1973); D.S. Marynick and W.N. Lipscomb, Proc. Natl. Acad. Sci. U.S.A. **79**, 1341 (1982); L. Throckmorton and D.S. Marynick, J. Comput. Chem. **6**, 652 (1985).

[54] D.S. Marynick (unpublished).

[55] S.K. Estreicher, in *Advanced III-V Compound Semiconductor Growth, Processing and Devices*, edited by S.J. Pearton, D.K. Sadana, and J.M. Zavada, MRS Symposia Proceedings No. 240 (Materials Research Society, Pittsburgh, 1992), p. 643.

[56] S.K. Estreicher, A.K. Ray, J.L. Fry, and D.S. Marynick, Phys. Rev. Lett. **55**, 1976 (1985); S.K. Estreicher, Phys. Rev. B **37**, 858 (1988).

[57] See, e.g., S.K. Estreicher, L. Throckmorton, and D.S. Marynick, Phys. Rev. B **39**, 13 241 (1989).

[58] C.G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[59] M.A. Roberson and S.K. Estreicher, Phys. Rev. B **49**, 17 040 (1994).

[60] T.S. Shi, S.N. Sahu, J.W. Corbett, and L.C. Snyder, Sci. Sin. **27**, 98 (1984).

[61] A. Mainwood and A.M. Stoneham, J. Phys. C **17**, 2513 (1984).

[62] B.D. Patterson, E. Holzschuh, W. Kündig, P.F. Meier, W. Odermatt, J.P.F. Sellschop, and M.C. Stemmet, Hyperfine Interact. **17-19**, 605 (1984).

[63] S.K. Estreicher, Mater. Sci. Forum **148-149**, 349 (1994).

[64] F. Buda, L. Guido, L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 294 (1989).

[65] D.E. Boucher and G.G. DeLeo, Phys. Rev. B **50**, 5247 (1994).

[66] See, e.g., the review by A.B. Denison, H. Graf, W. Kündig, and P.F. Meier, Helv. Phys. Acta **52**, 460 (1979).