

Lowest-energy site for hydrogen in diamond

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We investigate the locations, electronic energy levels and motion of hydrogen in diamond with tight-binding total energy calculations and Molecular Dynamics simulations. A lowest energy site for hydrogen in diamond is found. It is a sixfold degenerate site (with respect to the C-C bond), giving rise to a dangling bond and to a deep electronic level in the energy gap. The motion of the hydrogen atom in the diamond crystal is jumplike between these stable sites, starting at above ~ 400 K. It is a coupled-barrier diffusion, with an activation energy of 0.9 eV.

I. INTRODUCTION

There is an abundance of hydrogen (H) in both natural and chemical vapor deposition (CVD) grown diamond.^{1,2} Its presence in the lattice may affect the physical properties of this interesting material; it has been shown that H is attracted to boron in *p*-type diamond,^{3,4} and passivates electrically active defects.⁵ However, a microscopic picture of the motion of H in diamond and the effects of H on the electrical properties of diamond are still controversial.

In the present paper, we present results of tight binding (TB) calculations on the behavior of H in diamond. In contrast to previous first-principle and semiempirical calculations^{6,7} where only relaxation of H in several common interstitial sites was carried out, we find the most probable site for H in diamond by simulating the annealing of the sample. We find that (i) the lowest energy position that an H atom occupies in diamond is a new site, that, to the best of our knowledge, has not been studied previously. It is a sixfold degenerate site with respect to the C-C bond, which we denote by ET (*Equilateral Triangle*), and illustrate in Fig. 1. (ii) H at this new site was found to create a dangling bond that induces an electronic energy level ~ 0.5 eV above the middle of the energy gap of diamond, i.e., it is a deep donor state. (iii) The diffusion of H in diamond proceeds via a jumplike mechanism between ET degenerate sites around the same bond, and at higher temperatures, also via jumps to neighboring ET sites associated with different bonds. The latter case also involves the jump of the nearest neighbor C atom of H; it is therefore a coupled-barrier diffusion mechanism.⁸

A detailed comprehension, at an atomistic level, of H in diamond is of basic importance, and requires understanding the relative energetics of different possible sites for H. The energies of several sites for H in diamond were recently calculated by different groups, using first-principle and semi-

empirical methods.^{6,7,9} In these calculations, first and second neighbor lattice relaxations^{6,7} were applied to carbon clusters terminated by H atoms, and full relaxation to carbon supercells.⁹ The BC site was found to be lower in energy than the T_d site, by amounts of 2.7,⁶ 1.9,⁷ and 1.6 eV.⁹ More recently,¹⁰ *ab initio* calculations showed that the energy of a H at the BC site is lower by 0.95 eV than at the T_d site. Different pathways for the motion of H in diamond were also considered,^{9,11-13} and various barriers were predicted for the migration of H in diamond, ranging from 0.4 to 5.1 eV.^{9,11-13}

Obviously, reliable results are obtained by *ab initio* methods, which need to be implemented to verify the present

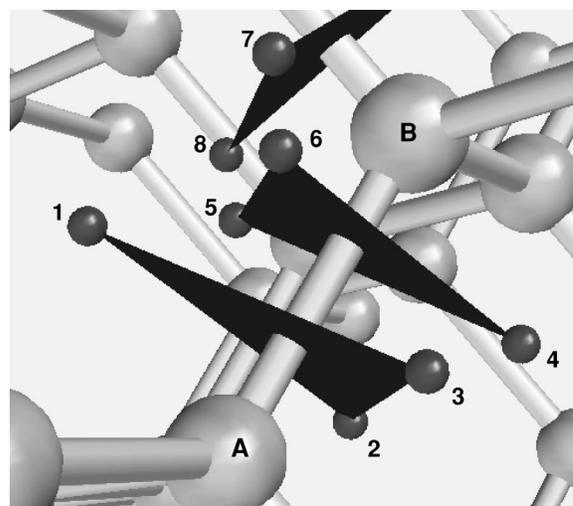


FIG. 1. Location of selected ET sites for H in the unrelaxed diamond lattice. Bright spheres are C atoms and dark spheres are the positions of the ET sites. The triangles 1-2-3 and 4-5-6 shown in the figure are equilateral, rotated with respect to each other by 60° around the same carbon-carbon bond (A-B), and perpendicular to it. The sites 7 and 8 surround an adjacent C-C bond.

findings. However, comparison of our results to those of Refs. 6,7, and 9 where *ab initio* and semiempirical methods were applied, gives confidence in our present approach, as discussed in more detail below.

II. CALCULATION METHOD AND VERIFICATION

In the present calculations, we use a TB model to describe the interactions between carbon and H atoms.¹⁴ The present model is made self consistent by the inclusion of local charge neutrality, and has been shown to be transferable to environments outside those included in the parameter fitting, like hydrocarbon molecules, diamond surfaces and amorphous diamondlike carbons.^{14,15} We have paid particular attention to the Brillouin-zone sampling for convergence of the supercell calculations.^{16–18} We use a small supercell of $64 + 1$ atoms and a larger one of $216 + 1$ atoms, and different sets of special k points. For H at high-symmetry sites (BC and T_d), convergence in the energy is already achieved with 2 special k points and the small supercell. For H at the ET site (to be discussed below), we use 10 special k points for accuracy with the small supercell. The calculations with the supercell of $216 + 1$ atoms and 2 special k points yield quantitatively the same results as those with the small one, justifying the use of the latter.

We first consider, like others,^{6,7,9,10} the BC and T_d interstitial sites for H in diamond. All the atoms of the samples are allowed to relax by the conjugate gradient algorithm. We initially use the tight binding parametrization of Ref. 14. We find, as found by the others, that H at the BC site is lower in energy than at the T_d site, however, by only 0.5 eV, a value smaller than the wide range of estimates obtained by others.^{6,7,9,10} Furthermore, our results are in full agreement with those of Ref. 9, regarding the structure of the atoms in the vicinity of the H atom at the BC site. In particular, we calculate the C-H bond length to be 1.17 Å (Ref. 19) and the C-C bond to increase by 52%, in full agreement with Ref. 9. The nearest neighbor atoms of H at a T_d site are found to relax by ~ 0.1 Å, also in very good agreement with Ref. 9. It should be noted that these lengths are slightly shorter than those found by others.^{6,7} We speculate that this is probably because in Refs. 6 and 7, local relaxation was applied to small H-terminated clusters, while in our work and in that of Ref. 9, full relaxation was applied to supercells.

Let us now consider the origin of the small energy difference found here between H at the BC site and H at the T_d site, and show that this has no noticeable effects on the motion and migration barriers of H in the crystal. The tight binding parameters for the C-H interaction¹⁴ were obtained from fitting to properties of the CH_4 molecule, as calculated by first principle models. Although the silicon crystal differs from diamond, we can adopt the approach used to determine the Si-H interaction parameters to the C-H parameterization needed here. In the case of H in silicon, the reference molecule is SiH_4 . However, to extend the tight-binding model to H in crystalline silicon (c -Si), the hierarchy of energies for H at different high-symmetry interstitial sites, as obtained from *ab initio* calculations, had to be reproduced. Boucher *et al.*²⁰ found that this hierarchy for H in c -Si is not maintained with the tight binding parameters obtained from SiH_4 . To properly describe H in c -Si, the authors, therefore, sug-

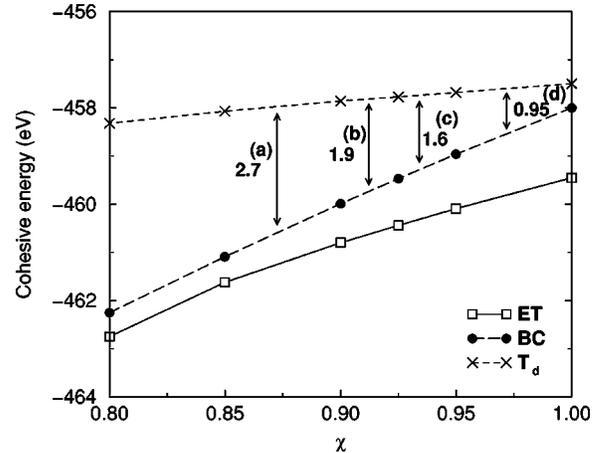


FIG. 2. The cohesive energy of H in diamond at three different interstitial sites (BC, T_d and ET), as a function of the multiplying factor χ (see text). The energy difference between H at BC and H at T_d , as calculated by others, are indicated. (a) Ref. 6, (b) Ref. 7, (c) Ref. 9, and (d) Ref. 10.

gested to decrease the strength of the Si-H repulsive potential obtained from SiH_4 , by using a multiplying factor $\chi \leq 1$. The optimum χ value found yielded the right hierarchy of energies for interstitial H in c -Si.

In our case, the tight-binding parameters deduced from CH_4 immediately lead to the right hierarchy for interstitial H in diamond, however with different relative energies than the *ab initio* data (see above). We find that the agreement of the relative energies with *ab initio* results can be improved by reducing the C-H repulsive energy, in the same way as suggested by Boucher for the case of H in c -Si. In Fig. 2, the cohesive energy of diamond with H at the BC and T_d interstitial sites is shown, as a function of the multiplying factor χ . It can be seen that the relative energy between H at BC and H at T_d can approach that obtained from other calculations (marked in the figure by arrows) by changing the value of χ .

In the rest of our investigation, the calculations of the energetics, the energy barrier and the motion of H in diamond are carried out with two different values for the multiplying factor: $\chi = 1$, which corresponds to the initial tight binding parametrization, and $\chi = 0.925$, which yields an energy difference of 1.7 eV between H at BC and H at T_d (see Fig. 2), well in the range of Refs. 6,7,9, and 10, and close to the *ab initio* pseudopotential result of Ref. 7. In both cases, the qualitative and quantitative results are similar. We thus present below only the results obtained from the initial parametrization ($\chi = 1$), unless stated otherwise.

III. THE STABLE SITE FOR H IN DIAMOND

As mentioned above, only common interstitial sites for H in diamond were investigated so far. Estreicher *et al.*⁶ suggested that for group-IV elements, bond lengths and bond strength determine the stability of interstitial H in the crystal. The C-C bond is the strongest and shortest among group-IV elements. Thus, in order to incorporate a H atom on a BC site in diamond, a larger relaxation of the C-C bond (52% of the C-C diamond bond length, as found here), with a larger amount of energy is required, compared to other group-IV

crystals. It is therefore plausible that a site *displaced* from the C-C bond may be energetically favorable for H in diamond.²¹

To search for such a site of lowest energy, we simulate an annealing process for a diamond sample, with a H atom initially located at the T_d site.²² We start the simulated annealing by molecular-dynamics calculations at 1200 K and then slowly lower the temperature down to 100 K, for 50 ps. We find that even at high temperatures, the system rapidly enters configurations where the H atom oscillates around equivalent sites (denoted ET) *away* from the BC and the T_d sites. Upon cooling, the amplitudes of oscillations of the atoms are reduced, however with no change in the equivalent configurations obtained at high temperature. The annealing process, as applied here, ensures that the final site of the H atom is a site of *global* minimum energy.²²

Next, we calculate the energy of the sample with a H positioned at such an ET site, by fully relaxing the supercell obtained after the annealing process. We also relax a sample initially in the ideal diamond lattice configuration, with H near the ET site. The same final configuration is obtained after relaxation, with exactly the same energy. We find this configuration to be lower in energy than that of H at the BC site by an amount of 1.4 eV. This newly discovered ET site is found here to be the *lowest energy* site for H in diamond.

At this stage, it is important to investigate the effect of the multiplicative factor, χ , on this result. In Fig. 2, we show the cohesive energy of the sample with H at the ET site, as a function of χ . It can be seen that the ET site remains the site of lowest energy for H in diamond, over the complete range of χ investigated.²³ With $\chi=0.925$ (which corresponds to an energy difference of 1.7 eV between H at BC and H at T_d), the energy difference between H at the BC site and H at the ET site is still rather large, ~ 1 eV. Thus, the ET site found here is not an artifact of the tight-binding parametrization and does indeed correspond to the most favorable site for H in diamond.

This site is six fold degenerate with respect to the C-C bond, and located at a distance of ~ 0.77 Å from an unrelaxed C-C bond, near the antibonding site. These six energetically equivalent sites are located around the C-C bond, at the corners of two equilateral triangles, which are rotated with respect to each other by 60° around the same unrelaxed C-C bond, are perpendicular to it, and are at a distance of $1/3$ of the bond length. In Fig. 1, we enumerate selected ET sites. Those numbered 1 to 6 surround one carbon-carbon bond (labeled A-B), while the sites 7 and 8 surround an adjacent bond.

In this configuration, the H atom is bonded to one C atom (say A-1 in Fig. 1), with a bond length of 1.08 Å. The initial carbon-carbon bond (A-B in Fig. 1) is broken, and relaxes by 43%. These may be some of the reasons for the ET site to be favored over the BC site: it involves less C-C relaxation and the C-H bond length remains close to the average bond length in organic molecules. The outward relaxation of the C atom that is not bonded to the H atom (atom B in Fig. 1) favors hybridization of sp^2 character for the bonding to its three nearest neighbors, and the creation of one dangling bond. We calculate the distance between the H atom and the unpaired C atom (atom B in Fig. 1) to be ~ 1.8 Å.

The presence of this dangling bond is confirmed when

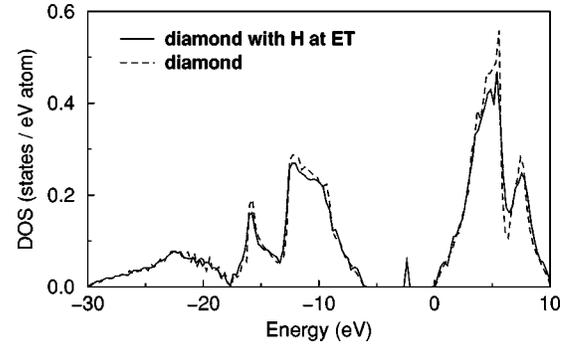


FIG. 3. DOS of pure diamond (dashed line) and diamond with H at the ET site (solid line). The zero of the energies is taken at the bottom of the conduction band.

electronic energy levels are calculated within the TB model. The calculation of the energy difference between the highest occupied and the lowest unoccupied orbitals in pure diamond yields ~ 5.8 eV, a value close to the measured energy gap in diamond of 5.48 eV,²⁴ and ~ 24.1 eV for the width of the valence-band, in excellent agreement with experiment (24.3 eV).²⁴ When we compute (with 60 special k points) the density of electronic states for diamond with H located on the newly found stable ET site, and compare it with that of diamond (see Fig. 3), a new state ~ 0.5 eV above the middle of the energy gap emerges; it is caused by the dangling bond created by the relaxation and the breaking of the C-C bond.²⁵

Due to this dangling bond, there is a strong tendency for another H atom to pair with the second carbon atom (atom B in Fig. 1). This C-H-H-C complex (one H at site 1 and another H at site 4 in Fig. 1, for example) is found by us to be lower in energy by 2.5 eV than the configuration proposed by P. Briddon *et al.*⁷, where one H is located at an antibonding site and the other at a BC site. As expected, we find that the bonding of the second H atom removes the dangling bond and eliminates the midgap state.

IV. COMPARISON WITH EXPERIMENT

The location of H in semiconductors (C, Si) is best determined experimentally by electron paramagnetic resonance¹ (EPR) or by the measurements of the hyperfine interactions of muonium (the light pseudoisotope of H) in the crystal.^{26,27}

The H1 center measured in EPR by Zhou *et al.*¹ and by Talbot-Ponsonby *et al.*² is associated with dangling bonds related to the presence of hydrogen in CVD diamond. It is speculated that H is bonded to one C atom, creating a dangling bond on the neighboring C atom, which is responsible for the EPR signal. This is similar to the atomic configuration around H at the ET site that we have found. Zhou *et al.*¹ conclude that the H atom is ~ 1.9 Å away from the unpaired electronic spin, in excellent agreement with our calculations (1.8 Å). Talbot-Ponsonby *et al.*² also measured the H1 signal in polycrystalline CVD diamond. They attribute this signal to H preferentially located on grain boundaries in the polycrystalline CVD diamond. Although our calculations deal with H in a bulk diamond, the ET site presented here is in accord with the model proposed by Zhou *et al.*¹

Muon spin resonance (μ SR) measurements²⁷ indicate that two paramagnetic forms of muonium exist: the “nor-

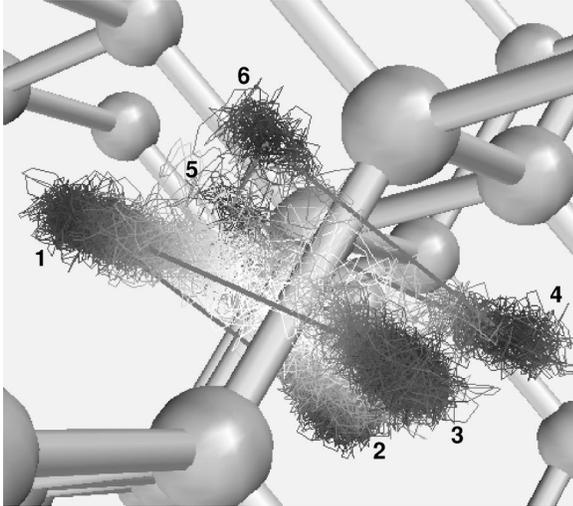


FIG. 4. Trajectory of the H atom at 1200 K, for 30 ps. The gray scale indicates the relative distance of H from ET sites (dark for short distances, bright for long distances). The C atoms are represented by spheres, in their equilibrium sites, for clarity. The lines join ET sites of the same equilateral triangle, to guide the eye.

mal” muonium (Mu), with an isotropic hyperfine interaction, and the “anomalous” muonium (Mu^{*}),²⁸ with an anisotropic hyperfine interaction.

Our findings also compared well with experimental results on the positions of muonium in diamond.²⁷ It is now well established that the anomalous muon (Mu^{*}) in semiconductors has small and highly anisotropic hyperfine parameters with $\langle 111 \rangle$ axial symmetry. Sahoo *et al.*²⁹ suggested that in an appropriate model for Mu^{*}, the unpaired electron should be in a delocalized orbital, comprised mainly of host atom orbitals directed towards the muon with a relatively small spin density at the muon. These conditions are fulfilled by the ET site, which is found to be close to an antibonding site. At high temperature, where the H atom jumps between ET sites around C-C bonds (see below), the axial symmetry should be recovered when averaging of the H motion is carried out. Furthermore, the dangling bond created when H is at a ET site contributes to the spin density at the proton, giving rise to the small values of the hyperfine parameters.

V. MIGRATION OF H IN DIAMOND

Next, we investigate the diffusion of H in diamond. First we qualitatively follow, for 50 psec, the trajectories that the H atom, initially placed at the T_d site, assumes at different temperatures, using MD calculations and visualization techniques^{30,31} to trace the path of the H atom. Only the Γ point is used to sample the Brillouin zone in these calculations. The equations of motion are solved by a velocity-Verlet algorithm, with a time step of 10^{-15} s, and the temperature is controlled by a Gaussian thermostat. We find that up to a temperature of ~ 400 K, the H atom vibrates around the initial T_d site. By ~ 600 K, it already finds its way to the nearest ET site, and jumps between the three equivalent ET sites of the same triangle (sites 1, 2, and 3 in Fig. 1, for example). Around 1200 K, the H atom begins to jump back and forth between the six ET sites around the same C-C bond. The trajectory of an H atom is depicted in Fig. 4 for 30

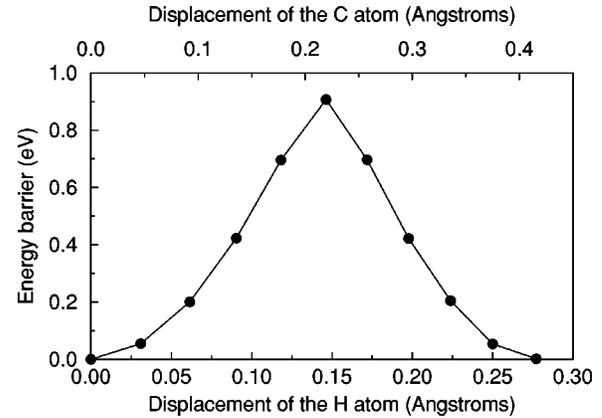


FIG. 5. Energy barrier for the adiabatic coordinated migration of H and its adjacent C atom. The top and bottom axis indicate the displacement of these two atoms.

ps at 1200 K. Finally, at a temperature of ~ 1700 K, it jumps to the nearest ET site of the neighboring bond (site 7 or 8 in Fig. 1, for example). At this stage, real diffusion sets in. It has to be noted that the temperatures mentioned above are not precise, but rather provide a hierarchy of the energetic barriers involved in the H motion in diamond. The present results can be compared with the experimental temperature of ~ 450 K at which the Mu-to-Mu^{*} transition occurs in diamond.²⁷

When a second H atom is added to the sample at an adjacent non-occupied ET site (as in our C-H-H-C complex mentioned above), the two H atoms are found to jump between the ET sites of their respective equilateral triangle, even at 1700 K, and are unable to jump to another ET site of an adjacent bond, for a simulation time of 50 ps. The presence of the second neighboring H atom should therefore reduce the possibility of diffusion.

In order to quantify the migration process of H in diamond, we evaluate the potential barrier that separates two adjacent ET sites on neighboring bonds (sites labeled 6 and 7 in Fig. 1, for example), as it is the relevant barrier for actual diffusion. We notice that the jump of H from one carbon-carbon bond ($A-B$ in Fig. 1) to the adjacent one (associated with site 7) involves the rebonding of bond $A-B$ and the breaking of the adjacent one. This change of bonding is due to a *coordinated motion* of both the H (from site 6 to 7) and the carbon (labeled B) atoms. Therefore the diffusion of H involves also the passage of the C atom over a barrier. Exactly such a coupled-barrier diffusion process has been found by Ramamoorthy *et al.*⁸ for diffusion of oxygen in silicon.

We therefore calculate the energy of the sample as a function of the positions of *both atoms* (H and adjacent C), in an adiabatic migration process. We move the H atom step by step from the initial relaxed site (number 6) to the final one (number 7), along the direction 6-7. Concurrently, the carbon atom (labeled B) is displaced step by step along the direction defined by its initial and final relaxed positioned. At each step, we relax the sample such that the H and the C atom are constrained to remain on the plane perpendicular to their respective directions of displacement. Four atoms are fixed on the faces of the supercell to prevent center of mass motion. This procedure yields the shape of the barrier for the coupled-barrier diffusion, shown in Fig. 5. As can be seen

from the figure, the barrier is symmetric, with a maximum of 0.9 eV at the center of the paths. It is found that during the coordinated motion, the distance between H and its adjacent C atom remains $\sim 1.08 \text{ \AA}$.

VI. CONCLUSION

In conclusion, a new stable site for a hydrogen interstitial in diamond was found, with an energy lower than that of H at the BC site. Hydrogen at this new site was found to create a dangling bond that induces a mid-gap state. This H related configuration is consistent with the results of EPR of hydrogen containing CVD diamond. We associate this site with the experimentally found anomalous muonium, Mu^* , in diamond. The motion of hydrogen in diamond was found to involve bond rearrangement, and can be described as a

coupled-barrier diffusion. The complex composed of the two H atoms at adjacent ET sites was found to be more stable than complexes proposed previously, and when formed, it greatly reduced the possibility of diffusion of H in diamond. We hope that the present findings will encourage further calculations on the energetics and the kinetics of H in diamond, using more accurate computational methods.

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