

***Ab initio* study of substitutional boron and the boron-hydrogen complex in diamond**

S. J. Breuer and P. R. Briddon

Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom

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Local-density-functional theory is used to determine the structure of minimum energy of a substitutional boron atom in diamond and a hydrogen atom bonded to that point defect. It is found that the substitutional boron is an on-site impurity with a vibrational frequency of 1288 cm^{-1} . It is also found that the hydrogen atom takes up a position in a $\langle 100 \rangle$ direction relative to the boron atom. This is in contrast to the structure of similar acceptor-hydrogen complexes in silicon and other tetrahedrally bonded semiconductors. The vibrational frequency associated with the stretching mode of the boron-hydrogen bond is calculated to be between 2540 cm^{-1} and 2655 cm^{-1} .

I. INTRODUCTION

Boron is a common and important impurity in synthetic diamond. As a dopant it adds an acceptor level and it is used to make the *p*-type material. Research continues into its use as a dopant, especially by its incorporation in chemical vapor deposition grown thin diamond films.¹ The implantation of boron atoms into thin films causes widespread microscopic structural damage. One of the post-implantation annealing methods currently being investigated is the exposure of the material to a hydrogen plasma.² Hydrogen diffusing through diamond has a singly occupied level in the band gap. In the presence of significant concentrations of boron atoms the hydrogen would be positively charged and, therefore, attracted towards the boron, eventually forming a defect complex.

In recent years extensive investigations have been carried out into the structures of the complexes formed by the passivation of shallow donors and acceptors by hydrogen. Without exception, these have all been found to

have C_{3v} symmetry. It has been found that when hydrogen forms complexes with acceptor impurities it prefers to sit approximately at the center of one of the bonds between the acceptor and a host atom (Fig. 1). For example, this has been shown to be the case for the boron-hydrogen complex in silicon³ and the beryllium-hydrogen complex in GaAs.⁴ In contrast, hydrogen atoms attach themselves in antibonding directions when forming complexes with donor impurities (Fig. 2). For example, in GaAs, a hydrogen atom bonds to a Si(Ga) in this position⁴ and in silicon it attaches itself in an antibonding direction to a silicon neighbor of a substitutional phosphorous atom.⁵

Both of these structures were used initially in the study of the boron-hydrogen complex presented here, but were both found to be unstable. When the equilibrium structure had been determined, the frequency of the highest frequency vibrational mode associated with the hydrogen was calculated. This frequency is important as the structure of the defect could be confirmed by its experimental measurement. In Sec. II we present details of the methods used in our calculations, in Sec. III we present our results for the substitutional boron and the boron-hydrogen complex, and finally in Sec. IV we give our conclusions.

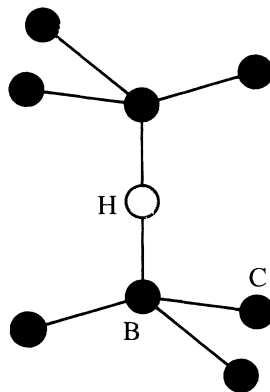


FIG. 1. The hydrogen atom at the bond-centered site between a boron atom and a carbon atom, a possible structure for the boron-hydrogen complex in diamond.

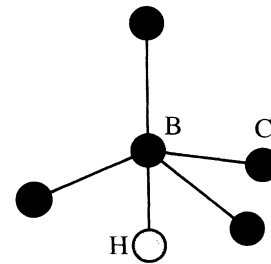


FIG. 2. The hydrogen atom attached to the boron atom at the antibonding site, a possible structure for the boron-hydrogen complex in diamond.

II. DETAILS OF THE CALCULATION

The method used involves the self-consistent solution of the Kohn-Sham⁶ equations obtained using the local-density approximation to density functional theory. The solid is simulated by using a large cluster. The basic cluster used in this investigation is $C_{70}H_{60}B$ (Fig. 3) which has 131 atoms, including 60 terminating hydrogen atoms and a central boron atom. It has tetrahedral symmetry before any atomic motion is allowed. A criterion for suitability satisfied by this cluster is that it has sites for the defect configurations with the terminating hydrogen atoms as fourth nearest neighbors. Thus the charge density at the site of the defect, at the center of the cluster, should not be significantly perturbed by the surface of the cluster. This approach has been used to determine the properties of defects in diamond previously, producing good agreement with experimental work.⁷ If the atoms are allowed to move in a pure diamond cluster of this size in such a way as to minimize the total energy then the resulting carbon-carbon bond length is within 1% of the experimental value for bulk diamond. The phonon spectrum can also be calculated to within 5% of the experimental result and, in particular, the Raman frequency is correctly reproduced at 1332 cm^{-1} . It can be concluded that for the properties under consideration here, cluster size is not a serious approximation. The pseudopotentials of Bachelet *et al.*⁸ are used for the boron and carbon atoms and the bare Coulombic potential is used for the hydrogens.

The charge density and wave function of the cluster are fitted using bases of Gaussian-type orbitals centered on the atoms and on the centers of certain bonds. These orbitals are made *s*-type and *p*-type as required by a multiplicative factor. In diamond the use of localized Gaussian orbitals avoids a problem usually encountered by the approach using plane wave expansions in supercells of a

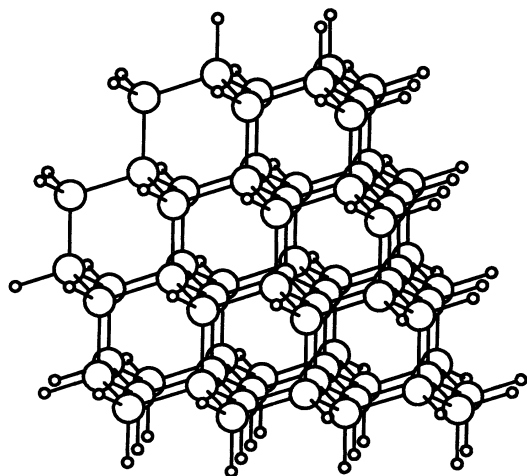


FIG. 3. The cluster $C_{70}H_{60}B$ used in the calculations. The hydrogens are the atoms with the smallest radii, at the surface of the cluster, and the boron atom is at the center of the cluster with a smaller radius than that of the carbon atoms.

very high cutoff frequency. This is due to the hardness of the pseudopotential required to model carbon atoms accurately. Around 500 orbitals were used to fit the charge density and 700 orbitals were used to fit the wave function of the cluster. The first and second nearest neighbors of the boron atom were allowed to move in each case so that the total energy of the cluster was minimized. The total number of atoms free to move was 17 for the substitutional boron and 18 for the boron-hydrogen complexes. Each defect structure was relaxed until the energy had converged to 10^{-5} a.u. The details of the method are essentially the same as that described in detail in a previous paper⁹ with modifications which will be described in a forthcoming paper.

The frequency associated with the vibration of the substitutional boron was below the Raman frequency of diamond. A Green function technique was therefore used to find the vibrational spectra of this defect as a perturbation from a perfect 131 atom diamond cluster. Second derivatives of the total energy with respect to displacements of the boron and its four neighbors were evaluated, giving a 15×15 matrix of interatomic force constants. The difference between this matrix and the corresponding matrix for the pure diamond cluster, $C_{71}H_{60}$, with the boron atom replaced by a carbon atom, then describes the perturbation caused by the defect. The corresponding vibrational frequencies can then be extracted using the Green function method by constructing the perfect lattice Green function and solving Dyson's equation. This is a standard procedure.¹⁰ An additional contribution to the technique is the *ab initio* evaluation of the perturbation matrix. The mathematical details of this approach will be given fully in a forthcoming paper. The calculation of the vibrational frequencies for the boron-hydrogen complexes was carried out by the *ab initio* generation of the dynamical matrix for the innermost six atoms, from which the frequencies can be found using standard techniques. The Green function technique was also used for this defect to find whether any other localized vibrational modes are present after the passivation of the substitutional boron.

III. RESULTS

A. The substitutional boron

The boron atom was put in the substitutional site at the center of the 131 atom cluster with the other atoms at the perfect diamond lattice positions. This defect was studied in the -1 charge state as would be observed experimentally either if the acceptor was ionized or in the presence of significant concentrations of other defects. In any case, it is well known that structural and vibrational properties of shallow impurities are not sensitively dependent on the charge state. When the innermost 17 atoms were allowed to move the surrounding atoms relaxed outwards from the boron atom, retaining the tetrahedral symmetry, with the boron atom remaining on center. The bonds to the first nearest neighbors of the boron increased by 3% and the bonds from those atoms to the

next shell of carbon atoms increased by 1%. The boron was displaced from its central position by distances of up to 1 Å. These largest displacements were in the antibonding direction towards the tetrahedral interstitial site and along the $\langle 100 \rangle$ direction. In all cases the boron was initially fixed at the displaced position while the surrounding 16 atoms were allowed to move until the equilibrium structure was found. Then all 17 atoms, including the boron, were allowed to move simultaneously, with the result that the boron always moved back to the on-center position with the tetrahedral symmetry being restored. This implies that substitutional boron is an on-site defect as expected.

The longer bonds of the defect lead to the force constants for the boron-carbon bonds being 5% weaker than those for carbon-carbon bonds in pure diamond. The vibrational density of states of the relaxed defect was found using a Green function technique [Fig. 4(a)]. The induced dipole moment produced by the vibration of this defect was also calculated [Fig. 5(a)]. This should correspond to the infrared absorption spectrum. The spectrum is overwhelmingly dominated by a peak at 1288 cm^{-1} . This is just below the Raman frequency at 1332 cm^{-1} so we would predict that substitutional boron gives rise to a resonance, not a local mode, even though boron is lighter than carbon. Similar calculations were carried out where the boron was treated as a mass defect only, without taking the change in interatomic couplings into account [Figs. 4(b) and 5(b)]. It is seen that the shape of the absorption in Fig. 5(b) is somewhat different from that in Fig. 5(a) but that the position of the peak is correctly given by this well known approximation. This is to be expected as the structural relaxation was no more than 3%. The isotopic shift in the peak due to replacing ^{10}B by ^{11}B was investigated. It was found that the peak

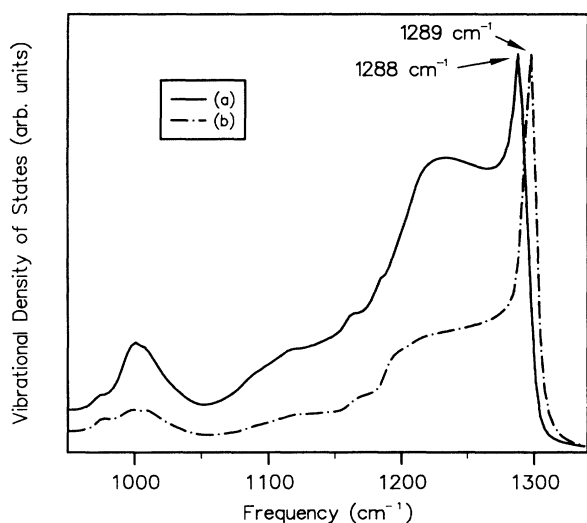


FIG. 4. The vibrational density of states for the substitutional boron atom. The units are arbitrary and the results have been scaled so that the two main peaks have the same height. The results for the relaxed defect are shown in (a) and those for the mass defect approximation are shown in (b).

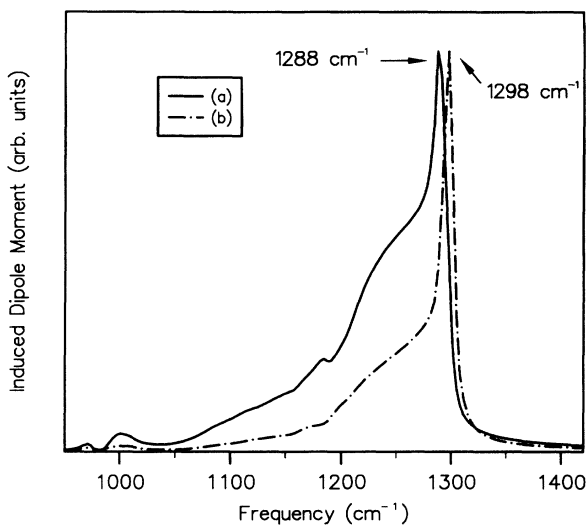


FIG. 5. The induced dipole moment for the substitutional boron atom. The units are arbitrary and the results have been scaled so that the two main peaks have the same height. The results for the relaxed defect are shown in (a) and those for the mass defect approximation are shown in (b).

shifted from 1288 cm^{-1} to 1211 cm^{-1} . The sharp peak seen in [Fig. 4(a)] is broadened considerably and the vibrational density of states begins to resemble that of bulk diamond, a reflection of the effectively small size of the perturbation from pure diamond of a substitutional ^{11}B atom.

B. The boron-hydrogen complex

As discussed in the Introduction, all previous acceptor-hydrogen complexes have been found to have C_{3v} symmetry and so the initial attempts to model the boron-hydrogen complex were based on structures with that symmetry. The hydrogen atom was put in the center of a boron-carbon bond. A symmetric relaxation was performed with the hydrogen forced to remain on the bond axis and the minimum total energy of the cluster was found. On relaxing the structure without that constraint the hydrogen atom moved completely out of the bond. It took up a position in virtually a $\langle 100 \rangle$ direction relative to the boron atom with a bond length of 1.1 Å. The boron itself was displaced in the $\langle \bar{1}00 \rangle$ direction by 0.1 Å. The energy of this $\langle 100 \rangle$ defect was found to be lower than that of the bond-centered defect by 0.7 eV. The hydrogen atom was also put at the antibonding site. On relaxation this also moved to an equivalent $\langle 100 \rangle$ displacement from the boron.

The stability of the $\langle 100 \rangle$ aligned boron-hydrogen complex (Fig. 6) and equivalent structures were investigated with respect to slight perturbations in the position of the hydrogen atom. The calculations showed that the energy surface around the structure which minimized the total energy had smaller scale detail. It appeared that small displacements of the hydrogen atom from along the ex-

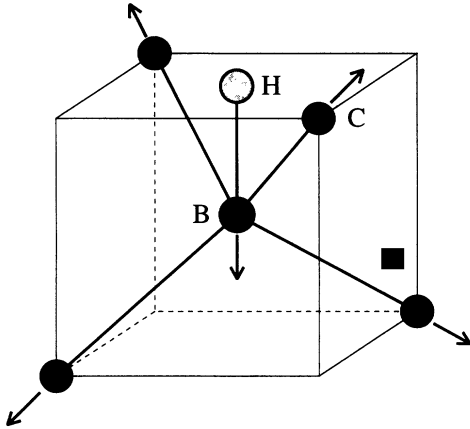


FIG. 6. The $\langle 100 \rangle$ aligned boron-hydrogen defect and the first nearest neighbor carbon atoms. The arrows indicate the direction in which the important relaxations of the atoms take place.

act $\langle 100 \rangle$ direction in the $[011]$ and $[0\bar{1}\bar{1}]$ directions gave a small but physically insignificant drop in the total energy. Any other perturbations of the hydrogen relaxed to the approximately $\langle 100 \rangle$ aligned structures. The magnitude of the drop in total energy is illustrated in Fig. 7. In this figure the relative total energy is shown as a function of the displacement of the hydrogen atom from an exact $\langle 100 \rangle$ position. At each point the hydrogen atom was kept fixed while the surrounding 17 atoms were allowed to move to obtain the equilibrium energy of the structure. In three dimensions the exact $\langle 100 \rangle$ direction alignment of the defect is a saddle point. The energy difference between the maxima and minima in Fig. 7 is

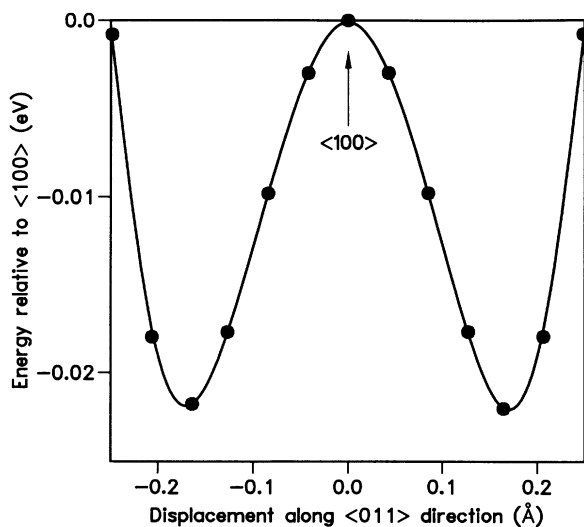


FIG. 7. The small-scale variation of the energy of the boron-hydrogen defect with displacement of the hydrogen atom along the $[011]$ and $[0\bar{1}\bar{1}]$ directions from the exact $\langle 100 \rangle$ aligned defect. The energies are relative to that with the hydrogen aligned along the $\langle 100 \rangle$.

only $\approx 0.02\text{eV}$, which is smaller than the estimated accuracy of the energy surface. In any case, whether this is an artifact of the calculation or not is irrelevant as the energy changes involved are smaller than the zero point energy of the defect. The observed physical system is expected to be the hydrogen moving on a flat-bottomed "valley" in the energy surface centered on the $\langle 100 \rangle$ displacement from the boron. The purpose of describing the details of the energy surface is to illustrate the difficulty in determining the vibrational properties of the defect with atomic motion having such a high degree of anharmonicity.

We now consider the vibrational properties of this defect. Three modes are expected to be principally associated with the motion of the hydrogen atom. The stretching of the boron-hydrogen bond should have the highest frequency of these, and there should be two modes associated with the perpendicular vibration of the atom along the flat-bottomed energy surface, known as "wagging" modes. The determination of the vibrational frequency is made more complicated by the shape of the energy surface because the harmonic approximation cannot be used for the "wagging" modes. However, motion of the hydrogen atom along the $[100]$ direction is almost decoupled from motion in a perpendicular direction. The frequency of the mode associated with the stretching of the boron-hydrogen bond could therefore be determined independently of the "wagging" modes. The result obtained was 2540 cm^{-1} for the structure of minimum total energy. This is far lower than a typical carbon-hydrogen bond-stretching mode and indicates that the hydrogen atom in this complex is only weakly bonded to the boron atom. When the hydrogen atom was forced to lie exactly along the $\langle 100 \rangle$ direction, the frequency increased slightly to 2655 cm^{-1} . The results from the Green function analysis showed that no other modes appeared above the Raman frequency due to the addition of the hydrogen atom. The boron-hydrogen bond stretching mode was, therefore, the only localized vibrational mode associated with this defect. The flat shape of the energy surface for motion of the hydrogen perpendicular to this suggests that the "wagging" modes should have anomalously low frequencies.

IV. CONCLUSIONS

The substitutional boron atom in diamond remains on site when relaxed from different starting positions. There are no localized vibrational modes associated with this defect even though boron is lighter than carbon. Instead it gives rise to a resonance at 1288 cm^{-1} . This frequency was also determined by taking the mass defect approximation. The value obtained was 1298 cm^{-1} , which shows that the approximation would be acceptable in this situation. The isotopic shift in the peak due to replacing ^{10}B by ^{11}B was from 1288 cm^{-1} to 1211 cm^{-1} .

The structure of the boron-hydrogen complex which minimized the total energy of the cluster was aligned along the $\langle 100 \rangle$ direction. The boron-hydrogen bond stretch mode has a frequency estimated to be between

2540 cm^{-1} and 2655 cm^{-1} , depending on the position of the hydrogen in a flat-bottomed minimum in the energy surface. The anharmonicity of this energy surface makes it impractical to determine any "wagging" modes involving the hydrogen atom. In any case, this strong boron-hydrogen bond-stretching mode gives the most characteristic frequency associated with the defect and should be experimentally observable in diamonds containing sufficient concentrations of boron and hydrogen. The results of a Green function analysis show that there are no other

localized vibrational modes apart from that associated with the hydrogen atom. It is hoped that by providing details of the vibrational properties of the equilibrium structures obtained this will aid future investigations.

ACKNOWLEDGMENT

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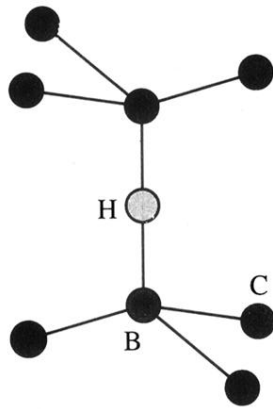


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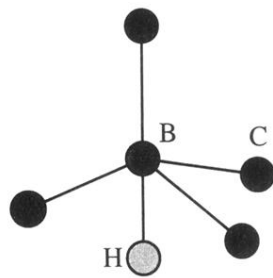


FIG. 2. The hydrogen atom attached to the boron atom at the antibonding site, a possible structure for the boron-hydrogen complex in diamond.

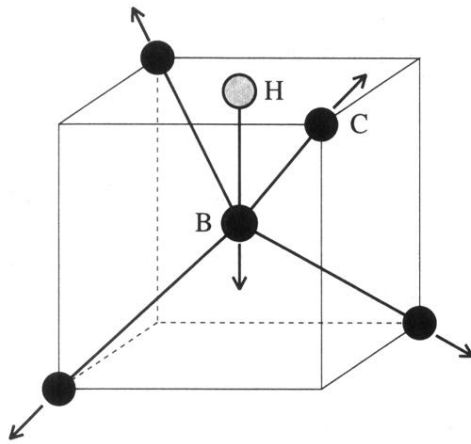


FIG. 6. The $\langle 100 \rangle$ aligned boron-hydrogen defect and the first nearest neighbor carbon atoms. The arrows indicate the direction in which the important relaxations of the atoms take place.