

The vacancy–nitrogen–hydrogen complex in diamond: a potential deep centre in chemical vapour deposited material

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S2903

(<http://iopscience.iop.org/0953-8984/15/39/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 15:16

Please note that [terms and conditions apply](#).

The vacancy–nitrogen–hydrogen complex in diamond: a potential deep centre in chemical vapour deposited material

J P Goss¹, P R Briddon¹, R Jones² and S Sque²

¹ School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

² School of Physics, The University of Exeter, Exeter EX4 4QL, UK

E-mail: J.P.Goss@ncl.ac.uk

Received 30 July 2003

Published 19 September 2003

Online at stacks.iop.org/JPhysCM/15/S2903

Abstract

Following recent experiments leading to the assignment of a trigonal vacancy–nitrogen–hydrogen complex in single-crystal chemical vapour deposited diamond, we have employed first-principles density functional supercell and cluster techniques to examine the structure and properties of such a defect. We find that the trigonal defect where H bonds directly to the nitrogen atom is unstable and instead a planar structure with H bonding to carbon is the ground state. The complex is expected to be thermally stable as well as optically, magnetically and electrically active. We also discuss the dynamic properties of the complex, and tentatively propose a trigonal form of the defect made up from a superposition of the three equivalent C_{1h} configurations.

1. Introduction

Recent electron paramagnetic resonance (EPR) experiments performed on single-crystal chemical vapour deposited (CVD) diamond intentionally doped with ^{15}N have produced evidence of an important defect in such films [1]. The defect, with an effective spin of $S = 1/2$, has been interpreted as a complex of hydrogen with the NV-centre with H bonded directly to N. The spin state and the presence of ionized substitutional nitrogen in the material suggests the ‘NV–H’ defect is negatively charged.

However, the proposal of a nitrogen–hydrogen bond in such a complex is somewhat surprising for several reasons:

- (i) Although in neutral molecules C–H and N–H bonds have comparable bond strengths [2], this pertains to three-fold coordinated N. For *four-fold* coordinated N–H, as in the proposed structure, C–H bonds are significantly stronger. This can be placed on a quantitative basis by considering the reactions $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ and $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$ which cost 4.5 and

0.9 eV respectively [2]. The fact that four-fold coordination is usually associated with positively charged N can be understood by considering the population of bonding and antibonding combinations of orbitals on the N atom: NH_4^+ has bonding combinations that resemble methane. The addition of another electron populates an antibonding combination of one N–H pair, thereby breaking the bond.

- (ii) The formation of multi-nitrogen centres with a single vacancy is favoured because replacing a C atom with nitrogen effectively removes a dangling bond—the N sites are fully satisfied in terms of the bonding. Energetically the formation of vacancy–impurity complexes and vacancy aggregates can be understood to a reasonable degree by simply counting the number of unsatisfied bonds, so that the formation of a divacancy, for example, is energetically favoured because it eliminates two dangling bonds relative to two isolated vacancies. Based on this principle an interstitial H atom would bond to a carbon neighbour of the vacancy in the NV–H complex, resulting in a complex with two rather than three dangling bonds.
- (iii) Theory predicts that the addition of a bond-centred H adjacent to a substitutional N atom forms a complex with the H closely bonded to the C neighbour with very little interaction with the N atom [3, 4]. This is a clear case of a defect where an H atom has the option to form a bond with N, C or both, and shows a preference for the carbon. Furthermore, in the case of the sulfur–vacancy complex, previous calculations seem to indicate that the H atoms bond first to the C dangling bonds [5].

In order to gain a better understanding of how an NV–H complex might behave, we first briefly review the relevant data pertaining to the related centres.

NV gives rise to optical transitions with zero-phonon lines (ZPLs) at 1.945 and 2.156 eV [6–11], arising from the negative and neutral charge states respectively [10, 11]. Experiment [12] has also shown that the acceptor level of NV is at 2.583 eV from a band edge.

Various other vacancy–nitrogen complexes are known to be stable in diamond, including V–N₂. Experimentally V–N₂ gives rise to the H2 and H3 ZPLs at 1.257 and 2.463 eV respectively. H2 and H3 are the negative and neutral charge states, indicating that the complex is electrically active. In general, removing C-related dangling bonds by the formation of V–N_n complexes generates more stable defects. This can be interpreted in terms of there being a larger energy saved by removing the C dangling bond than the interactions involving N lone pairs. When $n = 4$ one has the B defect which is believed to be electrically passive.

The location and properties of hydrogen in diamond are far less well understood. However, it is expected that, in line with other group IV materials, vacancies will form deep traps for hydrogen. Previous theoretical studies have predicted that vacancy–hydrogen complexes would be strongly bound [5, 13–15].

In this work we present the results of local density functional calculations using both atomic clusters and supercells to evaluate the stability and properties of the NV–H complex. We describe the method in section 2 and the results in section 3. We conclude in section 4.

2. Method

Local density functional calculations using both cluster and supercell methods were carried out using the AIMPRO (Ab Initio Modelling PROgram) [16, 17]. Where appropriate, the symmetry of the defect has been constrained during relaxation.

2.1. Cluster calculations

Cluster calculations employed hydrogen-terminated clusters based on the cluster representing bulk material: C₆₈H₆₆. This is centred at an atom site and consists of two complete shells of

C atoms which are only bonded to carbon atoms (i.e. not bonded to surface hydrogen). The cluster was first *fully* relaxed subject only to a tetrahedral symmetry constraint. The relaxed C–C bond lengths are all within $\pm 0.7\%$ of the experimental value for bulk diamond. In subsequent relaxations the surface C and H atoms were held fixed and all other atoms allowed to move to minimize the total energy via a conjugate-gradients scheme.

The wavefunction basis consists of two, four and five sets of s and p Gaussian functions centred on each H, C and N atom respectively. The charge density is fitted by a number of independent s Gaussian functions with different widths: three, four and five on each H, C and N atom respectively. The atoms are treated using the pseudo-potentials [18], except for hydrogen where the bare Coulomb potential is used.

2.2. Supercell calculations

The calculations were carried out in 64 atom cubic supercells and typically eight special k -points generated by a Monkhorst–Pack scheme (MP-2³) were used to sample the Brillouin zone [19]. As with the cluster calculations, pseudo-potentials are used for C and N to eliminate core electrons [18, 20]. The H and C wavefunction bases are composed of four independent sets of s and p Gaussian orbitals with four different widths, with an additional set of d Gaussians on each C and N site. The charge density is expanded in plane waves with an energy cut-off of 300 Ryd. The errors in the lattice constant and bulk modulus of diamond using this basis are less than 1 and 6% respectively. The direct and indirect band gaps are within 1 and 0.1% of previously published plane-wave LDA values (5.68 and 4.18 eV [21]).

2.3. Calculation of experimental quantities

Local vibrational modes (LVMs) can be estimated using standard techniques, with the dynamical matrix being constructed using a mixture of calculated values of the energy double derivatives in the region of the defect, with other regions using terms generated from valence force potential.

We use the formation energy of a defect X in charge state q defined by

$$E^f(X, q) = E(X, q) - \left(\sum_i \mu_i \right) + q(E_v + \mu_e) + \chi(X, q) \quad (1)$$

where $E(X, q)$ is the energy of the supercell containing the defect, μ_i are the chemical potentials of atom types i in the cell, and the sum is over all atoms. E_v and μ_e are the valence band top and electron chemical potential respectively, and $\chi(X, q)$ is a correction term that includes the electrostatic energy due to the supercell approximation as well as the quadrupole interaction and higher-order terms [22]. There is also an influence from the difference in asymptotic potential between a defective and bulk cell, although this is usually small enough to be neglected. Typically for charged cells the dominant term is the electrostatic term of the order of 0.1 eV for $q = \pm 1$. Binding energies are defined for the reaction $A + B \rightarrow C$ as

$$E^b(C) = E^f(A) + E^f(B) - E^f(C), \quad (2)$$

so that a positive binding energy represents a bound system.

An important quantity regarding the defect under consideration is the electrical activity. The acceptor and donor levels can be estimated by comparing the ionization energy or electron affinity of the defect cell with some known marker. It is convenient to use bulk material, as suggested previously [23]. Then, for example, a single donor and acceptor level can be evaluated by replacing E_v in equation (1) by $E(\diamond, 0) - E(\diamond, 1)$ and using

Table 1. Structural parameters for the NV defect in diamond. Bond lengths are in Å. Q refers to the overall charge state of the centre. C^* and C refer to carbon atoms in the first and second shells surrounding the vacancy, respectively. By symmetry, there are two types of $C-C^*$ bond. The negatively charged system has $S = 1$.

Method	Q	N-C	$\angle C-N-C$ (deg)	C-C*	$\angle C-C^*-C$ (deg)
Cluster	0	1.51	113.0	1.49, 1.50	113.1, 114.3
	-1	1.50	113.4	1.49, 1.50	113.1, 113.7
Supercell	0	1.46	113.0	1.47, 1.49	111.5, 113.4
	-1	1.46	113.2	1.48, 1.50	111.5, 112.7

$E_c = E(\diamond, -1) - E(\diamond, 0)$, where \diamond represents the bulk cell of the same size. Assuming that the terms in χ are similar for different cells this yields

$$E(0/+) = E_v + \{E(X, 0) - E(\diamond, 0)\} - \{E(X, 1) - E(\diamond, 1)\} \quad (3)$$

$$E(-/0) = E_c - \{E(X, 0) - E(\diamond, 0)\} + \{E(X, -1) - E(\diamond, -1)\}. \quad (4)$$

Optical transition energies can be calculated approximately using the Slater transition state method [4, 24]. This technique has previously been employed for vacancy-impurity defects in diamond [4] using atomic clusters. The same approach can be adopted using supercells; however, due to dispersion within the Brillouin zone an average is taken over a representative set of k -points. We have found that using a Monkhorst-Pack scheme [19] with 2^3 points gives a result that is converged to within less than 0.1 eV, which is sufficient given the inherent inaccuracies of the method.

The principal advantage of the cluster over the supercell approach is one of computational expedience. However, one must adopt the supercell approach for accurate formation and binding energies.

3. Results

3.1. The isolated NV defect

To place the subsequent results on a firm footing, we have first explored the key properties of an isolated NV centre. In table 1 we report the bond lengths and angles found using both the cluster and supercell approaches. The relaxation of the atoms away from the vacancy is consistent with previous calculations [25], although the magnitude is smaller at around 4% of a C-C bond length, independent of supercell/cluster approach.

We have estimated the location of the electrical levels of NV using the approach outlined in section 2. Using the 64-atom bulk cell as a marker, the $(-/0)$ level lies at $E_c - 3.3$ eV. This is in excellent agreement with experiment which locates the level at around $E_c - 2.6$ eV [12].

Using the formation energy of an isolated vacancy obtained using quantum Monte Carlo techniques, $E^f(V) = 6$ eV [26], we can calculate the binding energy of a neutral substitutional N defect with a neutral vacancy. It is found to be around 3.4 eV, which is smaller than the 4.7 eV previously obtained using a more approximate computational method [25]. This value is of course an over-estimate of the binding energy since the donor level of substitutional N lies above the acceptor level of the vacancy (as indicated by the presence of V^- in N-doped diamond), and thermodynamically the reaction should be $N^+ + V^- \rightarrow NV$. The binding energy for this reaction is lower than the neutral case by the difference in the location of the nitrogen donor level and the vacancy acceptor level. However, the calculated binding energy will remain of the order of several electronvolts, in line with the energy of a covalent bond. This supports the view that the nitrogen has removed a dangling bond from the vacancy.

The cluster calculations yield optical transition energies of ~ 1.4 and ~ 1.7 eV for the neutral and negative charge states respectively. Although these values are considerably lower than the experimental values, this is deemed reasonable agreement given the nature of the calculation; they are in reasonable agreement with previous calculations employing smaller clusters [4]. The supercell calculations yield 1.7 and 1.6 eV for the neutral and negative charge states, respectively, in reasonable agreement with the cluster calculations, and therefore in only semi-quantitative agreement with experiment.

3.2. NV-H complexes

We have placed hydrogen into the NV defect with the hydrogen atom initially located in proximity to either a carbon or the nitrogen atom, along $\langle 111 \rangle$ directions pointing into the vacancy. The relative total energies of the systems are listed in table 2. We have checked the convergence of these energies with respect to the Brillouin-zone sampling. Using an MP-4³ mesh resulted in changes in the total energies of less than 10 meV. Furthermore, increasing the plane-wave cut-off energy from 150 to 300 Hartrees has no appreciable effect on the total energy, and increasing the number of sets of d orbitals on the N atom from one to four also resulted in an unstable trigonal centre in the negative charge state. It should be noted that the electronic structure of the trigonal centre in the neutral charge state is essentially the same as NV⁻, i.e. $a_1^2 e^2$, and hence there are three multiplets associated with this system. In table 2, the $S = 0$ energies refer to an admixture of the two spin singlet multiplets associated with the one-electron configuration, and are therefore only an approximate value. As an additional check, we have calculated the relative energy of $S = 1$ and 0 configurations for NV⁻ without taking the full multiplet structure into account. The difference in the total energies of 0.5 eV is close to the value reported where the multiplet was considered explicitly [11], giving some confidence regarding the values in the table. It should be further noted that the e level is localized on the C atoms, and inaccuracies in the treatment of the multiplets are unlikely to affect the location of the H atom if bonded to the N site.

The overall agreement between the energies produced using the cluster and supercell approaches is very good. In particular, the lowest energy found for a trigonal N-H bonded complex is more than 0.4 eV above the ground state. This occurs for the positive charge state in line with the discussion in the introduction regarding four-fold coordinated nitrogen.

In the negative charge state, the energy difference between the H bonded to the C and N is 1.3 eV or more, always in favour of the H being attached to the C atom. The principal reason for the 0.3 eV difference between the cluster and supercell calculations is that in the supercell the relaxation breaks the weak N-H interaction and the H atom moves to a site on the trigonal axis closer to the three C atoms, whereas the H remains in proximity to the N atom in the cluster calculation (see bond lengths in table 2). For the supercell result, the symmetry-constrained geometry does not represent a physical structure, and in the absence of the symmetry constraint, even when the initial N-H separation is of the order of that in ammonium, the H atom *spontaneously* moves to form a bond with a C atom. Where the defect is constrained to have the N-H bond length of ammonia, the total energy is 1.9 eV above that of the ground state, similar to the energy found in the cluster calculation. We have also examined a structure where the H atom antibonds to the N atom, also forming a trigonal centre, but this is vastly higher in energy (6.4 eV) above the ground state in the negative charge state and can be discounted.

One must therefore conclude that local density functional theory does not support a model of an NV-H complex in *any* charge state where the hydrogen atom forms a bond with the nitrogen atom. As pointed out above, the energy difference between a C-H and an N-H

Table 2. Relative total energies of NV–H in diamond (eV). In each charge state the zero of energy is taken to be that of the lowest energy structure. Q and S refer to the overall charge and effective spin, respectively. Also listed are X–H bond lengths (Å).

Method		Sym.	Q	S	Energy	Bond length
	C–H	C _{1h}	–1	1/2	0.00	1.08
	N–H	C _{3v}	–1	1/2	1.69	1.18
Cluster	C–H	C _{1h}	0	0	0.00	1.06
	C–H	C _{1h}	0	1	0.33	1.09
	N–H	C _{3v}	0	1	1.19	1.12
	N–H	C _{3v}	0	0	1.57	1.11
	C–H	C _{1h}	+1	1/2	0.00	1.07
	N–H	C _{3v}	+1	1/2	0.43	1.07
	C–H	C _{1h}	–1	1/2	0.00	1.10
	N–H	C _{3v}	–1	1/2	1.31	1.78
Supercell	C–H	C _{1h}	0	0	0.00	1.08
	C–H	C _{1h}	0	1	0.26	1.11
	N–H	C _{3v}	0	1	1.07	1.18
	N–H	C _{3v}	0	0	1.56	1.20
	C–H	C _{1h}	+1	1/2	0.00	1.10
	N–H	C _{3v}	+1	1/2	0.61	1.11

configuration is least in the positive charge state, consistent with the four-fold coordination of the ammonium ion, NH_4^+ . It seems unlikely that a positively charged centre would form in material where there are nitrogen donors, but a possible interpretation of the experiment is that NV-H^+ is formed as a metastable structure during growth and frozen in. This would require a considerable barrier to the transfer of the H atom from the N to the C site since it would have to survive above the growth temperature of $\sim 700^\circ\text{C}$.

We have investigated this barrier by relaxing the complex subject to a constraint $R_{\text{C-H}}^2 - R_{\text{N-H}}^2 = C$, with C constant and R representing the internuclear distances. Such an approach has been successful in a range of migration barriers in diamond, such as the self-interstitial [27]; however, one must exercise caution in interpreting such barriers where H is involved due to the low mass relative to the host. By varying the constant C we have obtained a static activation barrier of around 0.2 eV to break the N–H bond and form a C–H bond. This is inconsistent with the formation of a metastable statically trigonal defect, especially given that quantum mechanical tunnelling effects neglected in this computation would tend to reduce this barrier. The formation of a metastable structure during growth for the negatively charged defect does not stand up to scrutiny since there is *no barrier to reconstruction in the negative charge state*. However, given the relatively small barrier to reorientation of the positively charged defect, we have examined the barrier to move the H atom from one C dangling bond to another, using the same constrained minimization as before. The activation barrier is estimated at 0.4 eV. Importantly, the two sites for the H atom are separated by around 1 Å, and it is anticipated from previous calculations of C–H stretch modes that the amplitude of the oscillation in NV–H could be comparable to this distance [28]. A barrier height of 0.4 eV is too large for any substantial tunnelling between the three equivalent sites, but the calculation of a static barrier where the dynamic properties of the hydrogen atom are potentially important leads to some uncertainty in the actual barrier height. The likelihood is that there is

a relatively small barrier between equivalent minima, and combining this with the zero-point motion suggests that the centre may in fact be trigonal, not because of an N–H bond along the C_3 axis, but by tunnelling between the three equivalent C–H structures. Such a hypothesis requires testing using more sophisticated theoretical techniques than those employed in this study, or from experiment.

Taking the ground state structures obtained in our calculations, the binding energy can be estimated for the reactions



and



where H_{BC}^q is the bond-centred interstitial hydrogen centre in charge state q . The energy liberated in each case is 5.8, 6.8 and 8.1 eV for the three reactions listed in equations (5)–(7) respectively. The difference in the energies associated with reactions in equations (6) and (7) relates to the difference between the acceptor levels of H_{BC} and NV, the former therefore lying around 1.3 eV above the latter in these calculations.

We can estimate the electrical levels of NV–H using the approach outlined in section 2. The single acceptor and donor levels lie at $E_c - 3.1$ and $E_v + 0.7$ eV respectively. In material where there are comparable concentrations of substitutional N and NV–H, the negative charge state would be preferred.

As with the NV centre, we can also estimate the energy of the optical transitions associated with these defects, remembering that we only expect semi-quantitative values. We have examined the excitations for the planar geometries where the H is bonded to a C atom. The gap contains three one-electron levels of which two are filled in the neutral charge state. These can be thought of as the three states derived from the t_2 orbitals of the vacancy, and closely resemble the electronic structure of N_2V . For both the neutral and negative charge states there are then two types of transitions arising from excitations of electrons from the two filled levels to the empty levels. The neutral centre then has excitation energies of 1.1 and 2.3 eV, and the negative charge state has excitation energies of 1.0 and 3.4 eV. We note that the neutral and negative systems are electronically similar to the H3 and H2 optical centres respectively, and one therefore is unsurprised to see transition energies that are close to the experimental values for N_2V . Although the foregoing analysis is only semi-quantitative, we conclude that the optical properties of NV–H will more closely resemble H2/H3 than the 1.945 and 2.156 eV optical signals from NV.

We have also calculated the LVMS for a number of the centres. Since the most likely candidate in N-rich material is NV-H^- , we address this case first. The local modes are listed in table 3. There is no significant dependence on the mass of the N atom, as one would expect. In the neutral charge state the ground state structure has a stretch mode at 2697 cm^{-1} , compared to 1381 cm^{-1} where the H is ‘bonded’ to the N atom. The very low N–H stretch frequency is indicative of the weak bonding interaction between the H and N atoms in this geometry. In the positive charge state where the nitrogen–hydrogen bond is chemically justified, the stretch mode is 2144 cm^{-1} compared to 2771 cm^{-1} when the H atom is bonded to a C site. For $(\text{NV-H})^+$ with the N–H bond, the shift with D and ^{15}N is 557 and 6 cm^{-1} respectively. In all cases there is no symmetry selection rule that prevents the observation by infrared absorption, but there is evidence from both experiment [29, 30] and theory [4] that some hydrogen–carbon modes may have a small effective charge and therefore be difficult to detect. In addition to the X–H stretch modes, for ground state structures there are also bend modes close to the Raman frequency.

Table 3. LVMS (cm^{-1}) for the ground state NV–H complex in the positive, neutral and negative charge states.

Isotopes	(NV–H) ⁺	(NV–H) ⁰	(NV–H) [–]
¹² C–H	2771	2697	2827
¹³ C–H	2763	2689	2819
¹² C–D	2038	1986	2080
¹³ C–D	2026	1973	2067

4. Discussion and conclusions

The main conclusion from our calculations is that we find the complex formed by the aggregation of hydrogen, nitrogen and a lattice vacancy in diamond has C_{1h} symmetry, with the H atom bonded to a carbon rather than the nitrogen atom, in line with simple chemical considerations. The binding energy of hydrogen to NV is considerable, and therefore suggests that this complex would be very stable once formed. The presence of H in the defect leads to a complex which is approximately isoelectronic with N_2V and is expected to have similar electrical and optical properties.

We further note that calculations regarding other vacancy–impurity complexes also yield the same general behaviour. For example, preliminary calculations that we have performed show that a complex made up from substitutional boron, a lattice vacancy and a hydrogen atom also has H bonded to the carbon atom neighbouring the vacancy, rather than bonding to the impurity, and the most stable site for hydrogen in a complex with N_3V is also bonded to the C atom. This is also in line with simple chemical reasoning. It is possible that the static picture of the NV–H complex fails, and that the defect is dynamically trigonal via the tunnelling between the three equivalent structures with C–H bonds. This is likely to be true at elevated temperatures in any case.

One route to the formation of the NV–H complex is analogous to that of the passivation of boron in diamond by hydrogen. The process $B^- + H^+ \rightarrow B-H$ is believed to be possible due to H^+ having a small barrier to migration. Provided that the acceptor level of NV is lower than the donor level of H, this reaction would also hold for NV. Calculated donor levels using formation energies for interstitial H range from $E_v + 1.2$ eV [31] to $E_v + 2.6$ eV [4], and so the process of charge transfer between NV and H may or may not be possible. The migration barrier for neutral H is somewhat higher (around 2 eV) but a $NV + H \rightarrow NV-H$ path might be possible at the growth temperature. An alternative path could involve substitutional N–H pairs trapping mobile vacancies dissolved in from the surface. This is consistent with the theoretically large binding energy for the N_s-H pair (3.5 eV [4]), but one should note that vacancies have a high formation energy [26] and the equilibrium concentration of vacancies at the growth temperature will be small. Should NV–H be present in as-grown material, it seems likely that it was formed at the growing surface rather than subsequently.

References

- [1] Glover C, Newton M E, Martineau P, Twitchen D and Baker J M 2003 *Phys. Rev. Lett.* **90** 185507
- [2] Lide D R (ed) 1996 *CRC Handbook of Chemistry and Physics* 77th edn (Boca Raton, FL: Chemical Rubber Company Press)
- [3] Mehandru S P and Anderson A B 1994 *J. Mater. Res.* **9** 383–95
- [4] Goss J P, Jones R, Heggie M I, Ewels C P, Briddon P R and Öberg S 2002 *Phys. Rev. B* **65** 115207
- [5] Miyazaki T and Okushi H 2002 *Diamond Relat. Mater.* **11** 323–7
- [6] Davies G and Nazaré M H 1980 *J. Phys. C: Solid State Phys.* **13** 4127–36

- [7] Collins A T and Lawson S C 1989 *J. Phys.: Condens. Matter* **1** 6927–9
- [8] He X-F, Manson N B and Fisk P T H 1993 *Phys. Rev. B* **47** 8809–15
- [9] He X-F, Manson N B and Fisk P T H 1993 *Phys. Rev. B* **47** 8816–22
- [10] Mita Y 1996 *Phys. Rev. B* **53** 11360–4
- [11] Goss J P, Jones R, Breuer S J, Briddon P R and Öberg S 1996 *Phys. Rev. Lett.* **77** 3041–4
- [12] Steeds J W, Charles S J, Davies J and Griffin I 2000 *Diamond Relat. Mater.* **9** 397–403
- [13] Zhou X, Watkins G D, McNamara Rutledge K M, Messmer R P and Chawla S 1996 *Phys. Rev. B* **54** 7881–90
- [14] Mehandru S P, Anderson A B and Angus J C 1992 *J. Mater. Res.* **7** 689–95
- [15] Miyazaki T, Okushi H and Uda T 2001 *Appl. Phys. Lett.* **78** 3977–9
- [16] Jones R and Briddon P R 1998 *The Ab Initio Cluster Method and the Dynamics of Defects in Semiconductors (Semiconductors and Semimetals vol 51A)* (Boston, MA: Academic) chapter 6
- [17] Coutinho J, Jones R, Briddon P R and Öberg S 2000 *Phys. Rev. B* **62** 10824–40
- [18] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev. B* **26** 4199–228
- [19] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188–92
- [20] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993–2006
- [21] Liberman D A 2000 *Phys. Rev. B* **62** 6851–3
- [22] Makov G and Payne M C 1995 *Phys. Rev. B* **51** 4014–122
- [23] Jeong J W and Oshiyama A 2001 *Phys. Rev. B* **64** 235204
- [24] Slater J C 1960 *Quantum Theory of Atomic Structure* vol 2 (New York: McGraw-Hill)
- [25] Mainwood A 1994 *Phys. Rev. B* **49** 7934–40
- [26] Hood R Q, Kent P R C, Needs R J and Briddon P R 2003 *Phys. Rev. Lett.* at press
- [27] Goss J P, Coomer B J, Jones R, Shaw T D, Briddon P R, Rayson M and Öberg S 2001 *Phys. Rev. B* **63** 195208
- [28] Jones R, Goss J, Ewels C and Öberg S 1994 *Phys. Rev. B* **50** 8378–88
- [29] Pajot B, Clerjaud B and Xu Z J 1999 *Phys. Rev. B* **59** 7500–6
- [30] Markevich V P, Murin L I, Hermansson J, Kleverman M, Lindström J L, Fukata N and Suezawa M 2001 *Physica B* **302/303** 220–6
- [31] Wang L G and Zunger A 2002 *Phys. Rev. B* **66** 161202