

PROGRESS REPORT

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Abstract

Certainly! Here's an abstract for your first year PhD progress report!

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§1. INTRODUCTION

The final aim of my PhD is to be able to accurately model the effects of radiation damage in diamond over large time scales, taking in to account quantum mechanical effects.

§2. REORIENTATION OF HYDROGEN IN N₂VH

§2.1. **Calculation.** The N₂VHdefect consists of a vacancy (V) surrounded by two substitutional Nitrogens (N₂), with a Hydrogen bonded to one of the two remaining carbon atoms (H). C_{2v} symmetry is reported from EPR runs in both the X (8 – 12 GHz) and Q-band (30 – 50 GHz) range [1]. It is not energetically favourable for the Hydrogen to be sit statically

in the middle with C_{2v} symmetry; this would suggest that the Hydrogen atom is reorientating between the Carbon atoms fast enough that its position is appearing as an averaged position of the two equivalent sites, giving rise to a higher order of symmetry [2]. It has previously been shown for NVH⁻ that a tunnelling period of $\tau \approx 10^{-8}$, or a tunnelling requencey of 0.1 GHz, is required to shown an averaged symmetry in EPR [3]. It would therefore be of interest to calculate the energy required for this reorientation to occur, and thus potentially create a relationship between tunnelling frequency and temperature.

A nudged elastic band (NEB) calculation was performed in order to find the energy barrier of the tunnelling path [4]. This method finds a minimum energy path (MEP) between two different states, in this case the Hydrogen moving between two equivalent carbons. Firstly, a fully relaxed configuration of the two different states are required before any path optimisation can occur. A diamond lattice was set up with 64 atoms, one Carbon atom was removed, and two neighbours in the same plane were replaced with Nitrogen atoms, a Hydrogen atom was then placed near one of the two remaining carbon atoms. A geometry optimisation was then carried out in CASTEP, using the PBE functional, a plane wave cut off energy of 1 000 eV, and an equally spaced Monkhorst-Pack grid of (444). These values were chosen after a convergence study was performed, with the energy converging to 3 significant figures with these parameters. A finite size effects study should be conducted in the future, however 64 is a resonably sized unit cell for the accuracy required, as it is theorised that all the electrons surrounding the vacancy point towards it, limiting the negative effects of a small cell size [5]. The system was optimised until no force was over 0.05 eV Å⁻¹. This was then repeated for the other equivalent Carbon

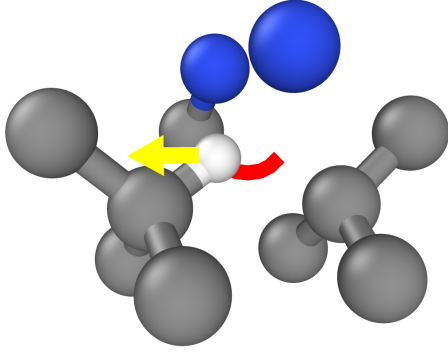


Figure 1: The NEB path of Hydrogen in N₂VH, where Nitrogen is blue, Carbon is grey, and Hydrogen is white. The *path* is shown in red, and is clearly curved, whilst the raw displacement is shown as a yellow arrow. Generated using OVITO [8].

atom. Their energies are within 0.001 eV, showing equivalent sites. A C-H bond length of 1.08 Å was found, this is consistent with results found in the literature of 1 ± 0.1 Å [6].

An initial ‘guess’ for the unoptimised path between the two systems is needed, for this, a simple a linear trajectory of the Hydrogen atom between the two Carbon atoms along the (110) plane was devised. The trajectory contains an odd number of images, this is to ensure that it captures the saddle point of the path that is, due to the symmetry of the system, likely to be in the middle of the trajectory.

The final, optimised, NEB path of the Hydrogen between the two equivalent carbon atoms, is seen in figure . It is of interest that the Hydrogen does not take the shortest straight linear path between each Carbon atom, but instead takes a longer curved path away from the two Nitrogen atoms, possibly avoiding excess electron density. The maximum energy found at the saddle point is 0.536 eV, with a full reaction path length of 1.1 Å, and a full width half maximum (FWHM) of 0.3781 Å. This differs from values found in literature, where the reported height and reaction path length are said to be 0.9 eV and 0.6 Å respectively [7]. There are many differences between these two calculations, namely that Peaker [7] uses a Gaussian basis set, whereas CASTEP uses a plane wave basis set, and the simulation cell is made up of 1 000 atoms, the increased number of atoms has the advantage of minimising finite size effects.

Peaker [7] takes the width of the barrier

as the *displacement* of the Hydrogen atom, the difference between the initial and final configuration. A higher displacement of 0.89 Å was found here, however taking the raw displacement of the Hydrogen atom does not account for the path it takes during reorientation, nor does it fully utilise the minimum energy path that the NEB calculation found. A more appropriate approximation would be to take the fully optimised path of the Hydrogen atom as the width of the barrier, and so to map the potential energy barrier to the Hydrogen path, instead of the reaction coordinate. This is reasonable as the majority of the movement stems from the Hydrogen, with the carbon atoms slightly relaxing under bond breaking and forming. The full path of the Hydrogen atom is 1 Å, only 0.1 Å more than the full reaction coordinate. The potential barrier height was found to be almost half of that found in the literature, this could be due to a more optimised MEP, or a more accurate basis. The *first* unoptimised MEP has a barrier height of 0.844 eV, much closer to that found in the literature.

§2.2. Analysis. With a barrier height and width determined it is now possible to calculate the probabilities of overcoming the barrier. As the barrier is a non-trivial shape, two different approximations will be made for different uses: approximating the barrier as a finite square potential, and the WKB potential.

For the finite square potential, it is common to take the FWHM as the width, and the saddle point as the barrier height. The classical rate of reorientation can be calculated as

$$\Gamma = A \exp\left(\frac{-E_a}{k_B T}\right) \quad (2.1)$$

where A is the attempt frequency, E_a is the activation energy, taken to be the barrier height, k_B is Boltzmann’s constant, and T is the temperature. The frequency in the direction of the barrier was found to be 40.87 THz. This would give a classical reorientation rate of $\Gamma = 0.0405$ GHz at room temperature, at 10 K this is approximately zero. At room temperature this is still quite fast, but an order of magnitude lower than would be required to see an averaged symmetry in EPR. As EPR is performed at temperatures at or below 10 K it is likely that the Hydrogen is quantum tunnelling.

Taking the finite square potential approximation, the probability the Hydrogen atom tunnelling can be calculated as

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right) \quad (2.2)$$

where a is the width of the barrier, taken to be the FWHM, m is the mass of the tunnelling particle, V is the potential energy of the barrier, and E is the energy of the particle. As an approximation the ground state energy of the Hydrogen atom can be taken as that of a simple harmonic oscillator

$$E_0 = \frac{1}{2}h\nu \quad (2.3)$$

where ν is the frequency of the oscillations. The frequency of the hydrogen atom was 40.87 THz (section 2.3), such that the ground state energy was thus 0.0845 eV. As EPR is typically performed at temperatures below 10 K, it is sensible to assume that the Hydrogen is in its ground state. This energy value can then be used in equation 2.2 to give a probability of tunnelling to be $P = 1.4 \times 10^{-5}$. The tunnelling rate can then be calculated similarly to 2.1 as shown below, where A is the attempt frequency.

$$\Gamma = A \cdot P \quad (2.4)$$

Giving a final tunnelling rate of 0.59 GHz for the square potential barrier. This is in the range of frequency for which an averaged C_{2v} symmetry would be measured by EPR, giving a similar result to other N_n VH defects.

A more accurate approximation of the nature of the potential barrier is the WKB approximation. This takes the form of

$$P = \exp\left(\frac{-4\pi}{h} \int_a^b \sqrt{2m(V(x) - E)} dx\right) \quad (2.5)$$

where a and b are the *turning points* of the barrier, such that $V(x) = E$. This approximation retains the shape of the barrier. This results in a rate of $\Gamma = 0.126$ GHz, once again, this is within the range to give an averaged symmetry.

§2.3. Phonon Calculations. In order to calculate the tunnelling rate, the attempt frequency must first be calculated. Just using the stretch mode as the attempt frequency is

a good approximation, as the Hydrogen takes a very particular path, and so the direction of its movement is important. This can be done through a finite displacement phonon calculation, allowing the calculation of the frequency at which the Hydrogen atom vibrates in the direction of the minimum energy path. This calculation uses the optimised system found in section 2.1. To find the frequencies and magnitudes at which the atoms vibrate, a finite-displacement phonon calculation was performed in CASTEP [9]. In this, each atom is separately moved a small displacement from its origin (in this case 0.02 Å), and the forces acting upon the atom calculated. This results in a $3N \times 3N$ *dynamical matrix* that contains the force created due to the displacement of atoms from the origin *i.e.* the force constants. More mathematically this is the second derivative of energy with respect to the atomic displacements, shown in equation 2.6. Where r_n is the position of an atom, and m_n is its corresponding mass.

$$\frac{d^2E}{dr_i dr_j} \frac{1}{\sqrt{m_i m_j}} \quad (2.6)$$

This dynamical matrix can then be diagonalised, to retrieve its eigenvectors and eigenvalues. The eigenvalues are the square of the wavenumbers, and the eigenvectors detail the strength of a mode and its direction. To calculate the frequency the Hydrogen vibrates in the direction of the MEP, the dot product between the eigenvectors, \hat{e} , and the *normalised* direction of the MEP, \hat{r}_H , is multiplied by the corresponding wavenumber of each eigenvector, as shown below.

$$\begin{aligned} \nu_{MEP} &= \sum_i^{3N} \nu_i (\hat{e}_i \cdot \hat{r}_H) \approx 40.872 \text{ THz} \quad (2.7) \\ &= 1363 \text{ cm}^{-1} \end{aligned}$$

This is of the correct order of magnitude for a H-C bond vibration, and is also close to theorised mode between 1375 and 1378 cm^{-1} [1, 7].

§2.4. Further Calculations. The approximations for the tunnelling rate gave results that would disagree with experiment, as they are lower than the frequency of EPR, however there are many possible reasons for large underestimates. One such reason is the calculation of the

attempt frequency, whilst taking the vibration in the order of the MEP is reasonable, it does not fully capture all the possible paths over the barrier. There is the possibility of there being an area around the MEP that is *valley* in the PES, such that it is possible for the Hydrogen atom to tunnel across a variety of different paths. This would greatly increase the tunnelling probability. To capture this behaviour, a path integral molecular dynamics simulation will have to be run. (EXPLAIN PIMD HERE). Before this can be done however, a suitable potential will have to first be identified. A suitable candidate is the MACE-MP potential (CITE), further investigations will have to be undertaken, and extra training of the potential may be required before it is suitable to run a full PIMD calculation.

§3. VACANCY MIGRATION IN A PURE DIAMOND LATTICE

There is much concern of how to remove vacancies from diamond, in order to create a perfect crystal. Annealing techniques are used to heat the diamond up to a certain temperature and cool it down, in hopes of making the vacancies turn mobile and rising to the surface, effectively eliminating themselves from the bulk. Previous experimental results have shown that this starts to occur at 600 K, however it could also be useful to know the energies required for a vacancy to migrate, and also the energy barrier involved for the formation of a vacancy [10]. Molecular dynamics simulations can provide an insight into how the mechanisms involved in vacancy migration, and to inform later experiments. Hu *et al.*, as shown in section 5.1, have used a Tersoff potential to model the vacancy migration of an atom from the second layer of a diamond (001) surface to the top layer. Their results showed that this process begins to occur at 1400 K, deviating from known experimental results. Hu *et al.* argue that is due to how the temperature of the diamond is measured in experiments, that the temperature of the surface is in fact much higher than measured, and so would align more with their findings. The results of Hu *et al.* are quite old, however the methods used are not out of date, so it is reasonable to try and recreate similar results, and expand upon their work using more state-of-the-art techniques.

The same system was set up as Hu *et al.*

described in section 5.1: a 1 fs timestep was used, as well as a 100 fs timestep for the velocity rescaling method, and a 1 000 fs timestep for the pressure rescaling method. There is no mention in the original paper what the timestep for the velocity rescaling method is, nor is a pressure rescaling ensemble used at all. The choice to use the NPT ensemble came from the need to ensure that the crystal can expand slightly under higher temperatures. Following Hu *et al.*, an initial system was created and relaxed at 300 K for 5 ps, before a vacancy was created in the second layer and it was allowed to relax again for another 5 ps. The final configuration of this system formed the starting configuration of all further simulations. The system was then allowed to run at temperatures in the 300–2 000 K range. Taking inspiration from Hu *et al.*, the positions of the atoms neighbouring the vacancy were extracted from the MD run. The atom with the lowest average distance to the vacancy site was taken to be the atom that was diffusing, which was then used for analysis.

§4. NV DEFECTS

§5. KEY TEXT REVIEW

§5.1. Hu *et al.* “The Diffusion of Vacancies Near a Diamond (001) Surface” by Hu *et al.* has played an important role in my research, influencing a large part of section . Hu *et al.* used molecular dynamics to investigate vacancy diffusion in diamond surfaces at various temperatures, calculating the diffusion coefficient and diffusion barrier. Knowing the properties of vacancy defects, and at what temperatures they are mobile such that they might escape to the surface is important when dealing with synthetic diamonds. The paper is limited in that it only deals with vacancies found in the second layer of the (001) surface. Other surfaces, such as the cleavage (111) surface, also play important roles in experiment, not to mention vacancies that are found further into the bulk, such as in the third or fourth layer. The limited scope of this paper has influenced my further research found in section .

They construct their simulation as a unit cell repeated equally 5 times in all 3 cardinal directions, with periodic boundary conditions along the x and y axes, and the surfaces in the z direction showing a (001) face. There is no men-

tion of the boundaries of the cell in the z direction, however as it is dealing with a surface diffusion, it is reasonable to assume that there is a sufficient vacuum gap, such that there are no external forces acting on the surface. The perfect diamond crystal is first allowed to relax for 5 ps at 300 K, before having an atom in the second layer removed, and then relaxed for another 5 ps. The final configuration of this system was then used as the starting point of all subsequent simulations, allowing for consistency between them all. The system is then ran for up to 35 ps at temperatures ranging from 300–2 000 K.

As it is impossible to precisely track a vacancy in a crystal, as it does not truly exist, Hu *et al.* opt instead to measure the displacement of the vacancy's nearest neighbours in the surface, as vacancies move by exchanging positions with one of their neighbours. It is only necessary to measure the positions in the surface, as Halicioglu [11] previously determined that it is energetically unfavourable for a vacancy to diffuse deeper into the bulk.

Hu *et al.* found that full vacancy migration is only achieved at and above 1 400 K, with simulations ran in the 1000–1 300 K range showing only a partial relaxation of the surface neighbours into an intermediate position which they remain in until the end of the simulation. For 1 400–1 800 K, the surface neighbour relaxes to the intermediate position for some time, before finally moving all the way to the vacancy site, implying that the vacancy has fully migrated to the surface. Hu *et al.* claim that this is the first time that the two-step migration phenomena has been observed, with the intermediate vacancy position being much closer to the neighbour's original site than the vacancy site. For 2 000 K the surface neighbour migrates to the vacancy site fully in one motion. These results differ to those seen in experiment, as mentioned in the paper, Davies *et al.* [12] have showed that in Type IIa diamond, the vacancy concentration greatly decreases after annealing at a temperature range of 973–1 023 K. This would imply that the vacancy is fully mobile, as was seen in the simulations above 1 400 K. This discrepancy is explained by Hu *et al.* to be caused by how the temperatures are read: Davies *et al.* are measuring the temperature of the substrate on which the diamond is grown, however the temperature of the surface is likely to be much hotter. Another cause of the higher required migration

temperature observed by Hu *et al.* could be due to the use of the Tersoff potential, which is likely to overbind in cases like these, stopping the vacancy from migrating at the correct temperature (CITATION NEEDED).

§5.2. **Peak 'er? I hardly know 'er!.** I'M LOCKED IN! Peaker [7] carries out computational simulations on a wide variety of point defects in diamond. All calculations were done using DFT implemented in AIMPRO [13], using the PBE exchange-correlation functional [14]. AIMPRO uses Gaussian basis sets centred on each atom, as opposed to the plane-wave method used for the original research in this paper. A 1 000 atom supercell is used before introducing any defects, leaving some systems with one fewer or one more atoms. Periodic boundary conditions are applied such that they satisfy Bloch's theorem [15].

Defects containing Nitrogen, vacancies, and Hydrogen were explored, where $n + m = 0, 1, 2, 3, 4$ in N_nV_m , this is clearly incredibly broad, so the entire paper cannot be covered in depth in this short review. The defects are lumped into groups depending on the sum of n and m , for each of these groups structural, electrical and vibrational properties are calculated, as well as the electronic structure and hyperfine interaction.

A section of the paper is devoted to the quantum tunnelling effects of different defects, including N_2VH , with a nudged elastic band calculation being performed, calculating the barrier height and width. Further calculations to find out the rate of tunnelling is not explored by the author however, however classical rates of site reorientation are estimated. The lack of concrete rate calculations was the inspiration for section 2.1 of this paper.

The binding energies of the defects were also investigated, with stability being correlated with an increased number of Nitrogen and Hydrogen in a defect. From this the energetics of defects combining to form new defects were calculated, including any intermediate stages.

"First principles study of point defects in diamond" was of great use to my research due its breadth, and despite its different calculatory methods, it will certainly be useful in the future.

§5.3. **Nitrogen in Diamond.** “Nitrogen in Diamond” is a comprehensive literature review of the Nitrogen defect centres in diamond [16]. The paper outlines the two main methods of preparing lab-grown diamonds, chemical vapour disposition (CVD) and high pressure high temperature (HPTP). Details are given on how different types of impurities occur during production and how to mitigate or encourage them. As diamond is by far the largest impurity in diamond, the main interest of the paper is the section detailing the properties that different Nitrogen-based defects have, including many ways they can be identified through different types of spectroscopy. The paper is far too large and varied for a full review, so a focused review of things that relate directly to the research carried out in this paper, and potential candidates for future research, will instead be conducted.

Of interest are the interstitial Nitrogen defects, N_i and N_{2i} , which are simply a Carbon atom replaced with one or two Nitrogen atoms respectively, in the case of N_{2i} , these two Nitrogen atoms are neighbours. EPR spectra have been suggested for the structure, however their signals are not supported by DFT calculations [17]. More research of this elusive defect is required, which could be carried out in the future.

Reorientation of Hydrogen in N_nVH defects, where n ranges from 1 to 3. All of these defects are formed around a central vacancy, with a Hydrogen in the middle of the vacancy, and Nitrogens replacing the surrounding Carbons to varying degrees. In the case of NVH , EPR spectra and hyperfine interactions all report a C_{3v} symmetry, which initially would imply that the Hydrogen is directly bonded to the Nitrogen, and thus sits in the centre towards the vacancy in the (111) plane. However the dangling bond on the Nitrogen would make this an energetically unfavourable position to be in [18]. This problem is rectified by identifying that the Hydrogen is in fact quantum tunnelling between the three carbon sites at rates similar to that of EPR, giving it an averaged C_{3v} symmetry [2]. The time scales do not in fact need to be *faster* than the rate at which EPR is run, it can in fact be an order of magnitude lower, with a frequency of roughly 0.1 GHz [3].

The more recently identified N_2VH defect also undergoes a similar reorientation, appear-

ing as an averaged C_{2v} symmetry instead of a C_{1h} symmetry under EPR [7]. Comprehensive calculations are still needed to determine the rate at which the Hydrogen tunnels, which is the inspiration for section 2.

N_3VH is the final member of the N_nVH family, as every bond pointing into the vacancy centre is fully saturated, making it unfavourable for N_4VH to form. The Hydrogen does not undergo rapid reorientation in this structure, as it is strongly bonded to the last remaining carbon surrounding the vacancy centre.

§5.4. Secret fifth hidden paper.

§5.5. **Formation of NV centres in diamond.** Deak et al. [19] carry out an *ab initio* study on Nitrogen, vacancy and nitrogen vacancy defects in diamond. To improve upon previous studies using local density and generalised gradient approximation exchange-correlation functionals, the HSE06 functional [20] was used in VASP [21], this is capable of reproducing all defect transition levels and internal transitions to within ~ 0.2 eV of experiment. A large 512 atom supercell was used to limit finite size effects, with other parameters being determined after initial runs with the quicker PBE exchange-correlation functional.

Formation and excitation energies are calculated for the various defects. The diffusion activation energies were also calculated using the nudged elastic band method, to improve accuracy, this was combined with density functional based tight binding calculations. This was done as most diffusion experiments take place at high temperatures, where most of the contribution to energy comes from phonons.

The concentration of NV centres was found to always be roughly 1 000 times smaller than that of N_s centres. This is due to the low equilibrium concentration of vacancies due to their high energy of formation. Even if a large number of vacancies were to be formed, there is a preference to form V_2 over NV. This differs during irradiation, where NV formation dominates over V formation. However during annealing after irradiation, V_2 once again begins to dominate, only short ranged vacancy migration can form NV centres. The formation of N_2V over NV was found to be depending on the concentration of Nitrogen, where the formation of

N₂V is heavily favoured when concentrations of Nitrogen reach over 1 000 ppm.

Overall this study provides highly accurate calculations for transition levels, excitation energies, migration barriers, and reaction energies for defect formation, even predicting missing data on charge transitions. It will be of much use to my future research.

§5.6. Migration in bulk diamond. Butorac and Mainwood [22] perform DFT calculations on defects containing vacancies, Nitrogen and Hydrogen, using SIESTA and the PBE exchange correlation functional, with the aim of calculating the energies of migration. For this, a relaxed structure of the defect is first found for both the initial and final structure of the migration process. Intermediate structures between the two are then generated through linear interpolation. The Carbon atoms *around* the impurity were allowed to relax until minimal forces were present, whilst the defect atoms, and the Carbon atoms at the edge of the supercell were not. This however gives an overestimate of the real barrier energies, due to the stress induced on the supercell caused by fixing the outer atoms.

For interstitial Hydrogen, the migration barrier between equivalent Carbon sites was calculated to be 2.8 eV at 0 K. The activation energy was found to increase with temperature, however due to the increased energy of the Hydrogen, the probability of switching sites will still increase with temperature.

For the NVH complex, the Hydrogen prefers to bond to one of three carbons, rather than the Nitrogen. Migration between equivalent Carbon sites is reliant on quantum tunnelling, when including vibrational effects, the barrier height drops from 1.4 eV to 1.1 eV, which readily allows for quantum tunnelling to occur. This is in agreement with the literature [2]. The stability of defects were also studied, showing for example that Hydrogen is easily trapped by a vacancy centre to form VH, as well as the favourable formation of NVH.

§6. FUTURE REASEARCH

As is evident from the literature review, the use of a larger system may be preferential during DFT calculations to limit finite size effects. The calculations done in this paper used a relatively

small 64 atom supercell for speed whilst trying to learn how to use CASTEP effectively, however in this future larger supercells should be used to gain more accurate results as done in the literature.

REFERENCES

- (1) C. B. Hartland, 'A study of point defects in CVD diamond using electron paramagnetic resonance and optical spectroscopy', 2014.
- (2) M. J. Shaw, P. R. Briddon, J. P. Goss, M. J. Rayson, A. Kerridge, A. H. Harker and A. M. Stoneham, *Phys. Rev. Lett.*, 2005, **95**, 105502.
- (3) A. M. Edmonds, 'Magnetic resonance studies of point defects in single crystal diamond', 2008.
- (4) G. Henkelman, B. P. Uberuaga and H. Jónsson, *The Journal of Chemical Physics*, 2000, **113**, 9901–9904.
- (5) C. Coulson and F. Larkins, *Journal of Physics and Chemistry of Solids*, 1971, **32**, 2245–2257.
- (6) C. Glover, M. E. Newton, P. M. Martineau, S. Quinn and D. J. Twitchen, *Phys. Rev. Lett.*, 2004, **92**, 135502.
- (7) C. V. Peaker, 'First principles study of point defects in diamond', 2018.
- (8) A. Stukowski, *MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING*, 2010, **18**, DOI: {10 . 1088 / 0965 - 0393/18/1/015012}.
- (9) K. Refson, P. R. Tulip and S. J. Clark, *Phys. Rev. B*, 2006, **73**, 155114.
- (10) G. Davies, S. C. Lawson, A. T. Collins, A. Mainwood and S. J. Sharp, *Phys. Rev. B*, 1992, **46**, 13157–13170.
- (11) T. Halicioglu, *Thin Solid Films*, 1993, **228**, 293–296.
- (12) G. Davies, S. C. Lawson, A. T. Collins, A. Mainwood and S. J. Sharp, *Phys. Rev. B*, 1992, **46**, 13157–13170.
- (13) P. Briddon and R. Jones, *physica status solidi (b)*, 2000, **217**, 131–171.
- (14) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

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- (15) F. Bloch, *Zeitschrift für Physik*, 1929, **52**, 555–600.
 - (16) M. N. R. Ashfold, J. P. Goss, B. L. Green, P. W. May, M. E. Newton and C. V. Peaker, *Chemical Reviews*, 2020, **120**, PMID: 32048841, 5745–5794.
 - (17) M. K. Atumi, J. P. Goss, P. R. Briddon, F. E. Shrif and M. J. Rayson, *Journal of Physics: Condensed Matter*, 2013, **25**, 065802.
 - (18) J. Goss, P. Briddon, R. Jones and S. Sque, *Journal of Physics: Condensed Matter*, 2003, **15**, S2903.
 - (19) P. Deak, B. Aradi, M. Kaviani, T. Frauenheim and A. Gali, *PHYSICAL REVIEW B*, 2014, **89**, DOI: 10.1103/PhysRevB.89.075203.
 - (20) A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *The Journal of Chemical Physics*, 2006, **125**, 224106.
 - (21) G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
 - (22) B. Butorac and A. Mainwood, *Diamond and Related Materials*, 2008, **17**, Proceedings of Diamond 2007, the 18th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide, 1225–1228.