Point and extended defects in chemical vapour deposited diamond

H Pinto¹, R Jones¹, J P Goss² and P R Briddon²

¹School of Engineering, Mathematics and Physical Sciences, University of Exeter, Stocker Road, Exeter, EX4 4QL, United Kingdom
²School of Electrical, Electronic and Computer Engineering, Newcastle University, NE1 7RU, United Kingdom
E-mail: pinto@excc.ex.ac.uk

Abstract. Homoepitaxially grown single crystal CVD diamond has a dislocation arrangement not seen in natural IIa diamond. Whereas in the latter, dislocations lie on (111) planes along [1\bar{1}0] directions, dislocations in CVD diamond lie nearly along the [001] growth axis and are arranged in bundles with almost four fold rotational symmetry. Their large strain is easily seen in birefringence and we model the arrangements in the bundle to account for the singular behaviour of the birefringence when the polarisers are rotated with respect to the crystal. The optical absorption spectrum of brown CVD diamond displays a continuum similar to that found in brown IIa natural diamonds but in addition broad point defect induced bands. We investigate the suggestion that the 2.38 eV (560 nm) peak is related to V\textsubscript{NH}. We suggest that the breadth of these bands is related to the large structural change when the defect is excited.

1. Introduction

Natural brown type IIa diamonds owe their colour to multi-vacancy defects introduced by plastic deformation [1, 2, 3]. Positron annihilation studies show that clusters of perhaps 50 vacancies exist and are optically active [4]. The clusters have also been seen by TEM experiments [5]. These clusters are not found in diamonds which have been treated to remove the colour or in naturally colourless diamonds. Although CVD diamonds are often brown, positron annihilation experiments do not reveal the presence of large vacancy clusters. In CVD brown diamonds, the brown colour is lost following anneals at temperatures lower than that needed for natural brown diamonds. It may be that the colour arises from vacancy disks [3] or graphitic forms of carbon.

In type IIa diamond, dislocations are often found on \{111\} planes and lie along \langle110\rangle direction. This is not the case in CVD diamonds where they lie in bundles close to the \{001\} growth axis. Previous modelling [6] has shown that the cores of individual dislocations can be reconstructed and the straight dislocation along \{001\} has a competitive core energy with dislocations with zig-zag segments lying along \{101\} and \{011\}. Many of these grown-in dislocations occur in bundles, and such is their strain that they are easily seen in birefringence. Remarkably, the birefringence exhibits an approximate four fold rotational symmetry which implies that the same numbers of dislocations are found in each of the four (110) quadrants. In section 2 we review possible arrangement of the dislocations in the bundle.

The absorption spectrum for a brown CVD diamond not only shows the continuous absorption seen in natural browns but also broad absorption bands around 1.4, 2.38, 3.44 and 4.5 eV. The last is due to neutral substitutional nitrogen centres [1, 7]. Of particular interest is the band at 2.4 eV which can result
in a pink colouration of the diamond. We discuss in section 3, the assignment of this absorption band and why their spectra are so broad.

2. Birefringence of dislocation bundles in CVD diamond

Homoepitaxial CVD diamond contains bundles of edge and mixed dislocations of density about $\sim 10^5 \text{ cm}^{-2}$, lying approximately along the [001] growth direction [8]. Although the dislocations lie close to the (001) directions, they fan out at an angle of a few degrees in $\langle 110 \rangle$ directions. Detailed studies using X-ray topography show that, in many cases, the dislocations are observed in groups of four or more lines diverging from a defect on or near the substrate. Where only four lines are observed to emanate from a given point, the dislocations deviate from [001] in such a way that their projections onto the (001) plane lie along $\langle 110 \rangle$. Often, those with projections along [110] or $[\overline{1}10]$ have [110] Burgers vectors, and those with projections along [$1\overline{1}0$] or $[\overline{1}10]$ have [110] Burgers vectors. These dislocations are predominantly of edge type [9]. Diamonds containing such bundles exhibit a birefringence with a few strikingly bright regions with a characteristic pattern consisting of four approximately equally bright petals as shown in figure 1. There is a close connection between these four petalled defects and dislocations. X-ray topographs reveal that the regions where birefringence is seen, coincides with dense bundles of dislocations [9].

The four petalled pattern shown in figure 1 is not invariant under a rotation of the crystal about [001], i.e., the pattern changes with the directions of the crossed polarisers (figure 2). Thus, the strain field is linked to the underlying crystallography as expected from a dislocation model and is not the case for a spherical inclusion. The additional lobes seen when the polarisers are parallel to $\langle 100 \rangle$ are weaker than the bright lobes seen for the case when the polarisers lie along $\langle 110 \rangle$.

The spatial extent of the birefringence in the (001) plane is about 13% of the crystal size or about 300-400 $\mu$m, given that the crystal is about 3 mm in size. Clearly, the birefringence of a single dislocation does not extend over this distance, and the resultant strain due to a bundle of many dislocations must be considered.

We note that the dislocations arise only in the epilayer and not the underlying substrate. Since dislocations cannot terminate within the crystal, the bundle must be composed of dislocation dipoles with zero net Burgers vector. We have found [10] that the four petalled pattern arises from a compact defect on the substrate surface with dimensions less than 20 $\mu$m. We discuss here possible arrangements...
2. Birefringence of a single edge dislocation

The strain fields of a bundle of dislocations can be found using isotropic elasticity theory by summing the strains due to individual edge dislocations. The principal values of the strain tensor and their directions are then calculated. The phase difference between the two polarised components of the light ray at the exit of the crystal is

$$\delta = 2\pi(n_1 - n_2)t/\lambda,$$

where $n_1$ and $n_2$ are the refractive indices of the crystal along the principal directions of strain, $\lambda$ is the wavelength (550 nm), and $t$ is the optical thickness of the crystal taken to be 2.52 mm. The refractive indices are related to the strain through the strain-optic coefficients $p_{ij}$. For stressed cubic materials,

$$n_1 - n_2 = -n^3(p_{11} - p_{12})(\epsilon'_{11} - \epsilon'_{22})/2,$$

where $\epsilon'_{ii}$ are the principal values of the strain tensor and $n$ the refractive index of diamond.

We have previously calculated $p_{11} - p_{12}$ to be $-0.3$ [11], and this compares favourably with experiment [12].

Thus, light polarised along the principal direction associated with $\epsilon'_{11}$ moves with the slower speed if $\epsilon'_{11} > \epsilon'_{22}$. This direction corresponds with tensile strain. We note that $\delta$ is simply related to the shear strain $(\epsilon'_{11} - \epsilon'_{22})/2$ and hence a map of $\delta$ gives the shear strain field in the (001) plane. The intensity of birefringence is given by $I = E^2\sin^2(2\phi)\sin^2(\delta/2)$ where $\phi$ is angle between a principal axis of strain and a polariser [13].

For an edge dislocation lying along $z$, with the Burgers vector of magnitude $b$, taken to be $a/\sqrt{2}$, and parallel to $x$, the strain tensor $\epsilon_{ij}$ and its principal values $\epsilon'_{ii}$ are well known and lead to a shear strain of [14]

$$\epsilon'_{11} - \epsilon'_{22} = -2Ax/r^2, \quad \theta = \frac{1}{2}\tan^{-1}(y^2-x^2)/(2xy).$$

Here $A = b/(4\pi(1-\nu))$, $\nu$ is Poisson’s ratio, $r^2 = x^2 + y^2$ and $\theta$ the angle between the Burgers vector and a principal direction of strain. We note that $n_1 - n_2$ decreases with distance from the core as $1/r$.

The strain field, proportional to $\delta$, and birefringence of a single edge dislocation with Burgers vector along [100] are shown in figure 3 for the cases when the polariser is along [100] and [110]. The birefringence reveals a characteristic dipole pattern which turns into a four petalled pattern when the crossed polarisers are turned through 45°. The patterns can be simply understood from the principal strains and their directions given above. However, the shear strain map and birefringence of a single edge dislocation cannot describe the four petalled defect and alternative models must be considered.
2.2. The four petal defect

X-ray topography shows that the petalled defect is associated with groups of edge dislocations emanating from a defect on or near the substrate surface and fanning out along \( \langle 110 \rangle \) directions. Many of these dislocations have [110] Burgers vectors and lie about 3-5\(^\circ\) off [001] in the (110) plane, while those with [01\(\overline{1}\)] Burgers vectors lie at a similar angle to [001] but in the (01\(\overline{1}\)) plane [9]. Here we shall investigate the strain field of the simplest arrangement having this structure consisting of a linear array of dislocations in each quadrant. We note that this arrangement has a four fold rotational axis and such a symmetry is necessary to explain the strain field of the four petalled defect shown in the lower part of figure 4. The other four petalled defect lying in the upper part of figure 4 possesses two fold rotational symmetric strain field which has been discussed earlier [10].

We placed 20 edge dislocations in the first quadrant all lying along \([\sin \chi, \sin \chi, \cos \chi]\) and intersecting the (001) plane at equidistant points along [110] as indicated schematically in figure 5(a). The dislocations all have the same \(a/2[1\overline{1}0]\) Burgers vector. The separation of individual dislocations in each arm is 0.1 \(\mu m\). Dislocations in the other three quadrants are found by rotating those in the first quadrant.

The dislocations introduce additional half-planes outside the core of the defect, which produce a net compression along the tangential direction and a radial tensile field. This is necessary to reproduce the radial slow axis shown in figure 4.

Figure 5 shows the calculated strain field and birefringence. The strain map, figure 5(b), reveals a four petalled pattern with dark arms corresponding with zero shear strain along \( \langle 110 \rangle \) as indeed observed. Since \( \delta \) is zero along the four \( \langle 110 \rangle \) directions, it follows that the birefringence vanishes along these directions for all directions of the polariser. This accounts for the four fold pattern seen in birefringence for polarisers lying other than along \( \langle 100 \rangle \). For points along say [100], we find that the principal axes
Figure 4. Phase difference |sin(δ)| between the two polarised waves at the exit of the specimen of thickness 2.52 mm showing the four petalled defect. The dashed lines parallel to the [100] and [010] edges of the specimen indicate the principal directions of strain for the slow direction of light propagation. Note that for points along [100], the direction of the slow axis is also along this direction. Figure provided by P. Martineau. Colour version online.

of strain also lie along ⟨100⟩ directions and in fact the tensile axis lies along this [100]. This is also in agreement with the experiment as shown in figure 4.

Consider now the birefringence for polarisers lying along ⟨100⟩. In this case, the four ⟨100⟩ directions are also dark as these directions coincide with the principal axes of strain. Figure 5 shows the birefringence map for this case and we find 8 arms in agreement with observation. The long exposure time required to reveal this structure is also in agreement with the theory as shown when figure 2 and figure 5 are compared. Finally, we note that the extent of the birefringence is around 300 μm and consistent with the observations.

2.3. Summary
We have analysed the strain field and birefringence of several linear arrays of dislocations which could be responsible for a number of petalled defects seen in single crystal CVD diamonds. The strain field of a single edge dislocation as well as its birefringence cannot explain the magnitude of the birefringence associated with the four petalled defect. The birefringence of four linear arrays of edge dislocations located on four arms lying along ⟨110⟩ directions with ⟨110⟩ Burgers vectors, leads to a strain field with four bright petals along ⟨100⟩ as observed. The birefringence associated with the defect is sensitive to
Figure 5. The calculated strain field and birefringence of the four arm defect. (a) Projection of dislocation lines onto (001). The dislocations are inclined at angle $\chi = 3.5^\circ$ to [001] and are separated by 0.1 $\mu$m. The projection shows the four fold symmetry of the bundle and the directions of the Burgers vectors. (b) Delta or strain map of the bundle, (c-f) birefringence for polarisers at angles of 0, 15, 30, and 45$^\circ$ to [100]. Note the extent of the birefringence is about 300 $\mu$m and that there is a weaker birefringence when the polarisers are parallel to [100] than at an angle of 45$^\circ$ with [100]. The birefringence shows 8 bright lobes in the first case and 4 in the second. Scale along x and y is in $\mu$m.

The directions of the polarisers. If these are along ⟨110⟩, then four bright lobes are seen also along ⟨100⟩. If the polarisers are parallel to ⟨100⟩, then eight weak lobes are seen. Such patterns reflect the four fold symmetry of the defect. With the arrangement of dislocations and Burgers vectors shown in figure 5(a), with the extra half planes of atoms in each dislocation lying outside the core, the principal axis of strain associated with the slower polarised ray is radial, as observed. The birefringence is seen to extend to
3. Absorption peaks in CVD diamond

Figure 6 shows the absorption spectrum of a brown CVD diamond. In addition to the continuum responsible for the brown colour in natural IIa diamonds, broad absorption peaks are detected at 2.38, 3.44 and 4.5 eV.

The peak at 4.5 eV is due to neutral substitutional nitrogen [15] while the 3.44 eV peak has been related to negatively charged nitrogen-hydrogen vacancy centres (V\textsubscript{NH}\textsuperscript{−}) [16]. This centre is after N\textsubscript{0}, the most dominant one detected by electron paramagnetic resonance [17]. It exhibits photo- and thermo-chromism [16] as an anneal around 800 K leads to the loss of neutral nitrogen donors as well as the intensities of the 2.38 eV (520 nm) and 3.44 eV (360 nm) bands. Following this anneal, the concentration of VNH\textsuperscript{−} as measured by EPR [17] and the intensity of a broad band centred at 1.37 eV (900 nm) increases. We review here the calculations of the optical properties of these defects carried out previously [18], and we investigate the origin of the lack of a zero phonon line and the breadth of the 3.44 eV and 1.37 eV bands.

Figure 7 shows the structure of the VNH defect along with that of VN\textsubscript{2}. It is clear that the two defects are very similar. Further, the band structures of VNH\textsuperscript{−} and VN\textsubscript{2}\textsuperscript{−}, shown in figure 8 are strikingly similar with each defect having three gap levels.

Although density functional theory is unable to describe optical transition energies accurately, we have used the errors in the transitions for VN\textsubscript{2} to correct the transitions for VNH. In a similar way, we can correct the acceptor level of VNH from the error we make in the same level for VN\textsubscript{2}.

We found [18] the spin 0 state is more stable than spin 1 for VN\textsubscript{2} and VNH. The vibrational modes of neutral (S = 0) and negative VNH defects are listed in table 1. The value for VNH\textsubscript{0} in the S = 0 configuration is in good agreement with one observed at 3123 cm\textsuperscript{−1} [16, 19] associated with VNH\textsubscript{0} and
Figure 7. VN\textsubscript{H} and VN\textsubscript{2} defects. Note that if the H atom was moved to lie on top of its carbon neighbour, the defect would have the same structure and symmetry and be isoelectronic with VN\textsubscript{2}.

Figure 8. Band structures along high-symmetry paths in the Brillouin-zone and in the vicinity of the band gap with $E_\text{v}$ aligned to zero for the spin singlet configurations of VN\textsubscript{2}(0) (left), and VN\textsubscript{H}(0) (right). Filled and empty symbols indicate filled and empty bands, respectively, with the underlying shaded area indicating the bands in a defect-free supercell of the same size. Note there are three localised gap levels.

Table 1. C–H stretch mode frequencies (cm$^{-1}$) calculated for VN\textsubscript{H} in the neutral and negative charge states. These values are obtained using the GGA.

| Defect | $q = 0$, $S = 0$ | $q = 0$, $S = 1$ | $q = -1$ |
|--------|-----------------|-----------------|---------|
| VN\textsubscript{H} | 3190            | 2858            | 2941    |

supports a spin-singlet ground state of VN\textsubscript{H}.

For VN\textsubscript{2}, which has $C_{2v}$ symmetry, the three gap levels have in ascending energy, $b_1$, $a_1$ and $b_2$ symmetry. Although, VN\textsubscript{H} does not have $C_{2v}$ symmetry, we shall refer to the gap levels as $b_1$, $a_1$ and $b_2$. The two highest in all three defects, $a_1$ and $b_2$, originate from bonding and anti-bonding orbitals made up primarily of dangling bonds on the two carbon radicals, The lowest $b_1$ level is localised on the N atoms while the level arising from C-H falls deeper in the valence band.

Both defects support internal $a_1 \rightarrow b_2$ optical transitions in the neutral (process I) and negative (process II) charge states as well as charge transfer transitions. The $b_1 \rightarrow b_2$ transition is dipole forbidden. Thus, each defect is expected to possess at least four optical transitions as charge transfer can take place by either by exciting a valence electron to a $b_2$ level for the neutral defect (process III),
Table 2. Calculated and experimental transition energies (see figure 9).

| Defect | $E_1$  | $E_2$  | $E_3$  |
|--------|--------|--------|--------|
| VN$_2$ | 1.297  | 0.969  | 2.7    |
| VNH    | 1.129  | 0.84   | 2.3    |

| Corrected value, eV |
|---------------------|
| VN$_2$              |
| 2.46                |
| 1.26                |
| 3.4                 |
| VNH                 |
| 2.3                 |
| 1.1                 |
| 3.0                 |

| Experimental values, eV (nm) |
|-----------------------------|
| VN$_2$                      |
| 2.46 (504)                  |
| 1.26 (984)                  |
| 3.4 (365)                   |
| VNH                         |
| 2.38 (520)                  |
| 1.37 (900)                  |

or exciting a electron from the $b_2$ level to the conduction band for the negatively charged defect (process IV). These four lowest energy optical transitions are schematically shown in figure 9.

The internal transition energies for neutral ($E_1$) and negatively charged ($E_2$) VN$_2$ are found by evaluating the total energies for the two single particle determinantal wave functions. These yield 0.97 eV for VN$_2^-$ and 1.3 eV for neutral VN$_2$. The former is in reasonable agreement with experimental value of 1.26 eV for the H2 optical centre [20] but the latter is in poor agreement with the experimental value of 2.46 eV [21]. We suppose this is because of errors in the correlation energy. As discussed above, we correct the energies for VNH by adding the error in the energies for VN$_2$. Table 2 gives the corrected transition energies.

Previously we used density functional theory to place the acceptor level of the VN$_2$ defect at $E_v+2.7$ eV [22]. This can be compared with an experimental value of $E_v+3.4$ eV based on a study of the photochromacity of VN$_2$ [23]. This energy is close to a weak absorption band of VN$_2^0$ labelled H13 [24]. Hence, the H13 absorption band is due to a charge state change involving the transfer of an electron from the valence band to the defect as in $\text{VN}_2^0 + e \rightarrow \text{VN}_2^- + h$. The acceptor level of VN$_2$ can also be evaluated and is given in table 2. Similarly we used the error found for VN$_2$ to correct the acceptor level of VNH, table 2.

4. Summary
In summary, VNH has four optical transitions shown schematically in figure 9. Each charge state has an internal transition and we label these transitions as processes I and II. There are also two transitions involving the valence or conduction band and a change in the charge state either by excitation of a valence electron creating VNH$^-$ (process III) or by ionisation of VNH$^-$ with electron emission to the conduction band (process IV).

The acceptor level of the defect establishes the minimum energy required for a charge state change from neutral to negative leading to a free hole. For a photochromic effect, the hole must be trapped by a nearby different defect. The defect then remains in the negative charge state and the internal absorption due to the neutral one is bleached. Thus, the acceptor level referenced to the valence band top is the bleaching energy for the neutral defect. Recovery can take place by the reverse process, or by exposure to light enabling electron emission from the negative defect to the conduction band. In the latter case, the minimum energy for recovery of the neutral defect is the distance of the acceptor level to the conduction band. These energies are known for VN$_2$ and are given in table 2. These experiments have shown that H2 is bleached with light of energy greater than 2.06eV (600nm) (process IV), and recovers with intense light of energy 3.4eV (365 nm, process III) [23]. The sum of the energies being the band gap
Figure 9. Configuration energies of $\text{VN}_2$ and $\text{VNH}$ defects showing the five states involved in the visible and UV optical transitions. The lowest line denotes the ground state energy $E = E_0$ of the crystal with a neutral defect. The next line denotes the energy of the ground state crystal and an internally excited neutral defect $\text{VN}_2^0$. The third is the energy of the crystal with a free hole and the charged defect $\text{VN}_2^-$ in its lowest energy state. The fourth represents the energy of the crystal with a hole and the internally excited charged defect $\text{VN}_2^{*+}$. The top line is the energy of a free electron in the conduction band and a hole in the valence band with the defect neutral and in its lowest energy state, i.e. the band gap energy $E_0 + E_g$. The energies of processes I, II and III are denoted by $E_1$, $E_2$ and $E_3$. $E_3$ is just the acceptor level of the defect referred to the valence band top. Assuming weak lattice relaxation, process IV has energy $E_g - E_3$.

confirms that the photochromic effect is due to a charge state change with an acceptor level at $E_g + 3.4\text{eV}$. Importantly, the effect is not limited by ionisation of the trap which is probably nitrogen. In principle, observations of a photochromic effect in $\text{VNH}$ could yield its acceptor level but, from the similarity of its properties with $\text{VN}_2$, we expect such a level to be close to that of $\text{VN}_2$.

Table 3. Vertical absorption and emission energies as well as zero phonon lines (ZPL) calculated for $\text{VN}^-$, $\text{VN}_2^-$ and $\text{VNH}^-$.

|                  | Vertical absorption (eV) | Vertical emission (eV) | ZPL (eV)  |
|------------------|--------------------------|------------------------|-----------|
| $\text{VN}^-$   | 1.95                     | 1.55                   | 1.74      |
| $\text{VN}_2^-$ | 1.36                     | 0.87                   | 1.08      |
| $\text{VNH}^-$  | 1.12                     | 0.52                   | 0.80      |

It is clear from figure 6 that the absorption bands due to $\text{VNH}$ are very broad. This is reminiscent of colour centres in alkali halides where it is related to a large structural change when the defect is excited and shown schematically in figure 10.

We have examined the effect of relaxation of the excited state on the vertical absorption and emission energies of $\text{VNH}^-$, $\text{VN}^-$ and $\text{VN}_2^-$ found by calculating the total energy differences between the ground and excited states when the structures are frozen or when relaxed. These are given in Table 3. For $\text{VN}^-$
and VN$_2$ these energies differ by 0.4 and 0.5 eV which account for a weak zero-phonon line and broad vibronic sidebands. In VN$,^-$, the integrated intensity of the ZPL is only 3% of the overall absorption. For VN$^-$, the effect is larger as the difference between the absorption and emission energies is now 0.6 eV. This we expect a weaker zero-phonon line which could explain why it is not seen. Sharp line luminescence is not detected from VN$^-$ and our theory suggests a broad spectrum starting around 0.5 eV.

5. Discussion
We find VN$_2$ and VNH posses three localised gap levels. The upper pair are related to bonding and antibonding orbitals on the two C radicals and the lower one comes from the N lone pair and the C-H unit. The positions of the highest occupied and lowest unoccupied levels of VN$_2$ and VNH are very similar and it follows that the optical activity of the three defects is also similar and derived from the properties of the two carbon atoms having dangling bonds. We have 4 electrons to distribute among these levels for the neutral defect and 5 electrons for the negatively charged defects. The ground and excited states of VN$_2$ have symmetry $^1A_1$ and $^1B_1$ respectively but their energy difference is calculated to be far too small. This reflects the fragility of the theory in treating excited states. In the negatively charged defect, the ground and excited states have $^2B_1$ and $^2A_1$ symmetry and their calculated energy difference is in fair agreement with the observed H$_2$ transition.

We expect VN$_2$ and VNH to possess similar optical properties to VN$_2$, and in particular similar internal optical transitions in the two charge states and similar acceptor levels. With this proviso we can discuss the absorption bands seen in CVD diamond. Table 2 shows that the two broad bands at 2.38 eV (520 nm) and 1.37 eV (900 nm) are internal transitions in VNH and VNH$^-$. This is supported by the bleaching and recovery data, which show these bands to be anti-correlated [16].

The 360 nm band is more contentious. It lies close to that required for a charge state change of VNH$^0$ (process III) and should be analogous with the H13 band in VN$_2$$^0$. However, it seems that this band does not anneal out at the same time as the 2.38 eV (520 nm) band indicating that a distinct defect is involved. Nevertheless, we recall that the intensity of the H13 band of VN$_2$ at 364 nm is weak, and we suppose that this is also true in VNH so that the broad 360 nm band hides the weak absorption where VNH$^0$ changes charge state. We remark that the existence of VNH$^-$ shows the defect has an acceptor level, and must absorb light with an energy close to this level. The weakness of the transitions may be because the dipole
matrix element is between an extended state in the valence band, and the localised \( a_1 \) state in the gap and this is smaller than the overlap between two localised gap states, as is involved in an internal transition. In the case of \( VN_2 \), the charge state change has been investigated optically with intense light of energy 600 nm and 364 nm (2.07 and 3.4 eV). Similar energies should effect photochromic behaviour in \( VNH \).

Finally, we note that the optical bands of \( VNH \) are anomalously broad. It appears that there a larger structural relaxation when \( VNH \) is excited than \( VN^- \) or \( VN^-_2 \). This would certainty broaden the spectra as the intensity of the ZPL relative to the broad vibronic side band would be \( \exp(-\Delta E/\hbar\omega) \). Here \( \omega \) is a typical phonon frequency taken to be \( \sim 500 \text{ cm}^{-1} \). This gives the Huang-Rhys factor of 3.7 required to give the ZPL intensity of \( VN^- \). \( \Delta E \) is the difference between the vertical absorption energy and the ZPL. Thus, the fractional intensities of the ZPLs are 3%, 1% and 0.4% for \( VN^- \), \( VN^-_2 \) and \( VNH^- \), respectively. Hence, broad absorption is to be expected for \( VNH^- \) with a weak zero phonon line.

6. Acknowledgements

L Houlsome, N Fujita, P M Martineau, M Gaukroger, D Fisher, R Khan and U Bangert are thanked for many valuable discussions.

References

[1] Jones R, 2009 Diamond Relat. Mater. 18 820–826
[2] Fisher D, Evans DJF, Glover C, Kelly CJ, Sheehy MJ and Summerton GC, 2006 Diamond Relat. Mater. 15 1636–1642
[3] Houlsome LS, Jones R, Martineau PM, Fisher D, Shaw MJ, Briddon PR and Öberg S, 2006 Phys. Rev. B 73 125203
[4] Mäki JM, Tuomisto F, Kelly CJ, Fisher D and Martineau PM, 2009 J. Phys. Cond. Matter 21 364216
[5] Bangert U, Barnes R, Gass MH, Bleloch AL and Godfrey IS, 2009 J. Phys. Cond. Matter 21 364208
[6] Fujita N, Blumenau AT, Jones R. and Öberg S and Briddon PR, 2007 Phys. Status Solidi A 204 2211–2215
[7] Nazaré MH and Neves AJT, 1987 J. Phys. C 20 2713–2722
[8] Martineau PM, Lawson SC, Taylor AJ, Quinn SJ, Evans DJF and Crowder MJ, 2004 Gems Gemol. 40 2
[9] Gaukroger MP, Martineau PM, Crowder MJ, Friel I, Williams SD and Twitchen DJ, 2008 Diamond and Related Materials 17 262–269
[10] Pinto H and R. J, 2009 J. Phys. Cond. Matter 21 364220
[11] Houlsome LS, Jones R, Shaw MJ and Briddon PR, 2006 Phys. Status Solidi A 203 3088–3093
[12] Lang AR, 2009 Diamond and Related Materials 18 1–5
[13] Born M and Wolf E, 2001 Principles of Optics, 7th edition, p 824 , Cambridge
[14] Bullough R, 1958 Phys. Rev. 110 620–623
[15] Jones R, Goss JP and Briddon PR, 2009 Phys. Rev. B 80 033205
[16] Khan RUA, Martineau PM, Cann BL, Newton ME and Twitchen DJ, 2009 J. Phys. Cond. Matter 21 36
[17] Glover C, Newton ME, Martineau P, Twitchen DJ and Baker JM, 2003 Phys. Rev. Lett. 90 185507
[18] Goss JP, Briddon PR, Pinho H and Jones R, 2010 Phys. Status Solidi A 207 2049–2053
[19] Fuchs F, Wild C, Schwarz K and Koidl P, 1995 Diamond Relat. Mater. 4 652–656
[20] Lawson SC, Davies G, Collins AT and Mainwood A, 1992 J. Phys. Cond. Matter 4 3439–3452
[21] Davies G, Nazaré MH and Hamer MF, 1976 Proc. R. Soc. London, Ser. A 351 245–265
[22] Goss JP, Briddon PR, Jones R and Sque S, 2003 J. Phys. Cond. Matter 15 S2903–S2911
[23] Mita Y, Nisida Y, Suito K, Onodera A and Yazu S, 1990 J. Phys. Cond. Matter 2 8567–8574
[24] Collins AT, 1983 J. Phys. C 16 6691–6694