Electron paramagnetic resonance studies of nitrogen interstitial defects in diamond


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EPR studies of nitrogen interstitial defects in diamond

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Abstract. We report on electron paramagnetic resonance studies of nitrogen-doped diamond that has been \(^{15}\)N-enriched, electron-irradiated and annealed. EPR spectra from two new nitrogen containing \(S = \frac{1}{2}\) defects are detected and labelled WAR9 and WAR10. We show that the properties of these defect are consistent with them being the (001)-nitrogen split interstitial and the (001)-nitrogen split interstitial–(001)-carbon split interstitial pair, respectively. We also provide an explanation for why these defects have previously eluded discovery.

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1. Introduction

Isolated vacancies and self interstitials are produced by the irradiation of diamond with particles of sufficient energy to displace carbon atoms. The production of primary and secondary irradiation damage defects has been intensively studied in intrinsic diamond. The neutral \((V^0)\) and negatively \((V^-)\) charged isolated vacancy have been thoroughly characterised by optical \([1, 2, 3, 4, 5]\) and EPR spectroscopy \([6, 7]\), and experiment and theory are in good accord. The activation energy for migration of \(V^0\) is 2.2 eV \([8]\), and in intrinsic diamond substantial concentrations of di-vacancies can be produced by annealing at 1100 K \([9]\). There is no evidence for excitation enhanced migration of the vacancy \([10]\), however the situation is far more complicated for the interstitial. Theoretically the (001)-split-self-interstitial \((I_{001})\) is by far the lowest energy configuration \([11]\), and this is the only one observed and characterised by EPR \([10]\) and optical spectroscopy \([12]\). For 1–2 MeV electron irradiation at \(\sim 100\) K the production of isolated vacancies and interstitials is identical \([10]\). However as the temperature is increased excitation enhanced migration of the interstitial with an activation energy of...
∼ 0.3 eV has been observed [13]. It is uncertain as to whether this enhanced mobility is due to electronic excitation of the neutral I_{001} defect or is characteristic of e.g. I_{001}^{-}. This result explains the production of di-interstitial aggregates upon room temperature irradiation [14], whereas post irradiation annealing shows that the activation energy for migration of I_{001} is 1.6 eV [13, 15]. Following annealing above the migration temperature of I_{001} a three interstitial aggregate has been observed by EPR [16] and a diamagnetic four interstitial aggregate predicted by theory [11].

Nitrogen is a common impurity in both natural and synthetic diamond and it is used as the basis for classifying diamond [17]: Type I diamond contains significant quantities of nitrogen as measured by Infra-red (IR) absorption; Type II diamond does not. Type I diamond is further subdivided into Type Ia, in which the nitrogen is present in aggregated forms, and Type Ib, containing mostly single substitutional nitrogen, N_{S}. Common forms of aggregated nitrogen in diamond are two nearest-neighbour substitutional nitrogen atoms, known as the A-centre, four substitutional nitrogen atoms surrounding a vacant lattice site (vacancy), called the B-centre, and three substitutional nitrogen atoms next to a vacancy, labelled N3 [17].

Much is known of the interaction of vacancies with nitrogen impurities. Charge transfer from the neutral single substitutional nitrogen (N_{S}^{0}) donor produces V^{-}

\[ V^{0} + N_{S}^{0} \rightleftharpoons V^{-} + N_{S}^{+} \]

Upon annealing above ∼900 K the stationary N_{S} readily traps vacancies to produce nitrogen vacancy complexes

\[ N_{S}^{0} + V \rightarrow NV^{0} \]
\[ NV^{0} + N_{S}^{0} \rightarrow NV^{-} + N_{S}^{+} \]

and both the neutral and negatively charged NV-centres are discussed extensively elsewhere [8, 18, 19]. Substitutional nitrogen pairs (A-centres) also trap mobile vacancies (although less efficiently than N_{S}) to produce N–V–N defects [8]; again neutral (H3) and negatively charged (H2) versions are produced [20, 21, 22, 23]. The NV centre anneals out at ∼ 1800 K, with the associated production of A-centres via vacancy-assisted aggregation

\[ NV + N_{S} \rightarrow N_{S}N_{S}^{-} + V \]
\[ N_{S} + V \rightarrow NV \]

\textit{etc}

[24]. High temperature annealing (under stabilising pressures) of nitrogen containing diamond usually results in specimens with detectable (at least by photoluminescence) concentrations of NV^{0/-} and NVN^{0/-}, which have been ’quenched’ in, but this will not be discussed further here [23, 25].

Our understanding of the fate of interstitials in nitrogen doped diamond is far less advanced. We know that (R1) di-interstitials are not produced in diamond doped with N_{S} when the concentration of nitrogen greatly exceeds that of the interstitials produced
by irradiation damage [26]. The production of isolated I\textsubscript{001} interstitials was not altered by the presence of N\textsubscript{0} \textsubscript{S} [26], indicating that even with the deep donor present the neutral charge state of I\textsubscript{001} is preferred. Once mobile we postulate that the I\textsubscript{001} interstitials are trapped by N\textsubscript{0} \textsubscript{S} producing N\textsubscript{I} \textsubscript{I} \textsubscript{001}

\[ \text{I}_{001} + \text{N}_{0}^{0} \rightarrow \text{N}_{1} \]  

where one of the atoms of the interstitial dumbbell is replaced by the nitrogen atom. It is unlikely that N\textsubscript{1} would dissociate but migrate as a unit [27], once mobile. Goss \textit{et al.} [27] predicted that the barrier to migration for N\textsubscript{I} \textsubscript{I} is substantially less than that for N\textsubscript{0} \textsubscript{I}. The capture of I\textsubscript{001} by N\textsubscript{1} would produce an R1 like di-interstitial with one of the three-fold coordinated carbons replaced with a nitrogen ([N\textsubscript{1}–I\textsubscript{001}]). Capture of N\textsubscript{1} by N\textsubscript{S} would produce N\textsubscript{2I} where both dumbbell atoms of the interstitial are replaced by nitrogens. Goss \textit{et al.} [27] proposed that this defect was responsible for the H1a local vibrational mode [28]. In the neutral charge state both N\textsubscript{1} and N\textsubscript{1}–I\textsubscript{001} would be paramagnetic and should be observable by EPR if not obscured by other defects; the detection of both is the subject of this paper.

We can postulate further that in diamond where the nitrogen is incorporated as A-centres mobile interstitials will be trapped by A-centres to produce N\textsubscript{2I} directly. Indeed this was the argument put forward by Goss \textit{et al.} to explain the different temperatures at which H1a is annealed into type Ib and type Ia diamond [27].

It has been shown that incorporation of nitrogen in HPHT diamond is growth sector dependent, with \{111\} sectors typically showing the highest N\textsubscript{S} concentration [29]. Burns \textit{et al.} [29] found that in a sample where the \{111\} sectors contained \sim 100 ppm (atomic parts per million) N\textsubscript{0} \textsubscript{S} the \{100\} sectors contained \sim 50 ppm N\textsubscript{0} \textsubscript{S} with the \{113\} and \{110\} sectors containing substantially less N\textsubscript{0} \textsubscript{S} at \sim 10 ppm and \sim 1 ppm, respectively. Thus following irradiation, it is important to bear in mind that we have to consider both the situations where \[ \text{N}_{0}^{0} \gg [\text{V}_0,\text{I}_{001}] \text{ and N}_{0}^{0} \ll [\text{V}_0,\text{I}_{001}] \] in a mixed growth sector sample. In the former we are likely to produce diamagnetic N\textsubscript{1} \textsuperscript{−} and [N\textsubscript{1}–I\textsubscript{001}] \textsuperscript{−}, in the latter paramagnetic N\textsubscript{1} \textsuperscript{0} and [N\textsubscript{1}–I\textsubscript{001}] \textsuperscript{0} when interstitials are mobile. Following the work by Goss \textit{et al.} [27] on the mobilities of N\textsubscript{1} \textsuperscript{0} and N\textsubscript{1} \textsuperscript{−} we might expect different concentrations of the defects in the different growth sectors. We have to consider carefully the consequences of different mobilities and stabilities in the two charge states.

2. Experimental

The sample used in this study is a synthetic mixed type IaA/Ib diamond. It was grown using a modified high pressure, high temperature (HPHT) synthesis method [30]: Atmospheric gases were removed from the growth capsule containing the solvent/catalyst and carbon source by heating it in vacuum. At a lower temperature, the removed gases were replaced with \textsuperscript{15}N enriched gases. The growth capsule was then sealed and the pre-treated reaction mixture was subjected to HPHT conditions.
in the diamond stable region. This produced a type Ib material, where > 95% of the nitrogen was $^{15}$N, with a mean bulk concentration of approximately 150 ppm $N_0^0$ [30].

The sample is made up of several different growth sectors. Through HPHT annealing > 80% of the $N_S$ in the high concentration sectors was aggregated to A-centres, making these sectors mixed type IaA, with an A-centre concentration of $\sim 60$ ppm and an $N_0^0$ concentration of $\sim 30$ ppm. In the sectors with low nitrogen concentration, little or no aggregation is likely to have occurred: if we assume that the low nitrogen sectors have a concentration of 1 ppm $N_0^0$ annealing at a temperature of 2300 K would only yield a 1% aggregation to A-centres, while the same annealing temperature would lead to $\sim 80$% aggregation to A-centres in sectors with 150 ppm $N_0^0$ [31, 32]. After the HPHT-annealing the sample was irradiated with 1.5 MeV e$^{-}$ to a dose of $4 \times 10^{17}$ electrons/cm$^2$ at room temperature leading to a vacancy ($V^0$ and $V^-$) concentration of $\sim 3$ ppm [10]. The mean bulk concentration of $V^-$ was determined from the EPR spectra recorded post-irradiation, figure 1b), to be $\sim 1$ ppm. The sample was subsequently annealed for 4 hours at 1100 K in an non-oxidising atmosphere, to create secondary irradiation defects such as NV-centres and possibly nitrogen-interstitial defects such as $N_I$, $N_2I$ etc.

The annealing time and temperature were chosen to remove all isolated vacancies [8].

Room temperature EPR spectra for the sample were collected using a Bruker EMX continuous wave X-band spectrometer with an operating frequency of $\sim 9.75$ GHz and a custom-built Q-band spectrometer, which has been described elsewhere by Twitchen et al. [14]. An Oxford Instruments Liquid Helium ESR900 flow cryostat was used with the Bruker EMX X-band spectrometer to perform measurements at cryogenic temperatures.

The presence of sectors with different defect concentrations in the sample is confirmed by the EPR spectra, see e.g. figure 1a), where it can be clearly seen that the $N_S^0$ EPR spectrum is made up of signals with components of different line widths [33]. For a nitrogen defect concentration of the order of 10 ppm or above the EPR line width increases roughly linearly with the defect concentration; for concentrations below 10 ppm the line width is determined by the interaction with the $^{13}$C present at natural abundance of 1.1% in the sample [33]. From this we can conclude that there are regions in the studied sample with defect concentrations below 10 ppm and other regions with defect concentrations up to an order of magnitude larger. As discussed in section 1 the \{110\} sectors may contain as little as 1 ppm of $N_S^0$. Consequently there is likely to have been regions of the sample where the vacancy concentration was roughly equal to the concentration of $N_S$. If $[N_S^0] \leq [V]$ in the low nitrogen sectors $V^0 + N_S^0 \rightarrow V^- + N_S^+$ so that in these sectors almost all of the $N_S$ is present as diamagnetic $N_S^+$. This assumption is supported by figure 1b), where the narrow component of the $N_S^0$ EPR spectrum is dramatically reduced compared to figure 1a).

Figure 1b) shows an EPR spectrum of the sample post-irradiation, where the large signal in the centre of the spectrum is from the negatively charged vacancy [6]. This is the region of the spectrum where the lines from the new defects appear, so that even if they were present in the sample post-irradiation but pre-annealing, they would not be detectable due to overlap with the negative vacancy signal.
Figure 1. X-band first derivative EPR spectra (black line) recorded with the magnetic field applied along (001) for the sample a) post-HPHT treatment but pre-irradiation and b) post-irradiation. Note that the $^{15}\text{N}_0$ EPR spectrum, marked with black arrows in figure a), is made up of components with different line-widths due to variation in concentrations of defects in different sectors of the sample. The much less intense lines of the $^{14}\text{N}_0$ EPR spectrum are marked with grey arrows in figure a). In figure b) note the large signal, with $^{13}\text{C}$ satellites, in the middle of the spectrum from the negatively charged vacancies present in the sample post-irradiation. For comparison, simulated spectra of the two new defects (grey line) are shown below the experimental spectrum, at approximately ten times the signal intensity expected from the concentration detected post-annealing. The vertical scale in figure a) is half that of figure b). Note that the narrow component of the $\text{N}_0^0$ EPR spectrum is dramatically diminished in figure b) compared to figure a). This is attributed to almost complete charge transfer from $\text{N}_0$ to $\text{V}$ in the low nitrogen sectors, see text for details.
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Figure 2. X-band second derivative experimental (thick black line) and simulated spectra at $f=9.752\,\text{GHz}$ with the magnetic field applied along $\langle 001 \rangle$. The solid grey line (——) shows the simulated WAR9 spectrum, the dashed grey line (- - - -) shows the simulated WAR10 spectrum, and the dotted black line (······) shows the $^{14}\text{N}_0^S$ spectrum. This line is used as a $g$-marker and the electronic Zeeman parameters of table 1 are referenced to the $g$-value $2.0024$ of $^{14}\text{N}_0^S$. [34] The grey dash-dotted line (—·—) shows the sum of all the simulated spectra.

3. Results

EPR measurements post irradiation and annealing revealed spectra from two previously unreported defects, labelled WAR9 and WAR10, each showing hyperfine interaction with one $\sim100\%$ abundant $I = \frac{1}{2}$ nucleus, see figure 2 and 3. The EPR spectra for the new defects both have line widths of $0.02\,\text{mT}$, like the narrow component of the $N_0^S$ spectrum. From the integrated intensity of the EPR signal of the WAR9 and WAR10 spectra the mean bulk concentration of these defects were found to be $0.10(1)\,\text{ppm}$ (atomic parts per million) each. In the same way the $^{15}\text{N}_0^S$ and $^{14}\text{N}_0^S$ mean bulk concentrations were determined to be $20(2)\,\text{ppm}$ and $0.72(7)\,\text{ppm}$, respectively. The sample also contains $0.6(1)\,\text{ppm}$ of NV$^-$. 

X-band EPR roadmaps for the new defects were produced by recording spectra with the magnetic field applied at $5^\circ$ increments in a $\{110\}$ crystallographic plane, see figure 5. Q-band EPR spectra were recorded with the magnetic field applied along the three principal directions $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, as well as two intermediate directions in a $\{110\}$ plane, see figure 6. The orientation of the applied magnetic field, $\mathbf{B}$,
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Figure 3. Q-band second derivative experimental (■) and simulated spectra at f=35 GHz for WAR9, WAR10 and $^{14}$N$_{0}$S with the magnetic field applied along $\langle 111 \rangle$. The upper solid grey line (—) shows a simulation using the WAR10 parameters from table 1 and the lower dashed grey line (---) shows a simulation using a spin Hamiltonian with lower g-symmetry and no hyperfine interaction for WAR10, which fits the X-band data. The parameters for WAR9 and $^{14}$N$_{0}$S are the same for both simulations. Only the simulation including a hyperfine interaction for WAR10 yields a satisfactory fit to the experimental data.

respect to the crystallographic directions was determined from the position of the $^{15}$N$_{0}$S EPR lines.

In a $^{14}$N-doped sample the central transition of the N$_{0}$S EPR spectrum with its associated satellites appears in the same field range as the entire WAR9 and WAR10 spectra. Figure 4 shows a simulated EPR spectrum with the magnetic field applied parallel to $\langle 001 \rangle$ from approximately 20 ppm of $^{14}$N$_{0}$S overlaid on a simulation of the detected concentration of WAR9 and WAR10 but with the hyperfine interaction scaled with the ratio of nuclear Zeeman values for $^{14}$N and $^{15}$N [35]. As can be clearly seen in this figure, the WAR9 and WAR10 signals are almost impossible to separate from the $^{14}$N$_{0}$S EPR spectrum, illustrating the importance of isotopical substitution of nitrogen for the detection of these two defects. The WAR9 and WAR10 lines are centred around $g \approx 2.002$ and all found within a 0.5 mT range of fields at X-band and 1.0 mT at Q-band as can be seen in figures 5 and 6.

No change in the EPR spectrum for WAR9 and WAR10 was detected down to the lowest measured temperature of 10 K. The intensities of the WAR9 and WAR10 EPR
signals have not been found to change on annealing the sample up to a temperature of 1800 K.

4. Analysis of the data

The X-band EPR spectra from the two new defects were fitted to the spin Hamiltonian

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - g_N \mu_N \mathbf{B} \cdot \mathbf{I}$$

(2)

with an electronic spin $S = \frac{1}{2}$ and nuclear spin $I = \frac{1}{2}$ from a $^{15}$N nucleus, varying the electronic Zeeman interaction, $\mathbf{g}$, and the hyperfine interaction, $\mathbf{A}$, see table 1. The WAR9 defect was constrained to have orthorhombic $C_{2v}$ symmetry and the WAR10 defect was constrained to have a $\{110\}$ mirror plane. Removing these constraints did not significantly improve the quality of fit. The parameters yield an excellent fit to the experimental data for all magnetic field directions for both the X- and Q-band measurements, as can be seen in figures 2, 5 and 6. The lines in the X-band spectra at $\sim 347.93$ mT, for all orientations of the magnetic field, are due to the central transition of the $^{14}$N$_S^0$ spectrum. This line was used as a $g$-marker and the determined electronic
Figure 5. X-band EPR line positions for different orientations of the applied magnetic field in the crystallographic (110) plane. The points (■) represent experimental peak positions and the lines show simulated peak positions for WAR9 as solid lines (——) and WAR10 as dashed lines (---) using the fitted parameters of table 1. The dotted line (·····) shows the position of the central $^{15}\text{N}_S$ peak, see also figure 2.

Table 1. Spin Hamiltonian parameters for the two new $^{15}\text{N}$ containing defects with directions $[\theta, \varphi]$, where $\theta$ is the angle from the crystallographic $[001]$ direction and $\varphi$ is the angle from $[100]$ measured towards $[010]$ in the (100) plane.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAR9</td>
<td>2.00343(10)</td>
<td>2.00272(10)</td>
<td>2.00268(10)</td>
</tr>
<tr>
<td></td>
<td>$[90^\circ, 45^\circ]$</td>
<td>$[180^\circ, 45^\circ]$</td>
<td>$[90^\circ, 315^\circ]$</td>
</tr>
<tr>
<td>WAR10</td>
<td>2.00344(10)</td>
<td>2.00272(10)</td>
<td>2.00269(10)</td>
</tr>
<tr>
<td></td>
<td>$[90.1(2)^\circ, 45.0(2)^\circ]$</td>
<td>$[179.9(2)^\circ, 45.0(2)^\circ]$</td>
<td>$[90^\circ, 315^\circ]$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$A_1$ / MHz</th>
<th>$A_2$ / MHz</th>
<th>$A_3$ / MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAR9</td>
<td>8.30(5)</td>
<td>7.85(5)</td>
</tr>
<tr>
<td></td>
<td>$[90^\circ, 45^\circ]$</td>
<td>$[180^\circ, 45^\circ]$</td>
</tr>
<tr>
<td>WAR10</td>
<td>1.00(4)</td>
<td>-1.01(4)</td>
</tr>
<tr>
<td></td>
<td>$[44.8(3)^\circ, 45.0(7)^\circ]$</td>
<td>$[134.8(3)^\circ, 45.0(7)^\circ]$</td>
</tr>
</tbody>
</table>

Zeeman parameters are referenced to its literature $g$-value of 2.0024(5) [34].

It is possible to achieve an equally good fit to the experimental WAR10 line positions at X-band using a spin Hamiltonian with only an electronic Zeeman interaction with $C_{1h}$ symmetry keeping only the $\{110\}$ mirror plane. However, this does not yield a satisfactory fit to the Q-band data. This is illustrated in figure 3 which shows the experimental Q-band spectrum recorded with the magnetic field parallel to $\langle 111 \rangle$ together with two different simulated spectra: the top one is simulated using the spin Hamiltonian parameters of table 1 and the bottom one using the parameters obtained
Figure 6. Q-band EPR line positions for different orientations of the applied magnetic field in the crystallographic (110) plane. The points (■) represent experimental peak positions and the lines show simulated peak positions for WAR9 as solid lines (——) and WAR10 as dashed lines (---) using the fitted parameters of table 1. The dotted line (······) shows the position of the central ${}^{14}\text{N}^0$ peak.

when fitting the X-band WAR10 line positions assuming $C_{1h}$ symmetry and only an anisotropic electronic Zeeman interaction. Only the simulation involving a hyperfine interaction with $^{15}\text{N}$ fits both the Q-band and X-band data, see also figure 2. The hyperfine interaction is assumed to be with a $^{15}\text{N}$ nucleus for both WAR9 and WAR10 since this is the only $\sim100\%$ abundant $I = \frac{1}{2}$ nucleus in this sample.

5. Discussion

As can be seen in table 1 the two new defects have identical electronic Zeeman parameters, with orthorhombic symmetry and a $\langle 110 \rangle C_{2v}$ symmetry axis. The hyperfine interactions, on the other hand, are very different: For WAR9 the hyperfine interaction has the same $\langle 110 \rangle C_{2v}$ symmetry axis as the electronic Zeeman interaction and small anisotropy, while the hyperfine interaction in WAR10 has an isotropic component that is approximately zero and the symmetry is lowered to $C_{1h}$, keeping the $\{110\}$ mirror plane.

The WAR9 and WAR10 EPR spectra are detected after electron irradiation and annealing to 1100 K. However, since the EPR signal from negatively charged isolated vacancies [6] appears in the same region of the spectrum as WAR9 and WAR10, see
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Figure 1b) these defects would not be detected until the vacancies have been annealed out. There are therefore several possibilities for when the WAR9 and WAR10 defects are formed: The centres could be formed directly after the irradiation, which could provide an explanation for the fact that in samples containing $N_S$ no R1 is formed on electron irradiation [26]: WAR9 and WAR10 are formed instead. Another possibility is that WAR9 and WAR10 are formed after annealing at some temperature < 1100 K, the annealing temperature used in this study. For example, the isolated, neutral $\langle 100 \rangle$-split self-interstitial ($I_{001}$) giving rise to the R2 EPR spectrum is stable up to 700 K [10, 36]. The WAR9 and WAR10 defects could be formed as $I_{001}$ becomes mobile. It is of course also possible that these defects are only formed at the temperature the sample was annealed at. They would in any case not be detectable before the $V^-$ EPR signal has disappeared from the spectrum.

5.1. Model for WAR9

For the $\langle 001 \rangle$-split nitrogen interstitial, $N_I$, illustrated in figure 7b, we expect $C_{2v}$ symmetry and inclusion of one nitrogen atom and that it is formed after irradiation and possibly annealing. This defect should be EPR active with $S = \frac{1}{2}$ in the neutral charge state. The $\langle 001 \rangle$-split nitrogen interstitial model is an analog of the $(N-B)_{\text{I}}^+$ defect which gives rise to the EPR spectrum labelled NIRIM-4 [37]. In this centre the majority of the unpaired electron density is localised on the nitrogen atom with a minor amount on the boron; for $N_I$ we expect to have a filled $p_\pi$ orbital on the nitrogen atom and a half-filled $p_\pi$ orbital on the carbon atom, so that the majority of the unpaired electron probability density is localised on the carbon atom. Scaling the magnitude of the $^{11}\text{B}$ hyperfine interaction for NIRIM-4 [37] with the ratio of the $^{11}\text{B}$ to $^{15}\text{N}$ nuclear Zeeman values [35], we get $|A_1| = 13.5\text{ MHz}$, $|A_2| = 10.4\text{ MHz}$ and $|A_3| = 7.9\text{ MHz}$. The WAR9 defect has the required $C_{2v}$ symmetry and the right $S = \frac{1}{2}$ spin to be the neutral charge state of $N_I$. The measured $^{15}\text{N}$ hyperfine values for WAR9 of approximately 8 MHz, see table 1, are also in reasonable agreement with those calculated from comparison with the NIRIM-4 centre. $N_0^0$ is therefore a possible model for the WAR9 defect.

If the $N_0^0$ is sufficiently high, the $N_I$ may accept an electron from $N_0^0$ and become diamagnetic. The WAR9 spectrum has a narrow line width meaning that the signal comes from the low $N_S$ regions of the sample. In the high $N_S$ sectors we expect $N_I$ to be in the negative charge state, which would be diamagnetic (as well as having broader EPR lines). If Goss et al.'s [27] model of the H1a IR centre [28] as a di-nitrogen interstitial, $N_{2I}$, is correct its likely formation mechanism in Type Ib diamond is trapping of $N_I$ by $N_S$. Since H1a is formed on annealing at 950 K in Type Ib material, this suggests that the nitrogen interstitial is mobile at this temperature in the negative charge state. The neutral charge state of $N_I$ may have a much higher thermal stability so that this does not rule out the assignment of WAR9 to $N_I$. 
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5.2. Model for WAR10

For a nearest neighbour ⟨001⟩-split nitrogen interstitial – self interstitial pair, N$_1$–I$_{001}$, see figure 7c, in the neutral charge state we expect, as for N$_1$, a filled p$_\pi$ orbital on the nitrogen atom and a half-filled p$_\pi$ orbital on the carbon atom, yielding a defect with C$_{1h}$ symmetry and an $S = \frac{1}{2}$ ground state.

If we view the N$_1$–I$_{001}$ defect as analogous to the R1 EPR centre it is possible to estimate the hyperfine interaction from a simple dipole-dipole calculation between the unpaired electron probability density and the nitrogen nucleus. The inter-radical distance of the R1 centre has been calculated to be 1.7 Å [11], so we set this to be the distance between the N-atom and the C-atom with the partially filled p$_\pi$ orbital. From the $^{13}$C hyperfine interaction in the R1 centre it has been estimated that approximately 70% of the unpaired electron probability density is in the partially filled p$_\pi$ orbitals. Following Hunt et al. [10] we therefore assume 35% of the unpaired electron probability...
density to be centred a distance $X=0.6\,\text{Å}$ on either side of the C-nucleus along the $[1\bar{1}0]$ direction. This yields two contributions to the hyperfine interaction which were transformed to a common coordinate axes system and summed. The principal values of this hyperfine tensor are $A_1 = 1.6\,\text{MHz}$, $A_2 = -1.0\,\text{MHz}$ and $A_3 = -0.6\,\text{MHz}$ with $A_3$ parallel to $[1\bar{1}0]$. Assuming that 0.4% of the unpaired electron probability density is localised on the N-atom yields an additional uniaxial hyperfine contribution of the form $A_\parallel = -2b$ and $A_\perp = b$ with $b = -0.3\,\text{MHz}$ and $A_\parallel$ along $[1\bar{1}0]$. Adding this to the hyperfine tensor from the electron dipole calculation results in a calculated hyperfine tensor with $A_1 = -A_2 = 1.3\,\text{MHz}$ and $A_3 = 0\,\text{MHz}$, with $A_3$ still parallel to $[1\bar{1}0]$. This is the form and magnitude of the experimentally determined hyperfine interaction for WAR10, which also has the required $S = \frac{1}{2}$ spin state. The numerical values in the hyperfine calculation are very sensitive to the angle of the interaction, which is determined by the assumed C–N distance and position of the unpaired electron probability density along the $p_\pi$-orbital. The good numerical agreement between the calculated and experimental hyperfine interaction should therefore be viewed as fortuitous, but this calculation shows that a $N_{\text{I}}$–$I_{001}$ model in the neutral charge state for WAR10 is consistent with the form of the hyperfine interaction.

As for WAR9 the narrow EPR line width for WAR10 shows that it is only present in the low $N_S$ sectors. If $N_{\text{I}}$–$I_{001}$ were present in the high $N_S$ sectors it probably wouldn’t be detectable since in these regions it would be in the negative charge state and therefore diamagnetic. Since $N_{\text{I}}^-$ is mobile below the temperatures the sample has been annealed at $N_{\text{I}}$–$I_{001}$ may not be present in the high $N_S$ sectors at all.

### 6. Conclusions

We have discovered two new nitrogen-containing EPR-active defects in irradiated and annealed diamond, which we label WAR9 and WAR10. We demonstrate that the formation of these defects after electron-irradiation and annealing and their spin-Hamiltonian parameters are consistent with them being the $[100]$-nitrogen split interstitial ($N_\text{I}$) and the $N_{\text{I}}$–$\langle 001 \rangle$ carbon interstitial pair ($N_{\text{I}}$–$I_{001}$), respectively, both in the neutral charge state. The use of an isotopically enriched sample, where $> 95\%$ of the nitrogen was of the $^{15}\text{N}$ isotope, was the key to detecting these defects, since their EPR spectra overlap with the central transition of the $^{14}\text{N}_S^0$ EPR spectrum. The narrow line widths of WAR9 and WAR10 indicate that they are only present in the low nitrogen regions of the sample, suggesting that both $N_{\text{I}}$ and $N_{\text{I}}$–$I_{001}$ are electron acceptors and exist in the negative charge state in the presence of $N_S$. This also means that even though the average bulk concentration of WAR9 and WAR10 is only $\sim 0.1\,\text{ppm}$, they are important irradiation products in low nitrogen sectors of diamond, which may only account for a fraction of the whole sample. The assignment of WAR9 and WAR10 to $N_{\text{I}}$ and $N_{\text{I}}$–$I_{001}$, requires that both are stable to at least 1800 K. Other annealing data suggests that $N_{\text{I}}^-$ is much more mobile and has not survived annealing to 1800 K. The difference in mobility of $N_{\text{I}}^0$ and $N_{\text{I}}^-$ was suggested by theory [27]. Nevertheless at first
sight the survival of $N_0^0$ and $[N_1-I_{001}]^0$ is surprising. However, in the low nitrogen sectors $N_0^0$ may be mobile but not able to find a trap at 1800 K.

Further work is required on both the annealing of $N_0^0$ and $[N_1-I_{001}]^0$, as well as determining the fraction of nitrogen which can be tied up in interstitial complexes; our results suggest that they are not necessarily minor players and should be considered when using ion implantation to produce useful colour centres in diamond (e.g. NV$^-$).

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References

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