Electron paramagnetic resonance and photochromism of $N_3V^0$ in diamond

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Abstract. The defect in diamond formed by a vacancy surrounded by three nearest-neighbor nitrogen atoms and one carbon atom, $N_3V$, is found in the vast majority of natural diamonds. Despite $N_3V^0$ being the earliest electron paramagnetic resonance spectrum observed in diamond, to date no satisfactory simulation of the spectrum for an arbitrary magnetic field direction has been produced due to its complexity. In this work, $N_3V^0$ is identified in $^{15}$N-doped synthetic diamond following irradiation and annealing. The $^{15}N_3V^0$ spin Hamiltonian parameters are directly determined and used to refine the parameters for $^{14}N_3V^0$, enabling the latter to be accurately simulated and fitted for an arbitrary magnetic field direction. Study of $^{15}N_3V^0$ under excitation with green light indicates charge transfer between $N_3V$ and $N_s$. It is argued that this charge transfer is facilitated by direct ionization of $N_3V^-$, an as-yet unobserved charge state of $N_3V$.

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1. Introduction

Through careful advances in both processing and particularly synthesis, diamond has become a material with a great variety of technological applications including magnetic bio-imaging [1, 2], thermal management [3, 4, 5], ultra-hard tooling [6] and particle detectors [7]. Underpinning these technological applications have been advances in understanding of defect and impurity properties within diamond, and their behavior during synthesis and processing.

Nitrogen is probably the most common impurity in both natural and synthetic diamond [8]. It is incorporated during high pressure high temperature (HPHT) growth of diamond primarily as single substitutional nitrogen, $N_x$. Annealing can drive the aggregation of nitrogen into higher-order complexes — the nitrogen-vacancy family $N_nV$ (with $n = 1–4$) and $N_x-N_y$ (a substitutional pair defect, the so-called A-center) [9]. Electron paramagnetic resonance (EPR) and optical signatures have been identified for NV$^0$/$N_2$ [10, 11, 12], $N_2V_0$/$N_3V$ [13, 14], $N_4V_0$ [15, 16], and optical-only for $N_5V_0$ (known as the B-center) [17]. The charge state of each of these defects in nitrogen-rich diamond is defined primarily by the concentration of $N_x$, which is a donor with an ionization threshold of approximately 1.7 eV [18].

The $N_3$ absorption and luminescence band, with a ZPL at 2.988 eV (415 nm, Fig. 1(c)), is observed in the vast majority of natural diamonds and some treated synthetic diamonds. Indeed, its ubiquity in natural diamond has led to the development of a commercial categorization device which looks for the presence of the absorption band [19]. A complex EPR spectrum, (known as P2, Fig. 1(a)), is associated with the $N_3$ absorption band by correlation between the EPR and optical signatures [15]. Through careful electron nuclear double resonance (ENDOR) experiments, the EPR spectrum was determined to arise at a center containing three nitrogen atoms decorating a vacancy, $N_3V_0$ (Fig. 1(b)) [20, 16].

The exact production route of $N_3V$ is not known. Calculations on the diffusion of nitrogen indicate that the energy required for concerted exchange is too high (>6.3 eV [21, 22]) to contribute significantly at typical annealing temperatures (400–2200°C). Aggregation is therefore understood to be mediated by the migration of vacancies [23] and interstitials [24, 25]: the rate of aggregation can be increased by the non-equilibrium introduction of vacancies and interstitials [23], typically by electron irradiation. These two intrinsic defects dictate two distinct classes of aggregation behavior. In the vacancy-driven model, vacancies (which become mobile at >700°C) migrate to $N_x$, forming NV. NV can then diffuse by dissociation and subsequent re-capture of the vacancy [26], forming $N_2V$ when two NV centers annihilate and emit a vacancy (1600°C [27]). At higher temperatures (>1800°C [28, 9]) $N_2V$ then spontaneously emits a vacancy, forming $N_2$. On the other hand, the interstitial model describes aggregates in terms of nitrogen interstitials, primarily $N_1$ and $N_2I$ [29]. Nitrogen interstitials introduced by irradiation (or converted from $C_1$ by low-temperature annealing [24]) aggregate to $N_{2I}$ at temperatures as low as 650°C in nitrogen-rich diamond [29]: this complex anneals out at approximately 1500°C, enabling the reaction $N_{2I} \rightarrow C_1 + N_0-N_8$ [25, 30]. $N_2V$ is subsequently formed by capture of a vacancy at $N_x-N_8$ (>1600°C). In both models, the route to production of $N_3V$ and $N_4V$ is not clear, though it is speculated that they form by migration and aggregation of lower-order aggregates [25]. It is likely that both the interstitial- and vacancy-mediated aggregation models are viable and operate simultaneously, with the dominant model for a given sample depending strongly on the relative concentrations of different impurities and intrinsic defects.

Once produced, the $N_3V$ structure has $C_{3v}$ symmetry and hence there are four equivalent orientations of the defect within the diamond lattice, each defined by its unique (111) axis. Each nitrogen atom is covalently bonded to its three carbon nearest-neighbors, with its lone pair directed into the vacancy. We therefore expect the unpaired electron probability density to reside primarily on the carbon atom nearest-neighbor to the vacancy, with a commensurately small electron-nuclear hyperfine interaction with each of the nitrogen constituents. Using the vacancy-cage model of electronic structure in diamond (which explicitly deals only with those orbitals pointing in towards the vacancy) [31], the one-electron description of the $N_3V_0$ ground state is $a_1^2t_2^3e^4e_1^1c^1$ (with N and C indicating orbitals located primarily on nitrogen and carbon atoms, respectively), yielding a $^2A_1$ ground state and a $^2E$ excited state — in this model, only one other high-energy $^2A_1$ state is possible. This
is in stark contrast to NV−, which possesses the same one-electron symmetry but two fewer electrons and hence can generate a multitude of high-spin (S > 1/2) states [12]. The vacancy-cage model may explain the lack of observation of N3V−: addition of an electron to N3V0 leaves a closed-shell spin singlet with no bound optical transitions, precluding sharp optical transitions and observation by EPR. Nevertheless, some confusion surrounds the precise electronic structure of N3V0, with some calculations predicting weakly-bound excitonic-type states [32].

Due to its prevalence in natural diamond, the ability to quantify N3V0 concentrations is key in developing characterization and discrimination tools. The published spin Hamiltonian parameters (see Table 1) produce a satisfactory EPR spectral simulation only for an external magnetic field $B\parallel\langle001\rangle$. For all other directions, the published parameters produce a poor simulation: this presents a problem when attempting to quantify defect concentrations in crystals whose orientation is not known, or where experimental geometric constraints prevent the crystal being oriented along $\langle100\rangle$. As a result of the complexity of the 14N3V0 EPR spectrum (Fig.1(a)), very small changes to the spin Hamiltonian parameters have a dramatic effect on the quality of a simulation of the measured spectrum. The production of N3V0 in a 15N-doped diamond would greatly simplify the observed EPR spectrum (see 2.3) and enable revised spin Hamiltonian parameters to be obtained for higher-accuracy, arbitrary-direction quantification.

Exploiting recent advances in synthesis, we have measured 15N-doped synthetic diamond to determine more accurate spin Hamiltonian parameters for the N3V0 EPR center. As a consequence of nitrogen aggregation over geological timescales in natural diamond and the need for stabilizing pressure (>3 GPa) at annealing temperatures above 1600°C, the significant concentrations (>1 ppm) of both N3V and the donor Ns in this sample are unusual. We have therefore studied the photochromism behavior of N3V0 with a view to confirming the presence of N3V−, and to identify any associated optical features.

2. Methods

2.1. Sample

Atmospheric nitrogen is readily incorporated into diamond during HPHT growth if chemical nitrogen traps (“getter”) are not employed. The sample used in this experiment was grown using a HPHT growth capsule that was outgassed under vacuum and subsequently backfilled with an isotopically enriched N14N gas [34] with a nitrogen isotopic ratio of 14N:15N of approximately 5:95 (see [14] for further discussion of synthesis method). A total substitutional nitrogen concentration of 84(3) ppm was measured after growth. The sample was irradiated to a total dose of approximately $5 \times 10^{17}$ neutrons cm$^{-2}$ under atmospheric conditions at an estimated sample temperature of approximately 200°C [35] in order to introduce vacancies and interstitials. The sample was then annealed for 15 h at 1500°C in a non-oxidizing atmosphere to produce N2V and Ns-Ns, before a further 1 h anneal under HPHT conditions at a nominal temperature of 1900°C to create N3V.

After processing the sample was measured (by IR absorption) to contain 13N8 ≥ 20 ppm; 15N$^+$ ≈ 5 ppm; and (Ns-Ns)$^0 ≈ 40$ ppm. The concentrations are approximate as we do not have a suitable reference spectrum for 15N4V0; we estimate approximately 15 ppm nitrogen in N4V0 form by fitting an adapted 14N4V0 spectrum to the IR data. The total concentration of 15N3V0 generated by this processing regime was approximately 1.6(2) ppm, as measured by EPR. Photoluminescence (PL) measurements of the sample post-processing were dominated by N3V0, N2V0, NsV−, NV0 and NV−. The high levels of nitrogen aggregation at a moderate annealing temperature (1900°C) are ascribed to the abundance of vacancies and interstitials introduced by the neutron irradiation [23].

2.2. Spectrometers

EPR measurements were performed on a Bruker EMX X-band spectrometer equipped with a ER 4109HS cylindrical resonator and an ER041XG microwave bridge: measurements were collected at non-

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**Figure 1.** (a) EPR spectrum of a diamond containing 14N3V0, with the applied magnetic field $B\parallel\langle001\rangle$. The complex structure is due to electron-nuclear interactions with the three $I = 1$ 14N nuclei. (b) Atomic structure of N3V in diamond, with the $\langle111\rangle$ $C_{3v}$ symmetry axis highlighted. (c) UV-Vis absorption spectrum of a synthetic 15N-doped HPHT-grown diamond containing N3V0 (ZPL at 2.988 eV) and substitutional nitrogen (N0, absorption ramp starting at approximately 2 eV).
Table 1. The measured spin Hamiltonian parameters for the $N_3V^0$ defect. Parameters have been given for $^{14}$N-doped diamond by scaling the measured $^{15}$N hyperfine values by the ratio of the nuclear g-values $g_{14}: g_{15}$ ($g_{14} = 0.403761$ and $g_{15} = -0.566378$ [3]). The g-tensor values are calculated assuming that $^{14}N_3V^0$ has an isotropic g-value of 2.0024. θ measured from [100] toward [001]; quadrupolar rhombicity given as $\eta = (P_x - P_y)/P_z$. Blanks in $^{15}N_3V^0$ parameters indicate values are as $^{14}N_3V^0$. $A_{1-3}$ and $P_i$ given in MHz.

<table>
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<th>Zeeman</th>
<th>Hyperfine</th>
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<td>$g_{\parallel}$</td>
<td>$g_{\perp}$</td>
<td>$\theta(\circ)$</td>
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<td>2.0032(2)</td>
<td>35.26</td>
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<td>35.26</td>
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<td>$-10.46(5)$</td>
<td>$-15.85(5)$</td>
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saturating microwave power. A PerkinElmer Spectrum GX Fourier-transform spectrometer was used to perform infrared (IR) absorption measurements, and a PerkinElmer Lambda 1050 spectrometer for ultraviolet-visible (UV-vis) absorption measurements.

The Lambda 1050 is a dispersive spectrometer, with light from a halogen bulb being monochromated before it is incident on the sample. The spectrometer compares the light intensity through two different paths (sample path, reference path) in order to determine the absorbance of the sample. Any light source which affects the two optical paths differently will therefore manifest as a baseline offset and must be excluded: this aspect is critical for our photochromism measurements, where a 100 mW green laser was used to excite the sample during the measurement. A ThorLabs FES0500 2.480 eV (500 nm) cut-off short-pass filter was employed to isolate the detector during the measurement. Testing with and without the laser revealed an absorbance offset of +0.05 (on 1.25 from the sample) at 2.755 eV (450 nm) under laser excitation.

The visible absorption of $N_3V^0$ is a broad ramp starting at approximately 2.0 eV and increasing in intensity toward the ultraviolet (see underlying ramp of figure 1(c)) with a small feature at 4.59 eV (270 eV) [36]. The absorbance of this sample at >4.0 eV saturates our spectrometer, and hence any change in $N_3V^0$ concentration will manifest only as a small baseline offset to the ramp. We cannot distinguish change this from laser leakage in the spectrometer (as discussed above) and therefore changes in $N_3V^0$ were monitored by IR absorption, and $N_3V^0$ changes using visible absorption.

2.3. Spin Hamiltonian

The spin Hamiltonian for a single electron, multiple nucleus system is given by

$$H = \mu_B \mathbf{B}^T \cdot \mathbf{g} \cdot \mathbf{S} + \sum_i S_i^T \cdot \mathbf{A}_i \cdot I_i + I_i^T \cdot \mathbf{Q}_i \cdot I_i ,$$

with $i$ summed over the nuclei. These terms represent the electronic Zeeman, electron-nuclear hyperfine, and nuclear quadrupole interactions, respectively. Applying a magnetic field lifts the degeneracy of the electronic states $m_S$ via the Zeeman interaction, with transitions between the states driven by resonant high frequency magnetic fields (usually in the microwave region) — the electron paramagnetic resonance phenomenon. Each nucleus splits the electron resonance line into 2$I + 1$ lines, where $I$ is the nuclear spin of the isotope in question: 1 for $^{14}$N; 1/2 for $^{15}$N. For an arbitrary magnetic field $\mathbf{B}$ applied to $N_3V^0$ we therefore expect $3^I = 27$ ($2^4 = 8$) lines per symmetry-related orientation for the $^{14}$N ($^{15}$N) case. The $^{14}$N case is further complicated by the quadrupolar interaction, which is only nonzero for $I > 1/2$: this interaction enables so-called “forbidden” ($\Delta m_S = 1, \Delta m_I \neq 0$) transitions to acquire appreciable intensity, and can yield up to $27^2 = 729$ lines per symmetry-related orientation. The $^{15}$N case is therefore spectrally significantly less complex to interpret, yet can determine 7 of the 10 spin Hamiltonian parameters for the $^{14}$N spectrum.

3. Results

3.1. EPR

A typical EPR spectrum of the sample with an applied magnetic field $\mathbf{B}||\langle 001 \rangle$ is given in figure 2. $^{15}N_3V^0$ was identified by modifying the published Hamiltonian parameters for $^{14}N_3V^0$: the hyperfine interaction strengths were scaled by the ratio of the isotopic nuclear g-values ($g_{14} = 0.403761$ and $g_{15} = -0.566378$ [29]) and the quadrupolar interaction was removed.

Unlike the $^{14}$N spectrum (Fig. 1(a)), the interpretation of the $^{15}N_3V^0$ spectrum is relatively simple (figure 2). As a consequence of the $C_3v$ symmetry of the defect, all four symmetry-related orientations are equivalent when the external magnetic field is applied along $\langle 001 \rangle$ and only one $g$-value is observed. Furthermore, the hyperfine interaction for each nitrogen nucleus is also identical, and for three equivalent $I = 1/2$ nuclei at an $S = 1/2$ centre, a 1:3:3:1 intensity pattern is expected. In fact, the approximate pattern is 1:1:2:2:1:1, with the highest-intensity lines split by
second-order hyperfine effects. As expected, the spectrum is significantly simpler than in the \(^{14}\text{N}\) case.

Further spectra were measured with the applied magnetic field along \((1\ 1\ 0)\) and \((1\ 1\ 1)\), in addition to \((0\ 0\ 1)\). The spectra for all three orientations were fitted simultaneously: the obtained spin Hamiltonian parameters are given in Table 1. The revised \(^{15}\text{N}_3\text{V}^0\) spin Hamiltonian parameters were then used to improve the fit for \(^{14}\text{N}_3\text{V}^0\), where the only free parameters are those relating to the quadrupole interaction.

A second (natural) diamond with natural nitrogen isotope abundance (100\% \(^{14}\text{N}\)), and containing approximately 25 ppm of \(^{14}\text{N}_3\text{V}^0\) was studied. Once again, EPR spectra of three high-symmetry directions were measured and simultaneously fitted. The updated spin Hamiltonian parameters enable fitting of the \(^{14}\text{N}_3\text{V}^0\) spectrum along arbitrary directions (see Figure 3). It is interesting to note that the updated parameters all lie within the quoted errors of the published data; however, the spectrum is complex due to several interactions of similar magnitudes, and hence very small relative changes in the hyperfine, quadrupole and Zeeman interactions have a dramatic effect on the generated spectrum.

**Figure 2.** (a) Measured EPR spectrum of synthetic \(^{15}\text{N}\)-doped HPHT-treated sample with applied magnetic field \(B\parallel (0\ 0\ 1)\). Three paramagnetic systems are visible and labeled. The \(^{15}\text{N}_3\text{V}^0\) EPR spectrum is significantly simpler than the \(^{14}\text{N}\) analogue (Fig. 2(a)). (b) Zoom of marked area in (a). Top: Experimental spectrum (dotted) and generated \(^{15}\text{N}_3\text{V}^0\) spectrum (solid). Bottom: Experimental (dotted) and generated spectrum including \(^{15}\text{N}_{0,0}\), \(^{15}\text{N}_{x,0}\), \(^{15}\text{N}_{y,0}\), and an \(\text{N}_3\text{V}\) center consisting of one \(^{14}\text{N}\) and two \(^{15}\text{N}\) nuclei (\(^{14}\text{N}^{15}\text{N}_2\text{V}^0\)); prominent resonances for this spectrum are highlighted with arrows. The relative intensities of \(^{15}\text{N}_3\text{V}^0,^{14}\text{N}^{15}\text{N}_2\text{V}^0\) are consistent with the source nitrogen isotopic ratio.

**Figure 3.** EPR spectrum of a natural diamond with applied magnetic field \(B\parallel (1\ 1\ 1)\). Top to bottom: experimental data; spectrum generated using the spin Hamiltonian parameters given in Table 1; spectrum generated using the spin Hamiltonian parameters given in \[16\]. The calculated \(N_3^0\) spectrum was subtracted from the experimental data before fitting.

### 3.2. Photochromism

The negative charge states of NV and \(N_2\text{V}\) have both been identified; however, no negative analogue of \(N_3\text{V}^0\) has been identified by EPR, optical absorption or PL. Indirect evidence for \(N_3\text{V}^-\) was obtained in material with high \(N_3^0\) by monitoring the ZPL of \(N_3\text{V}^0\) at 2.988 eV (415 nm) in absorption while pumping with a filtered arc lamp: upon illumination with light of energy >1.65 eV the ZPL was seen to increase \[37\]. This energy was interpreted as the ionization threshold for \(N_3\text{V}^-\); as only the \(N_3\text{V}^0\) ZPL was monitored, no corresponding donor (or acceptor) was identified. No effect was observed when the same experiment was performed in material with low single nitrogen concentration.

Measurements of the sample at 110 K show an increase in \(N_3\text{V}^0\) of approximately 0.1 ppm (using the calibration coefficient in \[39\]) when illuminated by 100 mW at 2.33 eV (532 nm, Fig 4(a)). Measurements in the infrared record changes in \(N_3^+\) and \(N_3^0\) of \(-1.3(1)\) ppm and \(+1.3(5)\) ppm, respectively, when the sample is illuminated with 100 mW at 2.36 eV (525 nm, Fig. 4(b)). Taken together, these results suggest that illumination drives the process

\[
(N_3\text{V}^- + N_3^+ \rightarrow N_3\text{V}^0 + N_3^0)
\]

(1)

The excitation energies employed here are close to the photoionization threshold of \(N_3^0\) (approximately 1.9–2.2 eV \[40\] \[31\]). The energy for \(N_3^+ + \nu \rightarrow N_3^0 + h^+\) is 4.0 eV \[42\] and hence we cannot drive this process in our experiments. We therefore infer that our optical excitation is leading to ionization of \(N_3\text{V}^-\) directly, and during illumination we are driving process (1) in both the forward and backward direction due to consecutive ionization of \(N_3\text{V}^-\) and \(N_3^0\).

The historical lack of observation of \(N_3\text{V}^-\) is not unexpected: \(N_3\text{V}\) represents significant nitrogen aggregation in diamond, and it is unusual to observe high-order aggregates and single substitutional...
nitrogen in the same sample, as required for the initial \( N_s \leftrightarrow N_3V \) process to occur. The identification of the donor in this process as \( N_0 \) combined with previous ionization results \(^{37}\) indicates that the photoionization threshold for \( N_3V^- \) lies in the range \( 1.65–2.2 \text{ eV} \).

Evidently the change in \( N_3V^0 \) concentration cannot account for the entirety of the charge transfer. We expect the processes (\( N_2V^- + N_s^+ \rightarrow N_3V^0 + N_s^0 \)) and (\( NV^- + N_s^+ \rightarrow NV^0 + N_s^0 \)) to be occurring simultaneously: unfortunately, both charge states of NV were below absorption detection limits; and the bandblock filter used to exclude the laser light from the spectrometer also blocks the ZPL of both charge states of \( N_2V \). Subsequent absorption measurements in the range 1.37–2.18 eV (900–570 nm) did not identify any sharp features with or without illumination.

4. Conclusion

Recent advances in synthesis and processing have enabled us to create a sample with a significant quantity of \( ^{15}N_3V^0 \). Due to the dramatic simplification of the \( ^{15}N \) spectrum we have been able to refine the spin Hamiltonian parameters of both \( ^{15}N_2V^0 \) and \( ^{15}N_3V^0 \), this enables the fitting and hence EPR-based quantification of \( N_3V^0 \) with the sample in an arbitrary orientation relative to the applied magnetic field. Subsequent optical absorption measurements of the \( ^{15}N \)-doped sample under illumination have indicated charge transfer between substitutional nitrogen \( N_s \) and \( N_3V \). The simplest model consistent with our results suggests the presence of the as-yet unobserved charge state \( N_3V^- \). Careful absorption and photoluminescence measurements in the 1.65–2.2 eV range may identify features associated with \( N_3V^- \).

References

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