Electron paramagnetic resonance studies of the neutral nitrogen vacancy in diamond

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Despite the numerous experimental and theoretical studies on the negatively charged nitrogen vacancy center (NV$^-$) in diamond and the predictions that the neutral nitrogen vacancy center (NV^0) should have an $S=\frac{1}{2}$ ground state, NV^0 has not previously been detected by electron paramagnetic resonance (EPR). We report new EPR data on a trigonal nitrogen-containing defect in diamond with an $S=\frac{3}{2}$ excited state populated via optical excitation. Analysis of the spin Hamiltonian parameters and the wavelength dependence of the optical excitation leads to assignment of this $S=\frac{3}{2}$ state to the $^4A_2$ excited state of NV^0. This identification, together with an examination of the electronic structure of the NV centers in diamond, provides a plausible explanation for the lack of observation (to date) of an EPR signal from the NV^0 ground state.

The negatively charged nitrogen vacancy defect (NV$^-$) in diamond is a much studied ($>$150 papers since 2000) color center which has a zero phonon line (ZPL) at 1.945 eV (Ref. 1) and an $S=1$ ground state with long spin coherence time.[2] These properties have led to a great deal of interest in NV$^-$, focused primarily on developing quantum information technologies (e.g., single-photon source for quantum communication[3] and as a candidate for a qubit in solid-state quantum computation[4]).

The nitrogen vacancy consists of a substitutional nitrogen impurity and a nearest-neighbor lattice vacancy to create a color center with trigonal (C_{3v}) symmetry. It can be modeled using the defect-molecule approach[5] where it is assumed that the properties are determined by electrons in the dangling orbitals on the carbon and nitrogen atoms neighboring the vacancy. The C_{3v} point group requires that the three resulting linear combinations of orbitals must transform as a_1, a_1, and e. Labeling the dangling orbitals φ_N (for the nitrogen) and φ_a, φ_b, and φ_c (for the three carbon neighbors) we find that

$$a_{1N} = \varphi_N, \quad a_{1C} = \frac{1}{\sqrt{3}}(\varphi_a + \varphi_b + \varphi_c),$$

$$e = \frac{1}{\sqrt{2}}(\varphi_a - \varphi_b), \quad \frac{1}{\sqrt{6}}(2\varphi_c - \varphi_b - \varphi_a),$$

where the subscripts N and C indicate the singlet levels derived from nitrogen (a_{1N}) and carbon (a_{1C}) dangling orbitals, respectively. For NV$^-$ there are six electrons to be accommodated in these orbitals. Assuming that the order of these energy levels is $a_{1N} < a_{1C} < e$, the lowest-energy configuration $a_{1N}^2 a_{1C}^2 e^2$ gives rise to the many-electron states $^1A_1$, $^3A_2$, and ^1E. Promoting an electron from a singlet to the doublet gives the configuration $a_{1N}^2 a_{1C}^1 e^3$ and the many-electron states ^1E and ^3E. Electron paramagnetic resonance (EPR) and optical studies have identified $^3A_2$ as the ground state and have as-

sociated the 1.945 eV ZPL with a $^3A_2$ to ^3E transition.[1,6] Determining the order of the energy levels is a taxing theoretical problem, and the existence of at least one metastable state between the $^3A_2$ and ^3E states has been proposed to explain the photophysics of NV$^-$ (Refs. 6 and 7). The details of the $^3A_2$ (Refs. 8 and 9) and ^3E (Ref. 9) states are still being refined, but the ground state is reasonably well understood. The small nitrogen hyperfine interaction (A), the large nitrogen quadrupole interaction, and the large zero-field (D) splitting (dominated by exchange coupling) in the ground state arise because the unpaired electron probability density is almost entirely on the three carbon dangling orbitals. The nitrogen is bonded to three nearest-neighbor carbons with effectively a lone pair of electrons pointing into the vacancy.

The neutral nitrogen vacancy has five electrons with which to populate the one-electron levels, and the $a_{1N}^2 a_{1C}^2 e^1$ configuration gives rise to the many-electron ground state ^2E. Promoting an electron from a singlet to the doublet gives the configuration $a_{1N}^2 a_{1C}^1 e^2$ and the many-electron states $^2A_1$, $^4A_2$, and ^2E. The NV^0 ZPL at 2.156 eV has been shown to arise from a transition between an E ground and an A excited state.[10] The spin of these states was not determined in the uniaxial stress-splitting study of the ZPL, but the assignment of these states to ^2E (ground) and $^2A_1$ follows from simple electronic structure arguments. The $S=\frac{1}{2}$ ^2E ground state has not been detected by EPR which on first inspection is surprising. One would expect an electronic Zeeman g value (**g**) close to that of the free spin and a small hyperfine coupling (since there is no unpaired electron probability density on the nitrogen), so it is possible that the EPR spectrum is obscured by other paramagnetic defects. Overlapping spectra would make observation more difficult but it is hard to believe that this explains the lack of detection. A more likely explanation is that the dynamic Jahn-Teller distortion of the ^2E ground state[10] broadens the EPR lines sufficiently to preclude detection. Neither problem would apply to the $^4A_2$ excited state if

this could be populated by optical excitation. The $^4A_2$ excited state is expected to be relatively low lying (i.e., below the $^2A_1$ excited state), and since it is the only $S=\frac{3}{2}$ state, it is likely that it would have a sufficiently long lifetime for detection by EPR. The same argument applies to the $^5A_2$ state of the neutral vacancy which has been observed in optically excited EPR experiments.[11]

The NV center can be produced by irradiation damage and subsequent annealing in diamond containing single substitutional nitrogen (N_S). N_S is an effective trap for vacancies, which are mobile above about 900 K.[12] N_S^0 is a deep donor, and charge transfer to NV^0 produces NV^-; both charge states NV^0 and NV^- are routinely detected by photoluminescence (PL) in the same diamond.[2] Photochromism in NV centers has been reported[13] and related to photoionization of other defects (e.g., N_S^0). However, at the excitation intensities used here no photochromism was observed. Nitrogen or N_2 ion implantation can be used to produce NV centers in high-purity diamond at specified locations.[14] NV centers are found in as-grown nitrogen-doped diamond produced via chemical vapor deposition (CVD),[2] although it is not clear if they are grown in as a unit or produced by the capture of a vacancy (mobile at typical growth temperatures) at N_S. High-pressure and high-temperature (HPHT) annealing of natural diamond, to remove brown coloration,[15] also produces NV centers.[15] It is believed that the brown coloration comes from vacancy clusters;[16] vacancies released upon annealing are trapped at N_S defects, possibly produced by dissociation of nitrogen aggregates, and NV defects are quenched in as the temperature is reduced.

The sample used in this study was produced by a modified HPHT process in which the reaction mixture (carbon source and a solvent-catalyst) in the growth capsule was pretreated at a high temperature under vacuum to remove the vast majority of the atmospheric gases. At a reduced temperature the removed gases were replaced with ^{15}N-enriched gas and the capsule was sealed. The pretreated reaction mixture was then subjected to HPHT conditions in the diamond stable region of the carbon phase diagram.[17] In this way a N_S-doped diamond (~ 150 ppm N_S^0), enriched with $>95\%$ ^{15}N, was produced. The diamond was subsequently HPHT annealed to aggregate the majority of the nitrogen ($>80\%$ aggregation to nitrogen pairs or A centers), irradiated with 1.5-MeV electrons to a dose of 4×10^{17} cm^{-2} and annealed at 1100 K in a nonoxidizing atmosphere, to form NV centers. N_S^0 is a much more effective trap for vacancies than the A center[18] and the HPHT anneal reduced the N_S^0 concentration so that there was a high probability of producing NV^0, rather than predominately NV^-.

The sample contained several growth sectors, and since nitrogen uptake is strongly growth sector dependent,[19] the sample was inhomogenously doped. The average bulk NV^- concentration was determined to be 0.6(1) ppm from EPR spectra recorded in the dark. Both NV^0 and NV^- were detected in optical absorption and PL measurements, with the absorption data suggesting that these were present in similar concentrations.

EPR spectra were recorded at ~ 9.6 GHz using a Bruker EMX spectrometer equipped with an Oxford Instruments liq-
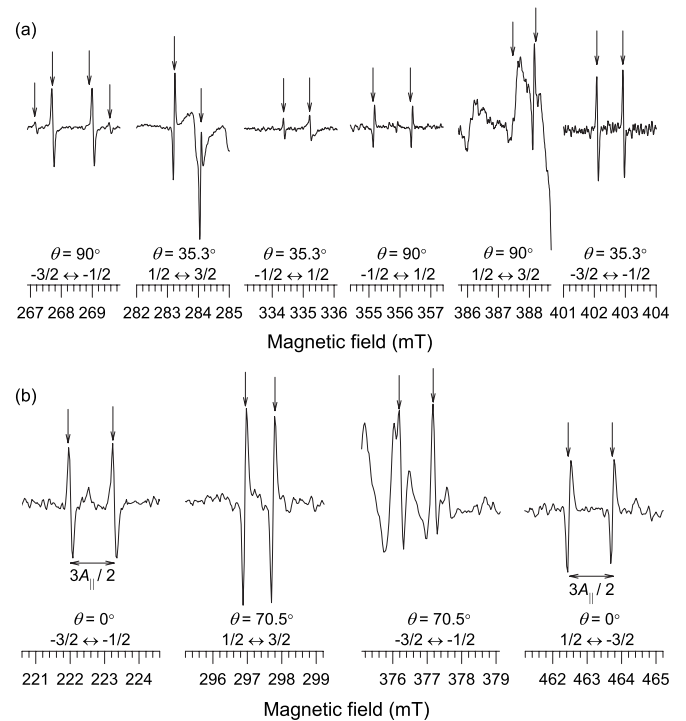

FIG. 1. EPR spectra recorded with (a) $\underline{\mathbf{B}} \| \langle 110 \rangle$ at 10 K and (b) $\underline{\mathbf{B}} \| \langle 111 \rangle$ at room temperature. The EPR transitions for the different sites are indicated by arrows and labeled with the appropriate values of S_z (e.g., transition $S_z = \frac{3}{2} \to \frac{1}{2}$). θ denotes the angle between the defect site symmetry axis and $\underline{\mathbf{B}}$. The smaller resonances seen around the lowest-field hyperfine pair in (a) are forbidden electron-nuclear double spin flips. The remaining structure originates from NV^-. In (b) the ^{15}N hyperfine splitting for the defect with principal axis parallel to the applied field is indicated; see also Table I.

uid helium ESR900 cryostat enabling measurements to be made between 4 K and 300 K. Light from a 200 W Hg-Xe arc lamp, appropriately filtered, was focused onto the sample. Figure 1(a) shows an EPR spectrum obtained with the magnetic field applied parallel to $\langle 110 \rangle$ (i.e., $\underline{\mathbf{B}} \| \langle 110 \rangle$) while the sample was illuminated with the output of the lamp in the region 300–700 nm. The spectrum shows a pattern of six pairs of lines. A trigonal defect in diamond has four symmetry-related copies orientated along $[111]$, $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}1\bar{1}]$ so that when $\underline{\mathbf{B}} \| \langle 110 \rangle$ the symmetry axis of two sets of defects makes an angle of $35.26°$ with the magnetic field and for the other two the angle is $90°$. Thus, for an $S = \frac{3}{2}$ trigonal defect with $\underline{\mathbf{B}} \| \langle 110 \rangle$, the g and D interactions (assumed axially symmetric about the trigonal axis) will produce two sets of three lines corresponding to the allowed EPR transitions ($\Delta S_z = \pm 1$). A hyperfine coupling (also assumed axially symmetric about the trigonal axis) with an $I = \frac{1}{2}$ nucleus will split each of the six lines into two, producing the pattern of six pairs of lines observed in Fig. 1(a). Figure 1(b) shows a corresponding EPR spectrum recorded with $\underline{\mathbf{B}} \| \langle 111 \rangle$. In this figure only four pairs of hyperfine lines are shown, since the $S_z = -\frac{1}{2} \to \frac{1}{2}$ transitions are obscured by the signal from residual N_S^0.

The angular dependence of all the EPR spectra for the

TABLE I. Spin Hamiltonian parameters for ^{15}NV$^0 \cdot g$, D, and A have principal axes along [111].

$g_\parallel$	$g_\perp$	D/MHz	$A_\parallel$/MHz	$A_\perp$/MHz
2.0029(2)	2.0035(2)	1685(5)	−35.7(3)	−23.8(3)

new color center is reproduced by setting $S = \frac{3}{2}$ and $I = \frac{1}{2}$ along with constraining g, D, and A to be axially symmetric about the trigonal axis of the defect. Spin Hamiltonian parameters for the new defect, determined from room-temperature data, are given in Table I.

The hyperfine interaction is approximately 10 times larger than for ^{15}NV$^-$ (Ref. 20) and $|A_\parallel| > |A_\perp|$, indicating that there is a small but significant localization of the unpaired electron probability density on the nitrogen. Since the nuclear g factor for ^{15}N is −0.5664, a negative sign is assigned to $A_\parallel$ and $A_\perp$. This has the consequence of setting D as positive, since only with $A_\parallel, A_\perp < 0$ and $D > 0$ can the position and intensity of the forbidden electron-nuclear double spin flips (see Fig. 1) be reproduced. It is also important to note that replacing ^{15}N with another $I = \frac{1}{2}$ nucleus (e.g., ^{1}H) does not yield a satisfactory fit to these transitions, regardless of the sign of A and D. This unambiguously identifies ^{15}N as the nucleus responsible for the hyperfine interaction.

The EPR spectrum for the new defect has only been observed when the sample is illuminated and, as can be seen from Fig. 1, is spin polarized. It is well known that for NV$^-$ optical pumping causes spin polarization of the ground state[6,7] with preferential population of the $S_z = 0$ spin sublevel,[21] giving rise to a large population difference ($\gg$Boltzmann) between the $S_z = 0$ and $S_z = \pm 1$. This results in the observation of EPR transitions in strong absorption and emission. Optical spin polarization of the $^5A_2$ excited state of the neutral vacancy in diamond has also been reported.[11] Figure 2 shows the variation of the room-temperature EPR intensity and hence spin polarization of the new $S = \frac{3}{2}$ color center, as well as NV$^-$, with the energy of the exciting light (varied using low-pass filters). For NV$^-$ it is known that the optical pumping involves the $^3A_2$ to ^3E ZPL at 1.945 eV (Ref. 1) and selective intersystem crossing (originating from anisotropic spin-orbit coupling) to a low-lying $^1A_1$ singlet.[9] The threshold at 1.9(1) eV observed for spin polarization of NV$^-$ is consistent with previous work.

The threshold for observation of the spin-polarized $S = \frac{3}{2}$ system is 2.2(1) eV, with preferential (but not equal) population of the $S_z = \pm \frac{1}{2}$ levels with respect to the $S_z = \pm \frac{3}{2}$ levels. Unlike the ground state of NV$^-$, the $S = \frac{3}{2}$ system could not be observed without optical excitation, even with extensive signal averaging; upon removal of the illumination, the signal disappeared in $\ll 1$ s. The magnitude of spin polarization did not vary strongly with temperature between 10 K and 300 K. The apparent requirement of optical excitation for EPR detection of the $S = \frac{3}{2}$ system invites the assertion that this is an excited state of a defect and all the experimental evidence strongly supports the association of this system with the $^4A_2$ excited state of NV^0. Spin-selective intersystem crossing to the $S = \frac{3}{2}$ excited state gives rise to the observed
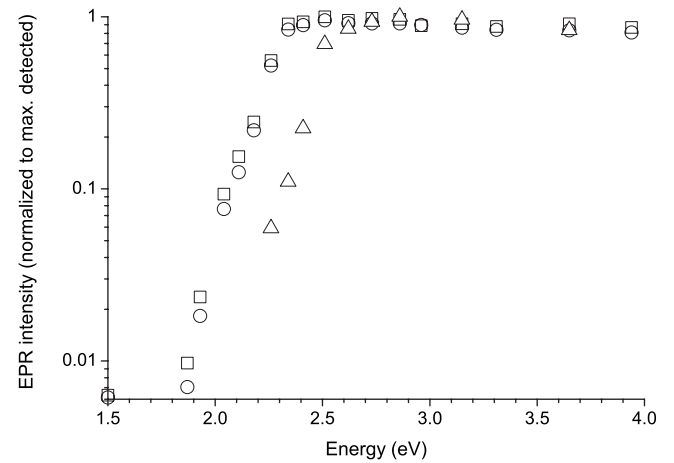

FIG. 2. Room-temperature EPR signal intensity as a function of optical excitation energy for the $S_z = \frac{1}{2} \rightarrow \frac{3}{2}$ transition of the $S = \frac{3}{2}$ defect ($\triangle$) and the $S_z = 0 \rightarrow 1$ ($\square$) and $S_z = -1 \rightarrow 0$ ($\bigcirc$) transitions of NV$^-$. The data were recorded with **B**$\|\langle 111 \rangle$ for the defects with their axes parallel to the applied field. Below 2.2 eV no EPR signal for the $S = \frac{3}{2}$ defect could be detected. The error in the cut-off energy is ± 0.1 eV.

spin polarization. Efficient spin polarization could increase the detection sensitivity by a factor of several hundred compared to that of a ground state in thermal equilibrium, and such a state would be below current detection limits.

There is now a considerable body of evidence supporting the assignment of the $S = \frac{3}{2}$ system to the $^4A_2$ excited state of NV^0. The symmetry of the EPR spin Hamiltonian parameters identifies this as a trigonal defect with a nitrogen atom on the trigonal axis. The production of the defect by irradiation damage and annealing in N$_S$-doped diamond concurrently with NV$^-$ adds further support to the assignment. The $^4A_2$ state is derived from the configuration $a_{1N}^2 a_{1C}^1 e^2$; hence, the unpaired electron probability density is expected to be predominately localized in the carbon dangling orbitals surrounding the vacancy, as is the case for NV$^-$. A large zero-field splitting arising from exchange coupling (cannot be dipolar in origin since $D > 0$) is therefore expected and observed. The data for the $^4A_2$ excited state of NV^0 indicate that approximately 6% of the unpaired electron probability density is localized on the nitrogen which is much larger than for the $^3A_2$ ground state of NV$^-$ (Ref. 22) which was derived from the configuration $a_{1N}^2 a_{1C}^2 e^2$. The properties of the $^3A_2$ ground state of NV$^-$ are insensitive to the order or energy separation of a_{1C} and a_{1N} levels, and the unpaired electron probability density on the nitrogen is negligible. However, for NV^0, if the order of a_{1C} and a_{1N} were reversed, then the configuration $a_{1C}^2 a_{1N}^1 e^2$ would still produce the $^4A_2$ excited state but now there would be significant unpaired electron probability density on the nitrogen and hence a large nitrogen hyperfine interaction. This is not likely, but it is probable that there is some mixing of the a_{1N} and a_{1C} one-electron levels and this gives rise to the observed nitrogen hyperfine interaction. It is worth noting that the experimental studies were greatly simplified using ^{15}N-doped diamond; the ^{14}N quadrupole interaction would have complicated the spectra. Measurements on similarly prepared ^{14}N-doped samples are

planned to determine the quadrupole interaction. ^{13}C hyperfine measurements would also be useful in confirming the localization of the unpaired electron probability density, but to date these satellites have been undetectable with a 1.1% natural abundance of ^{13}C.

The threshold for the optical excitation of the $S=\frac{3}{2}$ excited state matches the energy of the ZPL of NV^0, providing further evidence for assignment to the $^4A_2$ state. This state is expected to be low lying, with a sufficiently long lifetime (and spin lattice relaxation time) such that selective intersystem crossing could build up a spin-polarized population under conditions of optical excitation. If only 1% of the NV^0 defects were excited into the $^4A_2$ state, then spin polarization comparable to that measured for the NV$^-$ would produce the observed EPR intensity, assuming that NV$^-$ and NV^0 are in comparable concentrations, as was indicated by the optical absorption measurements. The lack of detection of the ground state is likely to be due to dynamic Jahn-Teller coupling which broadens the EPR lines, dramatically reducing the detection sensitivity (i.e., a tenfold increase in linewidth would reduce the detection sensitivity by a factor of 100). If this is the case, then application of uniaxial stress should lock the defect into a lower-symmetry configuration, enabling EPR and optically detected magnetic resonance studies of the ground state. No donor is required for the production of NV^0 (cf. NV$^-$), simplifying its production for applications exploiting the spin physics.

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