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# Electron spin resonance characterization of a multi-nitrogen complex in diamond

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**Abstract**

The W27 centre has been characterized by means of electron spin resonance in natural diamond. The centre exhibits spin $S = 1$, a large spin–spin coupling constant $D = 99$ mT, and a complex hyperfine interaction structure interpreted as originating from interaction of an $S = 1$ electronic system with five nitrogen atoms: two of these sites are equivalent and are located near the $S = 1$ electrons; three others are nearly equivalent and more remote. The centre is suggested to include a divacancy, where one vacancy, bound to two nitrogen atoms and one carbon atom, has trapped an extra electron, while the second vacancy is bound to three substitutional nitrogen atoms.

Nitrogen is a dominant impurity in diamond present in concentrations that may reach the atomic per cent level. In synthetic diamond, nitrogen is found dispersed as neutral single-substitutional atoms ($N_S^0$), which have been detected by electron spin resonance (ESR) as spin $S = 1/2$ centres, named P1 (see, e.g., the review of Ammerlaan 1990). In natural diamond, as a result of prolonged annealing at high pressures and temperatures, nitrogen has aggregated into clusters. In type IaA diamond, nitrogen is mostly present as $[N_S–N_S]^0$ pairs (A centres), while type IaB diamond is rich in complexes of four $N_S$ atoms surrounding a vacancy ($[4N_S–V]^0$ or B centres); both centres are ESR inactive. In both types of diamond a small part of the nitrogen may also form $[3N_S–V]^0$ $S = 1/2$ centres. A, B, and P1 nitrogen centres efficiently trap vacancies, forming $2N_S–V$, $4N_S–2V$, and $N_S–V$ complexes, respectively. $2N_S–V$ and $4N_S–2V$ defects are usually present in natural diamond in the neutral, ESR-inactive states. The $N_S–V$ complex is believed to exist in both the neutral and the negative charge states; however, only the $[N_S–V]^-$ state has so far been detected by means of ESR. It consists of a nearest-neighbour pair of a negative vacancy ($V^-$) and one $N_S$ atom; the $V^-$ part gives rise to an $S = 1$ centre, termed W15, exhibiting a relatively large spin–spin coupling constant $D = 102.7$ mT (Ammerlaan 1990).

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No other nitrogen–vacancy complexes have so far been reliably identified by means of ESR. Yet several $S = 1$ ESR centres exhibiting hyperfine (hf) interaction with two or more nitrogen atoms have been detected (Ammerlaan 1990). However, the scarcity of experimental data complicates their modelling. In the present work, we characterize one of those centres, named W27. Previously, it has been assigned the spin-Hamiltonian parameters $g \sim 2.00$, $S = 1$, $D = 96$ mT, with the principal axis tilted $\sim 10^0$ away from the $\langle 110 \rangle$ crystal axis. The centre exhibits hf structure due to interaction with two equivalent nitrogen sites; the hf splitting was $\sim$1.2 mT along the defect axis (J A van Wyk (unpublished), Ammerlaan (1990)).

In the present paper, the W27 centre has been detected by means of ESR in several natural IaB type diamonds—however, only after neutron irradiation to doses of $\sim 10^{18}$–$10^{19}$ neutrons cm$^{-2}$ and annealing at temperatures above 600 °C. At those temperatures vacancies in diamond become mobile and form nitrogen–vacancy complexes. The centre could not be detected in IaA diamonds subjected to a similar treatment. In the diamonds studied, the W27 centre dominated the ESR spectra with concentrations reaching 1 at. ppm.

Representative first-derivative Q-band ESR spectra from an irradiated and annealed IaB diamond are shown in figure 1. The spectra have been recorded at room temperature, using a microwave power $P_\mu = 5$ mW and a modulation amplitude of 0.07 mT, with the direction of applied magnetic field close to a $\langle 110 \rangle$ axis. The large applied $P_\mu$ did not result in saturation distortions; those only appeared at $P_\mu > 10$ mW. Several centres contribute to the spectrum of figure 1(a). However, we will focus here on the W27 spectrum, consisting of several widely spread groups of multiline structures. The groups originate from allowed ($\Delta S = 1$) transitions at an $S = 1$ centre, while their internal structure is caused by hf interaction with several nitrogen atoms. The $S = 1$ assignment is confirmed by detection of a single group of lines in the half-field region shown in figure 1(b). Zooming into the very left group of lines in figure 1(a) reveals an interesting pattern, presented in figure 1(c): the group consists of five major lines of relative intensities 1:2:3:2:1, separated by 1.2 mT; each of these lines is further split into about seven partially resolved lines, separated by 0.17 mT. This pattern could be best simulated by hf interaction with two equivalent nitrogen-atom sites ($^{14}$N, 99.63% natural abundance, nuclear spin $I = 1$), supposedly situated close to the $S = 1$ electronic system, and with three more remote and nearly equivalent nitrogen atoms. A similar narrow-line structure is also seen in the half-field spectrum shown in figure 1(b). It should be noted that in some samples this hf structure could not be resolved due to line broadening, which could explain it not being reported in previous work. The spectra of figure 1 were recorded at room temperature; however, no significant changes were observed when the sample was cooled down to 20 K. The intensity of the centre could be bleached by 25% by *in situ* $Ar^+$ laser illumination (457.9 nm, $\sim$1 W cm$^{-2}$). The post-illumination recovery occurred within a few seconds.

Angular maps of the W27 centre for rotation of the sample in a $\langle 110 \rangle$ plane are plotted in figure 2. Panel (a) shows the angular variation of the positions of the $\Delta S = 1$ lines (centres of the groups), while part (b) presents the map of the nitrogen hf splitting (two equivalent sites). An important feature observable in figure 2(b) is that the hf splitting has the smallest value for the most distant $\Delta S = 1$ lines while the largest splitting is observed for the inner $\Delta S = 1$ lines, thus suggesting that the principal axes of the spin–spin matrix **D** and hf matrix **A** are mutually perpendicular. In contrast, the hf splitting arising from the three remote nitrogen sites is largest for the most distant $\Delta S = 1$ lines, varying in the range 0.15–0.17 mT with magnetic field angle (angular map not shown).

Thin curves in figure 2 present the results of simulation using the spin-Hamiltonian parameters summarized in table 1. The complex character of the spectrum might result in some ambiguity in determination of the directions of the principal axes. Nevertheless, the following essential facts about the W27 centre could be reliably obtained from the simulation:

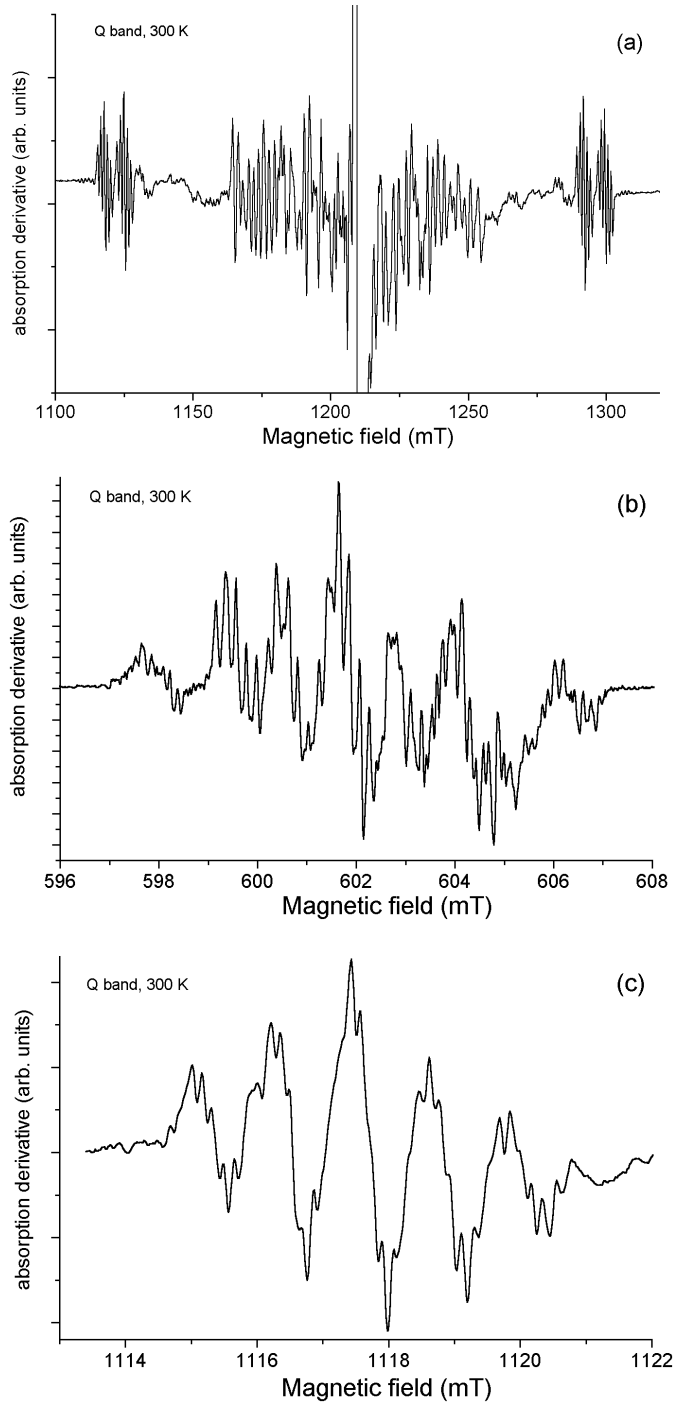


**Figure 1.** Q-band ESR spectra observed in natural IaB diamond at 300 K using a microwave power $P_\mu = 5$ mW and a modulation amplitude of 0.07 mT. The direction of the applied magnetic field $\boldsymbol{B}$ is close to a ⟨110⟩ axis. Parts (a) and (b) present spectra of allowed ($\Delta S = 1$) and forbidden ($\Delta S = 2$; half-field lines) transitions, respectively. Part (c) shows a magnification of the low-field part of spectrum (a). The sample was irradiated to a dose of $\sim 10^{19}$ neutrons cm$^{-2}$ and annealed at 1200 °C for 1 h.

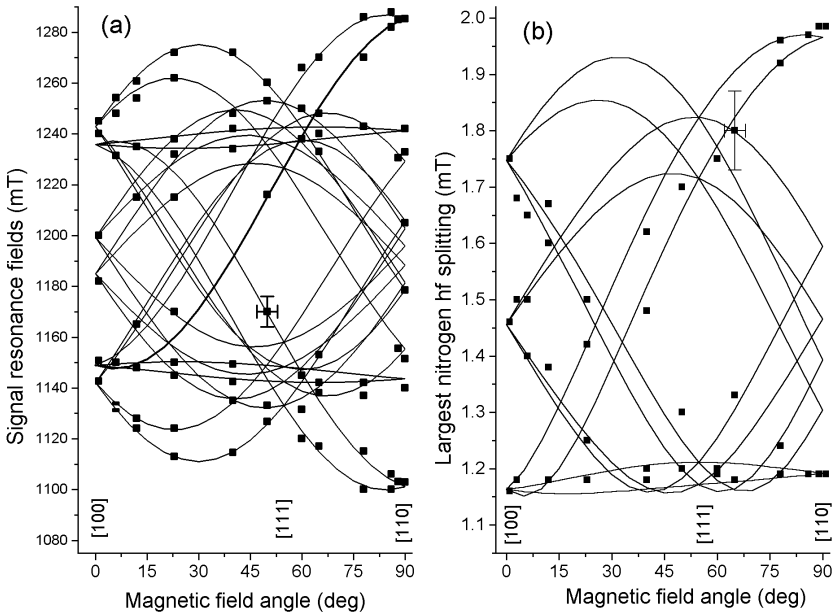


**Figure 2.** Angular maps of the W27 centre (300 K, Q-band) measured for rotating the sample in a ⟨110⟩ plane. Part (a) shows the angular variation of the resonance field values of the $\Delta S = 1$ lines (centres of the groups), while part (b) presents the map of nitrogen hf splitting (two equivalent sites).

**Table 1.** Spin-Hamiltonian parameters inferred for the W27 centre. The sign of the $D_1$ component is assumed to be positive as in the case for the W15 centre (Ammerlaan 1990). Values for **D** and **A** are in mT.

| Matrix | Principal values | | | Euler angles (deg) |
|---|---|---|---|---|
| **g** | 2.003(1) | 2.003 | 2.003 | — |
| **D** | 66(1) | −38 | −28 | (45, 25, 12) |
| **A**(2N) | 2.0(2) | 1.2 | 1.2 | (135, 25, 12) |
| **A**(3N)[a] | 0.17(1) | 0.15 | 0.15 | (45, 25, 12) |

[a] Nearly equivalent sites.

(a) The centre has a low symmetry ($C_1$ or nearly $C_{1h}$) with a symmetry axis in between the ⟨110⟩ and ⟨111⟩ directions.
(b) Its $D$-value of 99 mT is rather close to that of the W15 centre (102.7 mT).
(c) The centre includes (at least) five nitrogen atoms.

Two of them are equivalent and are located close to the $S = 1$ electron system; the electron density on these is ∼32%; the principal axes of the matrices **A** and **D** are perpendicular. Three other nitrogen atoms are nearly equivalent and more remote; the electron density on these is ∼1.5%; the principal axes of the matrices **A** and **D** are parallel.

Figure 3 presents a schematic diagram of the hypothesized structure for the W27 centre. It consists of a divacancy, where one vacancy, bound to two nitrogen atoms and one carbon atom, has trapped an extra electron, while the second vacancy is bound to three substitutional nitrogen atoms. Apparently, this model may comply with the experimental ESR results: it has

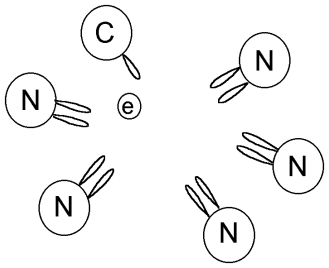


**Figure 3.** A schematic diagram of the proposed structure for the W27 centre. It depicts a divacancy, where five out of six basal carbon atoms (C) are replaced by nitrogen atoms (N). The defect has trapped an extra electron e.

low symmetry, it may result in a $D$-value which is close to that of the W15 centre ($[N_S–V]^-$), and the arrangement of nitrogen atoms agrees with the measured hf structure. It may be expected that the trapped electron can be ionized by light, as is observed experimentally. However, it should be added that although the model incorporates the key elements to account for the observed ESR properties, it is clear that final consolidation will require further experimenting.

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## References

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