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LETTER TO THE EDITOR

^{14}N ENDOR of the N2 centre in diamond

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Abstract. ^{14}N ENDOR in the N2 centre in diamond demonstrates that nitrogen is a constituent of the centre.

Many paramagnetic centres in diamond have been shown to involve nitrogen by interpretation of the hyperfine structure in the EPR spectrum produced by the nearly 100% abundant isotope ^{14}N. Indeed, apart from weak hyperfine lines from the 1.11% abundant isotope ^{13}C, most hyperfine structure that has been observed in diamond has been due to nitrogen.

This letter reports new measurements on the N2 centre, whose EPR spectrum does not have any resolved hyperfine structure, which show nevertheless that nitrogen is associated with the centre.

Shcherbakova *et al* (1975) first reported the EPR at about 9 GHz of the N2 centre, which occurs in all brown diamonds. Its EPR spectrum consists of a single broad line at $g = 2.003$. Brown diamonds, classified as type Ia, are characterised by strong absorption in the visible region which rises monotonically towards shorter wavelengths. Shcherbakova *et al* suggested that dislocations are responsible for this additional absorption. However, type II diamonds are known to contain high dislocation densities, but are markedly less brown. It therefore appears likely that the absorption is due to an impurity centre, which may be associated with a dislocation.

Shcherbakova *et al* reported that the depth of coloration of brown stones was closely linked with intensity of the N2 EPR line, suggesting that the N2 centre may also be associated with dislocations.

We have made two different types of new measurements on the N2 centre: (i) EPR at 17 GHz, and (ii) ENDOR at 9 GHz.

EPR at 17 GHz gives greater resolution than was possible in the original measurements at about 9 GHz. Because of strong microwave saturation, measurements were made only in the dispersion mode. Apart from the central lines of the previously reported W7 (Loubser and Wright 1973) and P1 (Smith *et al* 1959) centres, there are several small unidentified lines close to the N2 centre. The N2 centre appears to be isotropic with $g = 2.0030(2)$, whereas the small lines are anisotropic, and unsymmetrically disposed about the line from N2, which indicates that they are not associated with the N2 centre. Their presence makes it difficult to measure the width of the N2 line, but we estimate it to be about 0.1 mT peak to peak derivative line width, and we confirm that there is no resolved hyperfine structure.

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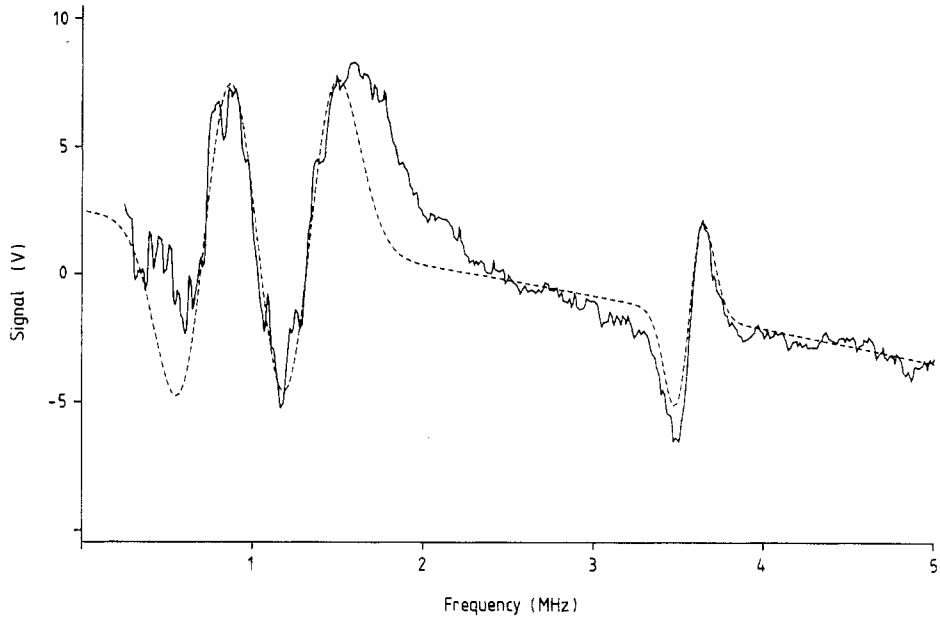

Figure 1. ENDOR spectrum of N2 compared with our fit to the spectrum shown by the broken curve.

ENDOR was performed at 9.303 GHz using a standard 115 kHz modulation of the external magnetic field, and frequency modulation of the radio-frequency. Figure 1 shows a typical spectrum for an arbitrary orientation of the magnetic field $\boldsymbol{B}$. Measurements at several orientations of $\boldsymbol{B}$ revealed no significant anisotropy of the spectrum. The poor quality of the spectrum may be because the spectrometer was operating near its low frequency limit set by RF matching.

Figure 1 shows that the ENDOR spectrum consists of three lines, two broad ones with peak to peak line width (Δ_{pp}) between 300 and 500 kHz, and a narrower one with Δ_{pp} = 170 kHz. The average frequency of the two broad lines is exactly equal to the ^{14}N nuclear Zeeman frequency in the applied field, which strongly suggests that they arise from a coupled system of an electron with $s = \frac{1}{2}$, and a nitrogen nucleus with $I = 1$ described by the usual spin Hamiltonian for such a system:

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

where the spectrum indicates that $|g_N \mu_N B| > |A| > |P|$, and the quadrupole interaction P is very much less than the ENDOR line width. Then one would expect ENDOR transitions at $h\nu = g_N \mu_N B \pm A/2$. The two low frequency ENDOR lines can be accounted for using this spin Hamiltonian with

$$g_N = 0.403\ \text{MHz} \qquad |A| \simeq 0.6\ \text{MHz} \qquad |P| \ll 0.3\ \text{MHz}.$$

In the EPR we would expect the characteristic three-line hyperfine structure, but this is not resolved since its overall splitting of 1.2 MHz is less than the observed line width of 3 MHz. The nuclear g-factor is a unique finger-print of ^{14}N, so these measurements show that nitrogen is involved in the N2 centre. The very small, approximately isotropic, hyperfine interaction indicates a very small localisation of the electron on the nitrogen.

The third, somewhat narrower, ENDOR line at 3.56 MHz corresponds to a nuclear Zeeman frequency in the applied field with $g_N = 1.407$. The nuclear g-factor of ^{13}C is 1.405 indicating beyond doubt that this is the nucleus responsible for this ENDOR. That only a single line at the nuclear Zeeman frequency is observed indicates that the process observed is either distant ENDOR or matrix ENDOR (Kevan and Kispert 1976), depending upon how the ^{13}C nuclei are coupled to the unpaired electron, or that the wavefunction of the unpaired electron is very extensive, with very small amplitude at any carbon atom. We have too little information about the electronic and nuclear relaxation processes to distinguish between these mechanisms. This ENDOR line merely tells us that carbon is involved in the defect, which gives us no specific information about the nature of the defect.

The significant new information revealed by these measurements is that nitrogen is involved in the N2 centre.

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