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Electron paramagnetic resonance investigations of nickel defects in natural diamonds

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Abstract. Electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectra of natural blue diamonds from the Argyle mine in Western Australia are reported for the first time. These diamonds are shown to contain the NE2 centre which has been observed primarily in synthetic diamonds and has been proposed to be Ni⁺ with three neighbouring nitrogens. A previously unreported EPR centre is observed and is found to have $S = 3/2$, $g = 2.02$ and superhyperfine interaction from one nitrogen. The results are found to be consistent with an Ni⁻ on a substitutional site with an N⁺ on a fourth nearest neighbour site. This defect is found exclusively in Argyle blue diamonds.

1. Introduction

The Argyle mine in Western Australia produces a relatively large number of coloured diamonds. The majority of these are brown but the highly valued pink diamonds are also found to a lesser extent. Both the pink and brown diamonds contain defects which are thought to be produced by plastic deformation. The colour of these diamonds is often believed to be related to these defects. However, it has been reported that also near colourless diamonds from the Argyle production suffer from severe plastic deformation. Another type of diamond which has a greyish blue colour is also found at the Argyle mine. It is extremely rare with only a few found each year and is not related to the semiconducting blue diamonds which contain boron [1].

The greyish-blue diamonds have not previously been extensively investigated. One optical spectroscopy study has been published to date [2]. It was found that these diamonds contain an unusually high concentration of hydrogen. The blue colour of these diamonds was believed to be related to these hydrogen defects.

This paper reports on the first electron paramagnetic resonance (EPR) study of these diamonds. In contrast to other diamonds from the Argyle mine these diamonds were found to contain nickel defects which have previously been observed in synthetic diamonds. More importantly a previously unreported EPR centre was also observed and it is proposed that this defect also contains nickel. This defect is found only in these diamonds.

A number of defects involving isolated nickel and nickel associated with nitrogen have been observed previously in synthetic diamonds. To provide some background to discuss our investigation of nickel defects in natural blue diamonds a brief review of the known centres is presented.

The first observation of a nickel centre in diamond was in a synthetic polycrystalline sample grown at high temperature and pressure from a nickel containing solvent [3]. The

centre gave rise to a single isotropic line at $g = 2.031$. Since it was present only in diamond grown from a nickel containing solvent it was attributed to nickel. It was later confirmed to be a nickel centre from the resolved hyperfine (hf) splitting [4]. This is the only centre where EPR confirmed the involvement of nickel directly. In other EPR investigations [5–8] EPR spectra assigned to nickel centres were only seen in synthetic diamond grown using nickel or a nickel alloy as catalysts. Furthermore, an isotope-related fine structure in the zero-phonon region of the 1.40 eV optical transition has conclusively shown that nickel is responsible for it [9].

A recent study using single crystals refined the g value of the centre showing Ni hf splitting to 2.0319 and, despite the fact that no zero field splitting was observed in the cw EPR spectrum, the electron spin of the centre was determined to be $S = 3/2$ using pulsed EPR techniques [5]. The Ludwig–Woodbury [10] model, which has been used for transition metals in silicon and germanium, was then used to assign this defect to a negatively charged nickel ion on a substitutional site. The Ludwig–Woodbury model predicts the following spin and electronic configurations for the different charge states of the substitutional and interstitial ions: Ni_i^+ , $S = 1/2$, $3d^9$; Ni_i^0 , $S = 0$, $3d^{10}$; Ni_s^+ , $S = 5/2$, $3d^5$; Ni_s^0 , $S = 2$, $3d^6$; Ni_s^- , $S = 3/2$, $3d^7$.

Two of the EPR centres found in synthetic diamonds grown from a nickel catalyst [6] were labelled NIRIM1 and NIRIM2. Both have an electron spin of $S = 1/2$ and, in accordance with the Ludwig–Woodbury model, were determined to be positively charged nickel on an interstitial site. The NIRIM1 centre gave a single line at $g = 2.0112$ although some structure was seen at lower temperatures. The NIRIM2 centre had trigonal symmetry and the following principal g values. $g_{\parallel} = 2.3285$ and $g_{\perp} \cong 0$. It was proposed that the NIRIM2 centre was a nickel interstitial defect with a trigonal perturbation from a nearby vacancy or carbon interstitial whereas the NIRIM1 centre was the unperturbed interstitial defect [6].

Optical transitions have also been found in diamonds grown from a nickel catalyst. These transitions occur at 1.4, 1.883, 2.51, 2.56 and 3.1 eV [11]. The transitions that were seen in any diamond were found to depend not only on the concentration of nickel but also of nitrogen [11]. Diamonds grown with a nitrogen getter, having therefore a low nitrogen content, show a dominant 1.4 eV ZPL [9, 11]. The NIRIM1 and NIRIM2 EPR centres are also seen in these diamonds with low nitrogen content. By contrast, diamonds grown without a nitrogen getter show stronger 1.883 and 2.51 eV lines are also the Ni_s^- EPR centre. It was proposed that the presence of substitutional nitrogen, a deep donor, produced changes in the Fermi level and hence a change in the charge state of the nickel defects [11].

More recently, studies involving the annealing of synthetic diamonds containing nickel have provided evidence that complex defects involving both nickel and nitrogen are formed in this process [7, 8, 12]. Nadolinny and Yelissev discovered three EPR centres that formed during the heat treatment at 2100 K and 5.5 GPa in diamonds containing both nickel and nitrogen [8]. These centres were labelled NE1–NE3. All had anisotropic g values with magnitudes between 2.00 and 2.14 and had characteristic superhyperfine (shf) splittings indicating interactions with two, three and three nitrogens respectively for the NE1, NE2 and NE3 centres. The EPR centres were also correlated statistically with optical features labelled as the S2 and S3 bands and a line at 523.2 nm (2.369 eV) but no direct correlation was made.

Further investigation by the same authors uncovered another four EPR centres. One, the NE4 centre, was present in as-grown diamonds and has trigonal symmetry with $g_{\parallel} = 2.0227$, $g_{\perp} = 2.0988$, and showed no shf splittings. The NE5, NE6 and NE7 centres were seen in

the heat treated diamonds but only during optical illumination. They all had anisotropic g values greater than 2 and had interactions with two, zero and one nitrogen, respectively. The centres NE1–NE5 were proposed to be an Ni^+ ($S = 1/2$, $3d^9$) in a di-vacancy position associated with zero to three nitrogens.

A series of optical absorption lines have also been observed in synthetic diamonds after heat treatment [12]. When diamonds, which initially showed the 1.883 and 2.51 eV lines, were annealed these lines decayed in strength and a new series of absorptions appeared. The most prominent of these was a vibronic band with a ZPL at 1.693 eV and a dominant 51 meV phonon energy. Associated with this band was a complicated series of lines between 2.2 and 2.6 eV. The 1.693 eV ZPL annealed out at temperatures over 1700 °C showing that it was a transient species. The maximum in the intensity of the 1.693 eV line was found to correlate well with the initial 1.883 eV line intensity. Some of the lines in the range 2.2 to 2.6 eV annealed out at this temperature and some remained, indicating that several separate defect species were being produced during the annealing. Again, complex defects involving nickel and nitrogen are proposed to account for these features.

These optical and EPR features have all been observed in synthetic diamonds. These defects would appear to be extremely rare in natural diamonds which have quite different origins. The NE1 and NE2 EPR centres have, however, been reported in natural diamonds from the Jakutii and Ural mines [13]. Also reported in [13] is a new EPR centre with $S = 1/2$, tetragonal symmetry, the parameters $g_{\parallel} = 2.0151$, $g_{\perp} = 2.2113$ and no shf structure.

2. Experiment

The diamonds examined in this work were six natural blue diamonds from the Argyle mine in Western Australia. The diamonds were of a grey-blue colour and generally of a rough shape with no discernible crystallographic faces. The largest stone was approximately 8 mm along its longest axis.

The cw EPR was performed on a Bruker ESP380e at room temperature using a standard rectangular cavity. The optical absorption spectra were recorded with a Cary 13 UV–vis spectrophotometer fitted with a diffuse reflectivity attachment. The spectra were recorded in transmission mode, but the diffuse reflectivity attachment was used as it contained an integrating sphere and good spectra could be obtained despite the poor optical quality of the samples. The optical spectra were recorded at room temperature. Fourier transform infrared (FTIR) spectra were obtained in the Department of Chemistry, Monash University, using a Perkin Elmer FTIR microscope attached to a PE 1600 series FTIR spectrometer.

The electron nuclear double resonance (ENDOR) measurements were performed on a home-built X-band spectrometer in the Physics Department at the University of Paderborn in Germany. The microwave source was a 120 mW YIG oscillator and double balanced mixers were used for detection. One mixer provides the absorptive signal while the other provides the dispersive signal which is used for the AFC of the source. The RF is generated with a computer controlled synthesizer and a broad band amplifier. A frequency range of up to 30 MHz could be achieved with this amplifier. The cavity with integrated helium flow cryostat worked in a TE_{011} mode and the RF field was produced by four silver rods in the cavity. For more details about the ENDOR spectrometer refer to Spaeth *et al* [14].

3. Experimental results

The FTIR spectra of the natural blue diamonds, figure 1, show strong absorptions below 1500 cm^{-1} indicating a high nitrogen content. The nitrogen is present predominantly in the form of B aggregates, which contain four nitrogens, and to a lesser degree as A aggregates, which are nitrogen pairs [15]. The concentration of nitrogen in the form of B aggregates is estimated to be 600 atomic ppm using the relation given by Woods *et al* [16]. Also present is a large platelet peak at 1376 cm^{-1} . Platelets are large extended defects that form during the aggregation of nitrogen in diamond [17]. The nature of the platelets is still controversial—they may be composed predominantly of nitrogen or be a precipitate of carbon interstitial atoms [18], perhaps with some nitrogen present. The presence of both the B aggregates and platelets indicates that, at some stage in their history, these diamonds have been subjected to high temperatures for extended periods. Several hydrogen related peaks are also present which have been previously reported by Fritsch *et al* [2]. The most prominent of these are the 3107 cm^{-1} and 3235 cm^{-1} peaks. The concentration of hydrogen in similar diamonds has been estimated to be 500 ppm [2]. Other lines are observed at 1404 cm^{-1} , 1434 cm^{-1} , 1498 cm^{-1} , 1546 cm^{-1} , 2784 cm^{-1} , 2852 cm^{-1} and 2924 cm^{-1} . The peaks in the regions of about 2200 cm^{-1} are two-phonon absorptions and are intrinsic to diamond.

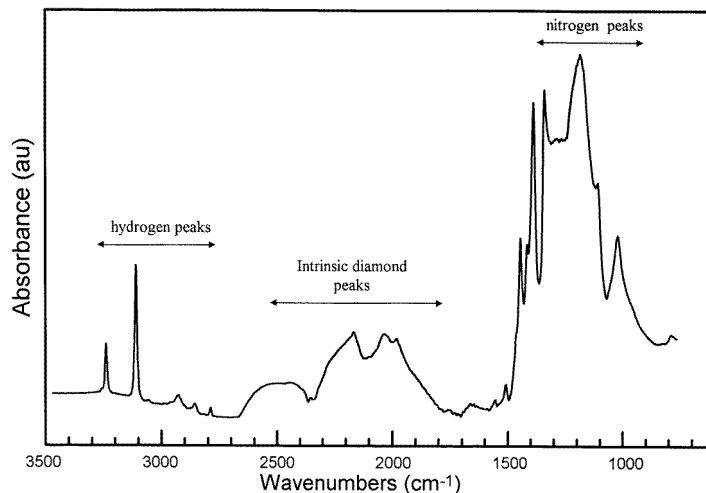


Figure 1. FTIR spectrum of Argyle blue diamond.

The room temperature optical absorption spectra, figure 2, of the natural blue diamonds have two dominant broad absorption bands, one centred at 1.71 eV (725 nm) and another at 2.25 eV (550 nm). It is presumably the peak at 1.71 eV which is responsible for the blue coloration. The peak at 2.25 eV is also of interest because of its similarity to a peak with roughly the same position and line width in optical absorption spectra of pink diamonds from the same mine. It is possible that the same defect is responsible in each case. However, as the absorptions are broad and with no sharp features to indicate zero phonon lines, it is difficult to draw any firm conclusions from optical absorption alone. The smaller features at approximately 2.25 and 1.48 eV are also reproducible, but it is not possible to identify them at this stage.

In the room temperature EPR spectra of the natural blue diamonds, figure 3, several nitrogen related EPR centres with g values close to the free electron value of 2.0023 are

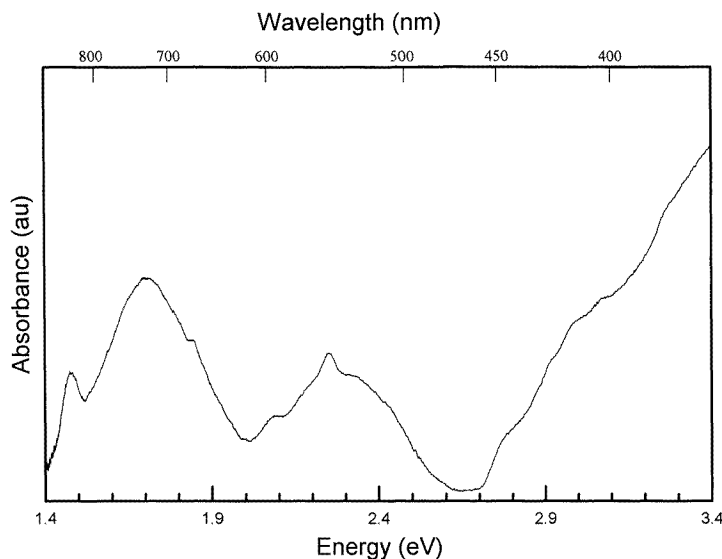


Figure 2. Optical absorption spectrum of Argyle blue diamond.

seen. The P1 centre, substitutional nitrogen, is seen as a well resolved triplet. The P2 centre which contains three nitrogens is also present in these diamonds although in this spectrum it is obscured by other partially resolved systems, possibly due to the OK1 and N2 centres [19]. In addition two other features at higher g values are also present in all of the blue diamonds. These are a broad isotropic line at $g = 2.02$ and a complicated series of lines centred at $g = 2.07$. The complicated spectrum is thought to be the result of shf splittings from at least three nitrogens. A centre involving three nitrogens had previously been described in nickel containing synthetic diamonds [8]. This centre, labelled NE2, was proposed to be Ni^+ in a di-vacancy position with three neighbouring nitrogens. Simulations of the EPR spectrum for the NE2 centre using the literature spin Hamiltonian parameters gave a good fit to the experimental spectrum observed by us. A complete angular dependence of this EPR centre was not recorded as the poor signal to noise ratio prevented a good resolution of the complicated shf splittings. It was only with the field along a [100] axis that a well resolved spectrum could be obtained.

The broad line, seen in figure 3 at $g = 2.02$, has not been previously reported. The line is roughly Gaussian in shape with a peak-to-peak linewidth of 1.4 mT. The linewidth does not appear to vary significantly with temperature or with orientation of the magnetic field and no structure could be resolved. It is difficult to verify this because the NE2 spectrum overlaps with this line and obscures the lineshape at orientations of the applied field away from a [100] axis.

ENDOR spectra recorded on the broad $g = 2.02$ line are shown in figure 4. The spectra were recorded at 55 K with a microwave power of $12 \mu\text{W}$. Long accumulation times were needed to achieve a satisfactory signal-to-noise ratio. The dominant feature in the ENDOR spectra was a peak at the Larmor frequency of ^{13}C indicating an interaction with matrix carbons. With the applied field close to a [100] axis another four lines were observed. These were arranged in two pairs with roughly equal spacing between them centred at 1.711 MHz and 3.020 MHz. These lines decreased dramatically in intensity as the applied field was

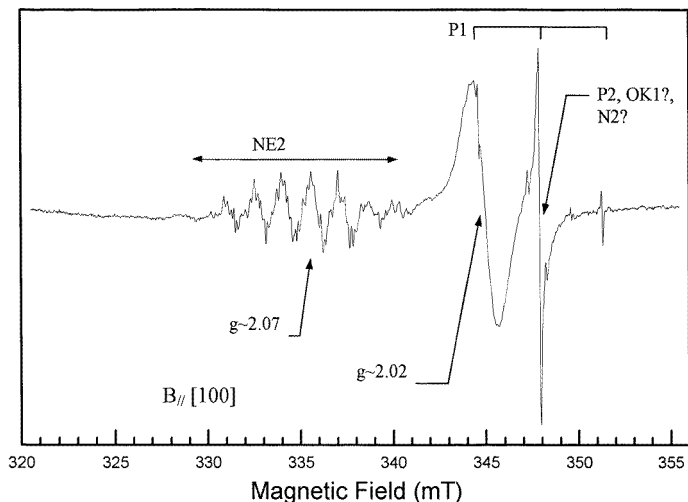


Figure 3. X-band room temperature EPR spectrum of Argyle blue diamond. The applied field is parallel to a [100] axis and the spectrum was recorded under the following conditions: microwave frequency = 9.76 GHz, microwave power = 10 mW, modulation amplitude = 0.1 mT.

rotated away from the [100] axis. There appeared to be some small variation in the line position, of the order of 10 kHz, but as the lines were only observed over a range of a few degrees it was not possible to determine the anisotropic part of the hf interaction with precision.

With these observations it was not possible to unambiguously assign the lines in the spectrum. However, an analysis of equation (1) [14], which shows the ENDOR frequencies to first order, does narrow the possibilities.

$$\nu_{ENDOR} = |m_s A - \nu_L + m_q P| \quad (1)$$

where

$$A = \frac{a + b[3 \cos^2(\theta_A) - 1]}{h} \quad (2)$$

$$\nu_L = \frac{g_n \mu_n B_0}{h} \quad (3)$$

$$P = \frac{3q[3 \cos^2(\theta_Q) - 1]}{h} \quad (4)$$

$$m_q = \frac{m_I + m_{I+1}}{2}. \quad (5)$$

Equation (2) describes the shf interaction with a and b the isotropic and anisotropic contributions. These quantities are related to the shf interaction tensor in the principal axis system, in the case of axial symmetry by

$$A_{xx} = A_{yy} = A_{\perp} = a - b \quad (6)$$

$$A_{zz} = A_{\parallel} = a + 2b. \quad (7)$$

θ_A is the angle between the applied field and x direction in this representation and h is the Planck constant. Equation (3) describes the nuclear Zeeman interaction with ν_L the Larmor frequency, g_n the nuclear g factor, μ_n the nuclear magneton and B_0 the applied

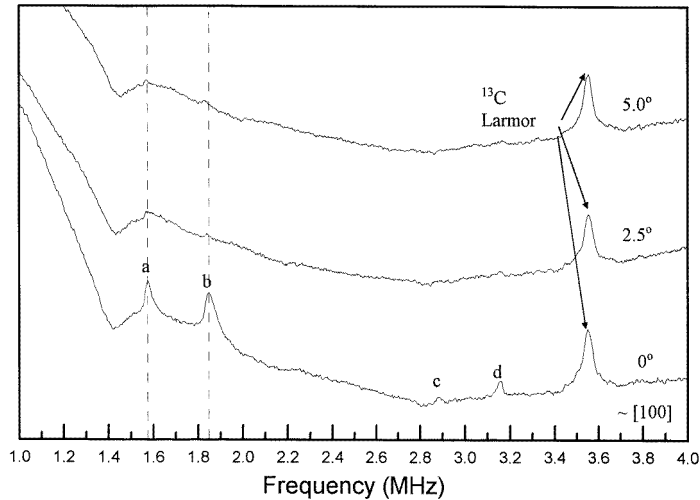


Figure 4. ENDOR spectra of Argyle blue diamond with the static magnetic field set at the broad resonance at $g = 2.02$ seen in figure 3. Magnetic field = 332.28 mT, microwave frequency = 9.3665 GHz, microwave power = 12 μ W, temperature = 55 K. For the lower trace the magnetic field was oriented parallel to a [100] axis. The middle and upper traces correspond to crystal rotations of 2.5 degrees and 5.0 degrees away from the [100] axis. A peak at 3.6 MHz, the Larmor frequency of ^{13}C , is seen at all orientations of the magnetic field. It is only with the applied magnetic field close to a [100] axis that a set of lines labelled a–d is observed.

magnetic field. Equation (4) describes the nuclear quadrupole interaction. The quadrupole coupling constant, q , is related to the quadrupole interaction tensor in the principal axis system, in the case of axial symmetry by

$$P_{xx} = P_{yy} = P_{\perp} = -q \quad (8)$$

$$P_{zz} = P_{\parallel} = 2q. \quad (9)$$

θ_Q is the angle between the applied field and z direction in this representation. In these equations m_s and m_I refer to the electron and nuclear spin states respectively and m_q is used to denote the two m_I states involved in the ENDOR transition where the quadrupole interaction is observed.

The most noteworthy feature of the experimental spectrum is the equal spacing between the two pairs labelled a–b and c–d in figure 4. We can see that this splitting could, in principle, be due to any of the terms in equation (1). If we neglect the last term and assume $S = 1/2$, the splitting can be either to $2A$ or $2\nu_L$. In the first case each pair would be centred at ν_L . The experimental values do not correspond to the Larmor frequency of any nucleus at this field so we can discount this possibility. Likewise, a nucleus with a Larmor frequency corresponding to the second case with a splitting of $2\nu_L$ cannot be found. We can then assume that the splitting is due to the last term in equation (1) and involves a quadrupole interaction with a nucleus with $I = 1$.

To explain the position of the two pairs, a–b and c–d, we can look at three possibilities. If we assume $S = 1/2$ then the two pairs could correspond either to the $m_s = 1/2$ and $m_s = -1/2$ manifolds or to two different sites with different orientations to the magnetic field. In the first case the separation between the centre of each pair would be equal to $2\nu_L$ and again we find that a nucleus with this Larmor frequency does not exist. If the two pairs

correspond to different sites with their principal axes at different angles to the magnetic field then the quadrupole splitting would not be identical for the two pairs. Therefore, both of these possibilities can be discounted. In the third possibility, $S = 3/2$, and the two pairs correspond to the $m_s = 1/2$ and $m_s = 3/2$ manifolds. In this case the position of the centres of the pairs would occur at $|A/2 + \nu_L|$ and $|3A/2 + \nu_L|$. The Larmor frequency of ^{14}N at this field is 1.0227 MHz and if we assume $A = 1.336$ MHz good agreement is found with the experimental line positions. The calculated positions for the centres of the pairs a–b and c–d are then 1.691 and 3.026 MHz which correspond well with the experimental values of 1.711 and 3.020 MHz.

Using equation (1), for the ENDOR frequencies to first order, we find that the model that best explains the number and position of the peaks in the ENDOR spectrum involves a defect with $S = 3/2$ and $I = 1$. We assume that both the shf and quadrupole interactions have the same principal axis along a [100] direction. The parameters that are calculated from the fitting are then $A_{\parallel} = 1.336$ MHz and $P_{\parallel} = 92$ kHz if we take $\theta_A = \theta_Q = 0^\circ$. As there will be sites with their principal axes along all six of the [100] directions we would expect to see lines corresponding to both A_{\parallel} and A_{\perp} . We therefore assume that the set of the lines corresponding to the perpendicular orientation occur below 1 MHz and are not resolved in the experimental spectra. The situation could, of course, be the reverse with the perpendicular component but not the parallel component. Without evidence to the contrary we will assume the former in the following discussion.

As these peaks in the ENDOR spectrum could only be resolved well with the field parallel to a [100] axis, the anisotropy of the shf interaction could not be determined with precision. The fact that a quadrupole interaction is observed implies that b in equation (2) is non-zero and hence there is some anisotropy in the shf interaction. The ENDOR frequencies for the $m_s = 1/2$ manifold appear to shift by a small amount of the order of 10 kHz within the 5 degrees in which the spectrum could be observed. If we neglect the quadrupole interaction then over 5 degrees we would expect a shift in the ENDOR frequencies of approximately 1% of b . Therefore for a shift of 10 kHz we obtain an upper estimate for b of 1 MHz. If b were significantly larger than 1 MHz, then this would produce a more noticeable angular dependence of the ENDOR frequencies.

4. Discussion

Observations of Argyle blue diamonds show that the colour is caused by a characteristic absorption band at approximately 725 nm (1.71 eV). The absorption spectrum shows no sharp lines or structure indicating vibronic bands and it is not possible to speculate on the defect responsible for the absorption from these spectra. A broad absorption band is also seen at 550 nm (2.25 eV) and it is possible that it is due to the same defect that is present in the Argyle pink diamonds.

A set of hydrogen related lines in the infra-red as observed by Fritsch *et al* [2] is also seen in the blue diamonds. These hydrogen defects had been related to the colour but no direct correlation has been established. The diamonds also contain high concentrations of nitrogen, >500 ppm predominantly in the B form. A statistical correlation between the nitrogen concentration and the hydrogen lines has also been observed [20].

The EPR spectra show P1 and P2 defects and other unresolved defects at $g = 2.00$. Of more interest are other lines at $g > 2.00$ which have also been observed. One of these has been identified as the NE2 centre which is believed to be a complex defect involving Ni^+ in a di-vacancy position with three nitrogens [8]. The other feature, a broad isotropic line at $g \cong 2.02$, has not previously been reported. Out of all these features only the last is observed

exclusively in Argyle blue diamonds. So far all the six Argyle blue diamonds that have been available for study have had this feature. Attempts to determine a direct correlation of the colour and the EPR line with $g = 2.02$ using optical detection of EPR (ODMR) were not successful due to the poor optical quality of the samples. Future experiments with specimens with polished faces might resolve this issue but the rarity of these diamonds presents some problems.

The broad EPR line has no structure even at 4 K and no apparent angular variation. It is therefore impossible to obtain any structural information directly from the EPR spectra. It is possible to make a number of inferences. Firstly the line has a g value greater than 2. This is unusual in diamond where the strong covalent bonding quenches the spin-orbit coupling. Out of all the EPR centres observed, by far the majority have g values close to the free electron value [21]. A g values greater than 2 is indicative of a more than half filled d shell. The centres associated with nickel all have g values greater than 2. The fact that another nickel related centre, the NE2 centre, is found in the blue diamonds also implicates nickel in the new EPR centre.

Synthetic diamonds have been produced that contain nickel in a wide variety of defects but none show this broad line. What then is different in the natural blue diamonds? One feature of the blue diamonds is the high concentration of hydrogen. Neither the EPR nor the ENDOR spectra show an shf splitting characteristic of hydrogen ($I = 1/2$) that would be expected if hydrogen were directly involved in the defect. The involvement of hydrogen could only be indirect such as a distant charge compensator.

The second major difference between the synthetic diamonds and the natural blue diamonds is the concentration and form of nitrogen defects. The natural blue diamonds show a higher concentration of nitrogen, and probably more importantly it is present predominantly in the B form. A large platelet peak was also observed. The nitrogen in the natural blue diamonds is much more aggregated than in the synthetic diamonds where the nitrogen is in the A form. This indicates the extensive annealing that the natural diamonds have experienced over geological time scales. It is reasonable to expect that other defects containing nickel and a number of nitrogens may have been produced in this process.

The ENDOR spectrum was consistent with an $S = 3/2$ and $I = 1$ defect where ^{14}N is the nucleus involved. This could be consistent with a nickel in an $S = 3/2$ spin state, Ni_v^- , with shf from a neighbouring ^{14}N nucleus or alternatively the nitrogen itself could be in an $S = 3/2$ spin state. Nitrogen has recently been observed in nitrogen implanted C_{60} in an $S = 3/2$ spin state [22]. No EPR spectrum associated with interstitial nitrogen has so far been observed although it would be expected to be paramagnetic [19] and theoretical calculations predict that a nitrogen interstitial in the tetrahedral site in diamond would give rise to an $S = 3/2$ state with an hf interaction of the same order of magnitude as that observed in our spectra [23]. This defect would be expected to have a g value close to the free electron value in contrast to the experimental value of 2.02 and no quadrupole splitting also in contrast to the experimental results.

The experimental results are therefore not consistent with a nitrogen interstitial in the tetrahedral site but do not rule out the possibility of a relaxed configuration. Theoretical calculations have, however, found that the migration energy of the nitrogen interstitial is sufficiently low that even at room temperature they would migrate and be trapped at other defects [24]. In this case nitrogen interstitials would not be observed.

The possibility that the broad EPR line in the blue diamonds is due to a nitrogen interstitial is therefore fairly small and the most likely model is a nickel defect in an $S = 3/2$ state interacting with neighbouring nitrogens. The $g = 2.0319$ defect in synthetic diamond has been shown to be $S = 3/2$ and is believed to be due to an Ni^- ion on a

substitutional site [6]. The defect observed in this study could therefore be substitutional Ni^- with a neighbouring nitrogen. This would be consistent with the presence of the NE2 centre in these diamonds which is also believed to involve both nickel and nitrogen [8].

Without the complete angular dependence of the ENDOR spectrum it is not possible to obtain enough parameters of the spin Hamiltonian to determine the exact structure of the defect. The order of magnitude of the quadrupole and shf interactions can, however, be used to give some information about the possible structures. For this we assume that the defect is Ni_s^- to give the $S = 3/2$ spin state and that the shf interaction is from a neighbouring N^+ .

The quadrupole interaction is thought to be caused by the point charge of Ni_s^- experienced by N^+ . It can be estimated by [14]

$$P_{\parallel} = 280.36 \frac{Q(1 - \gamma_{\infty})}{4I(2I - 1)} \frac{1}{R^3}. \quad (10)$$

P_{\parallel} is the element of the quadrupole interaction in MHz, Q is the electric quadrupole moment in units of $|e| \times 10^{-24} \text{ cm}^2$ and is equal to 0.0193 for ^{14}N , I is the nuclear spin, γ_{∞} is the Sternheimer antishielding factor and R is the separation between the Ni_s^- and the N^+ in ångströms. Neglecting the Sternheimer antishielding, values of P_{\parallel} for N^+ represent a lower limit of the quadrupole interaction. In table 1 this is given for various N^+ sites. According to this N^+ cannot be nearest neighbour (nn) because the experimental value of P_{\parallel} (0.09 MHz) is too small for that. Since γ_{∞} is not known for N^+ , we could only speculate on it. However, had we included Sternheimer antishielding, for the isoelectronic B^- ($\gamma_{\infty} \approx -3$), we would arrive at a position of N^+ beyond next nearest neighbours. Similarly, an estimation of the anisotropic shf interaction by the classical point dipole-dipole interaction suggests that N^+ cannot be nearest neighbour, for which the anisotropic shf constant would be significantly above the upper limit of 1 MHz, which was estimated from the experiment.

Table 1. Estimates of quadrupole parameters for different positions of nitrogen.

| N^+ position | R (Å) | P_{\parallel} (MHz) |
|-----------------------|---------|-----------------------|
| nn | 1.54 | 0.2 |
| nnn | 2.52 | 0.05 |
| 4nn-[001] | 3.56 | 0.01 |
| $[00\frac{1}{2}]$ | 1.78 | 0.1 |

The ENDOR spectrum indicates that the defect has a symmetry axis about [100] and it is therefore natural to consider structures that have this symmetry. Figure 5 shows the unit cell for diamond. It can be seen that the fourth nearest neighbour positions belong to the (100) class and are one unit cell spacing (3.56 Å) from the Ni_s^- . We also consider the interstitial position which is half a unit cell spacing from the Ni_s^- and is also in a [100] direction.

Regarding both symmetry and magnitude of the measured interactions, the most probable position is the 4nn position one unit cell spacing in the [100] direction. We also compare our experimental value for the quadrupole parameter with that obtained from the N^+ in the W7 centre [25]. The model for this defect has the N^+ in a third nearest neighbour (3nn) position relative to the major nitrogen that has the electron spin and has a similar magnitude for the quadrupole interaction ($P_1 = 0.13$, $P_2 = -0.13$, $P_3 = 0.0$ MHz). We therefore propose that the defect structure involves Ni^- on a substitutional site and a nitrogen on a 4nn position.

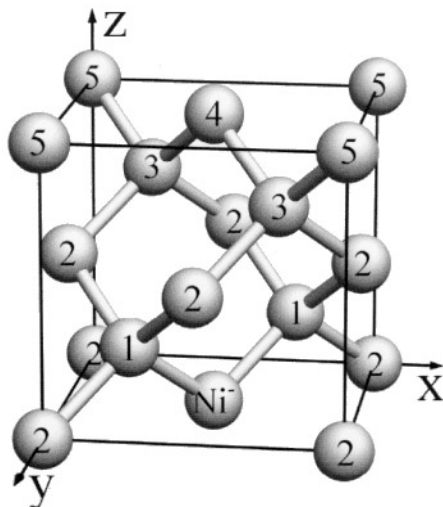


Figure 5. Unit cell of the diamond structure. An Ni^{2+} is shown on a substitutional position and the first to sixth nearest neighbour carbons are labelled. One of the six fourth nearest neighbour carbons is shown one unit cell spacing from the Ni^{2+} . The interstitial position in the centre of the unit cell can also be seen.

We now consider several arguments to account for the rather large linewidth of the EPR line. In contrast to Ni_s^- we do not observe a temperature dependence of the linewidth and hence spin–lattice relaxation does not determine the linewidth. Dipolar broadening from other paramagnetic species does not seem to account for the linewidth as we would expect the other EPR centres to be broadened by the same mechanism which is not observed experimentally.

The shf interaction from a single N^+ determined from the ENDOR spectra could only account for at most 0.06 mT of the linewidth. From the ENDOR spectrum we cannot determine the number of nitrogens that are involved. There are six 4nn sites and it is therefore possible that up to six nitrogens may be associated with the Ni_s^- . This would produce a Gaussian EPR lineshape. However, an analysis shows that only approximately 0.3 mT of the line width can be accounted for in this way. The high charge state of such a defect would also suggest a high formation energy and a low probability of it forming.

There are two other observations which could indicate the number of nitrogens involved. Firstly, the g factor of the EPR line appears to be isotropic. Secondly, we note that the ENDOR spectrum contains lines from both the $m_s = 1/2$ and $m_s = 3/2$ manifolds. This implies that the zero field splitting can be no larger than the EPR linewidth and therefore must be less than 40 MHz. This suggests that the Ni_s^- largely retains its local tetrahedral symmetry. If the defect involved had only one nitrogen we would expect some tetragonal distortion of the local environment of the nickel. This would result in anisotropic g values and a zero field splitting. This argument could be used to suggest that the defect has a symmetric structure with all six possible sites for the nitrogen occupied. However, as the nitrogen is proposed to be one unit cell distant from the nickel it is likely that the magnitude of this perturbation is quite small and may not produce noticeable effects.

Other diamonds from the Argyle mine, including the pink and brown coloured stones, are known to have large amounts of random strains resulting from plastic deformation. It is therefore possible that the blue diamonds also contain random strains and it is suggested

that this could explain many of the features observed. The random strain would produce a distribution of sites with different zero field splittings and g values. It would give rise to a broad isotropic Gaussian line as has been observed. A similar distribution of zero field splittings was observed with the Ni_s^- centre [5]. This would still be consistent with the observation of the $m_s = 1/2$ and $m_s = 3/2$ manifolds in the ENDOR spectra as a certain fraction of the defects would be unperturbed and have small zero field splittings. The random strains would also produce a distribution in the ENDOR frequencies. This may explain why only weak lines could be resolved on top of a broad baseline in the ENDOR spectra. The model proposed for this defect can therefore account for the features of the EPR and ENDOR spectra.

5. Conclusion

The results show that these blue diamonds contain nickel and a high concentration of nitrogen. The diamonds have been subjected to high temperatures over geological time scales. This has led to the formation of nitrogen aggregates and defects containing both nickel and nitrogen. One of these, the NE2 centre, has previously been observed in synthetic and natural diamonds and has been proposed to be Ni^+ in a di-vacancy position with three neighbouring nitrogens. The second has not been observed previously and occurs exclusively in Argyle blue diamonds. We propose that this defect is Ni_s^- with N^+ in a 4nn position. This defect has not been produced in synthetic diamonds and it appears that annealing over geological time scales is needed. Plastic deformation, which is common in other Argyle diamonds, also appears to play a role in these diamonds. The diamonds also contain high concentrations of hydrogen, which has previously been reported, but it is not clear how this is related to the nickel centres observed or the colour.

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References

- [1] Nassau K 1983 *The Physics and Chemistry of Color: the Fifteen Causes of Color* (New York: Wiley-Interscience)
- [2] Fritsch E, Scarrat K and Collins A T 1991 *New Diamond Science and Technology, MRS Int. Conf. Proc.* ed R Messier, J T Glass, J E Butler and R Roy (Pittsburgh, PA: Materials Research Society) pp 671–6
- [3] Loubser J H N and van Ryneveld W P 1966 *Nature* **211** 517
- [4] Samoilovich M I, Bezrukov G N and Butuzov V P 1971 *Pis. Zh. Eksp. Teor. Fiz.* **14** 551 (Engl. transl. 1971 *JETP Lett.* **14** 379)
- [5] Isoya J, Kanda H, Norris J R, Tang J and Bowman M K 1990 *Phys. Rev. B* **41** 3905
- [6] Isoya J, Kanda H and Uchida Y 1990 *Phys. Rev. B* **42** 9843
- [7] Yelisseyev A and Nadolinny V 1992 *Dokl. Akad. Nauk* **326** 524
- [8] Nadolinny V and Yelisseyev A 1994 *Diamond Relat. Mater.* **3** 1196–200
- [9] Davies G, Neves A J and Nazare M H 1989 *Europhys. Lett.* **9** 47
- [10] Ludwig G W and Woodbury H H 1962 *Solid State Physics* vol 13, ed F Seitz and D Turnbull (New York: Academic) p 223

- [11] Collins A T, Kanda H and Burns R C 1990 *Phil. Mag.* B **61** 797
- [12] Lawson S C and Kanda H 1993 *J. Appl. Phys.* **73** 3967
- [13] Mineeva R M, Speranskii A V, Titkov S V and Bershov L V 1994 *Dokl. Akad. Nauk* **334** 755
- [14] Spaeth J-M, Niklas J R and Bartram R H 1992 *Structural Analysis of Point Defects in Solids* (Berlin: Springer)
- [15] Clark C D, Collins A T and Woods G S 1992 *The Properties of Natural and Synthetic Diamond* ed J E Field (London: Academic) pp 35–79
- [16] Woods G S, Purser G C, Mtinkulu A S S and Collins A T 1990 *J. Phys. Chem. Solids* **51** 1191
- [17] Evans T 1992 *The Properties of Natural and Synthetic Diamond* ed J E Field (London: Academic) pp 181–214
- [18] Woods G S 1989 *Proc. R. Soc. A* **407** 219
- [19] Baker J M and Newton M E 1995 *Appl. Magn. Reson.* **8** 207
- [20] Chapman J 1997 private communication
- [21] *Landolt-Börnstein New Series* 1990, Group III, vol 22b, ed O Madelung and M Schulz (Berlin: Springer) pp 117–206
- [22] Murphy A T, Pawlik Th, Weidinger A, Höhne M and Spaeth J-M 1996 *Phys. Rev. B* **77** 1075
- [23] Overhof H 1997 private communication
- [24] Mainwood A 1994 *Phys. Rev. B* **49** 7935
- [25] Newton M E and Baker J M 1991 *J. Phys.: Condens. Matter* **3** 3591