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V A Nadolinny†, A P Yelisseyev‡, J M Baker§, M E Newton§, D J Twitchen§, S C Lawson‖, O P Yuryeva† and B N Feigelson¶

† Institute of Inorganic Chemistry, Novosibirsk 630090, Russia
‡ Institute of Mineralogy and Petrography, Novosibirsk 630090, Russia
§ Department of Physics, University of Oxford, Clarendon Laboratory Parks Road, Oxford OX1 3PU, UK
‖ DTC Research Centre, Belmont Road, Maidenhead, SL6 6JW, UK
¶ Research Centre 'Basis', Facultetsky per., 12, Moscow 125080, Russia

Abstract.   Electron paramagnetic resonance (EPR) and optical spectroscopy have been used to determine the structure and electronic state of nickel–nitrogen centres in natural diamonds and in synthetic diamonds enriched in ^{13}C. The latter were grown in an Fe–Ni–C solvent/catalyst system at 1750 K, under stabilizing pressure, by the temperature gradient method and afterwards treated at high temperature and pressure. The parameters and directions of the ^{13}C hyperfine structure (HFS) tensors for the NE1 centre were found to confirm the previously proposed model for this defect, with a nickel ion at the centre of a double semivacancy as the basic structural unit. In this unit the nickel atom has six atoms in its coordination shell. The NE1 centre has C_{2h} symmetry, and the two equivalent nitrogen atoms in the coordination shell lie in the symmetry plane. New data on the HFS of ^{14}N and ^{13}C for the NE5 centre, also with C_{2h} symmetry, indicated the same structural unit, but the two equivalent nitrogen atoms (and two equivalent carbon atoms) lie out of the symmetry plane and are related to one another by reflection in it. A new paramagnetic centre was found, labelled NE8, also with C_{2h} symmetry, with four equivalent nitrogen atoms in the coordination shell all lying out of the symmetry plane. This centre is responsible for the 793.6 nm vibronic system in absorption and luminescence spectra. The new data have allowed a reinterpretation of the HFS tensors for the NE2 centre, which has C_1 symmetry, suggesting that it has the same structure as NE1 but with one additional nitrogen atom in the coordination shell. The electronic states of these nickel-containing centres are discussed using the approach of Ludwig and Woodbury to transition metal ions in covalent crystals.

1. Introduction

For many years there has been difficulty in incorporating heavy elements as impurities into the diamond lattice. In spite of the fact that analytical methods show that almost all elements of the periodic table have been found as impurities inside diamond, only six elements have been unambiguous identified as bonding to the diamond lattice, namely nitrogen, boron, nickel, silicon, hydrogen and cobalt [1–6]. The only experimental proof, for many years, of the presence of heavy metals in the diamond lattice was the EPR spectrum of nickel, labelled W8, which was confirmed by the presence of ^{61}Ni hyperfine structure (HFS) when investigating samples enriched in ^{61}Ni [7, 8]. Attempts to use ion implantation techniques for incorporation of transition metal ions were unsuccessful, presumably because of the large sizes of transition

metal ions, the small lattice parameters and the metastability of the diamond phase at ambient pressure [9, 10]. Recently, in connection with the development of technology of both single crystal growth and diamond film synthesis, attempts have been made to incorporate various dopants into the diamond lattice during its growth. This has made it possible to study the structure of as-grown nickel defects and to show that Ni occupies a tetrahedral position, substituting for a carbon atom, and that it has an electronic spin $S = \frac{3}{2}$ due to the $3d^7$ state of the Ni^- ion [11, 12]. We will use a subscript s, as in Ni_s^-, to indicate a substitutional site.

The development of annealing technology for diamond crystals at high pressure and high temperature (HTHP) (5.5 GPa and up to 2500 K) made it possible to show that on annealing of the as-grown defect Ni_s^-, its environment changed producing a new centre, named NE4 [13, 14]. The activation of migration of nitrogen impurities on increasing the annealing temperature in the 1900 to 2500 K range results in the capture of impurity nitrogen atoms by the nickel NE4 defects. EPR study of annealed synthetic and natural diamonds has revealed a large family of nickel-related defects containing up to three nitrogen atoms. These centres have $S = \frac{1}{2}$ and g-values typical of d ions in an octahedral environment. It was proposed that these new centres are variants of a structure where one of the neighbours of Ni_s had been displaced to a distant interstitial position, to leave a vacancy adjacent to Ni_s, and the Ni atom had moved towards the vacancy so that it occupied the middle position in a nearest neighbour di-vacancy, VNiV. This is called a paired or double semivacancy [15], as there is only one missing atom. This structure is illustrated in figure 1. This was proposed as the structure of the centre NE4, with D_{3d} symmetry [14]. There are two planes through this structure which will be relevant to the discussion, which are illustrated in figure 1. One contains the VNiV fragment and two of the carbon ligands, say 1 and 2; the $(1\bar{1}0)$ plane for the VNiV fragment aligned along $[11\bar{1}]$. The other, (332), contains the other four carbon ligands (3–6) and the Ni atom at their centre, and is normal to the first plane, and almost normal to the [331] direction joining atoms 1 and 2. This double semivacancy structure has been proposed to account for optical experimental data for a silicon containing centre in diamond [16], and this has been supported by theory [17]; the structure has also been proposed theoretically for the structure of the phosphorus-vacancy centre in diamond [18].

The structure of observed nickel–nitrogen defects NE1–NE5 has been deduced from the principal values and directions of the g-tensors and the HFS-tensors of nitrogen atoms. For a more definitive determination of the defect structure, information about their carbon environment is required. An EPR and ENDOR study of ^{13}C enriched diamonds has usually been the way to obtain such data.

In the present paper the results of an experimental EPR study of the HFS of ^{13}C are described for the nickel–nitrogen defects NE1, NE2 and NE5 in diamonds which have been especially enriched in ^{13}C during growth. New data about the HFS from ^{13}C and more detailed analysis of the EPR spectrum of the NE5 defect at the Q-band, has allowed refinement of the structure of this defect. The investigation also revealed a weak spectrum due to a new nickel–nitrogen defect (labelled NE8), containing four equivalent nitrogen atoms.

Experimental details are discussed in section 2 and the measured data are discussed in section 3. The general method of interpreting the data is discussed in section 4 and the interpretation for specific sites in section 5. Some general comments on the structures of the defects are made in section 6 and the optical analogues of the EPR centres are discussed in section 7. In section 8 an analysis is given of the electronic state of the nickel–nitrogen defects using the approach developed by Ludwig and Woodbury [19] for transition metal ions in purely covalent structures.
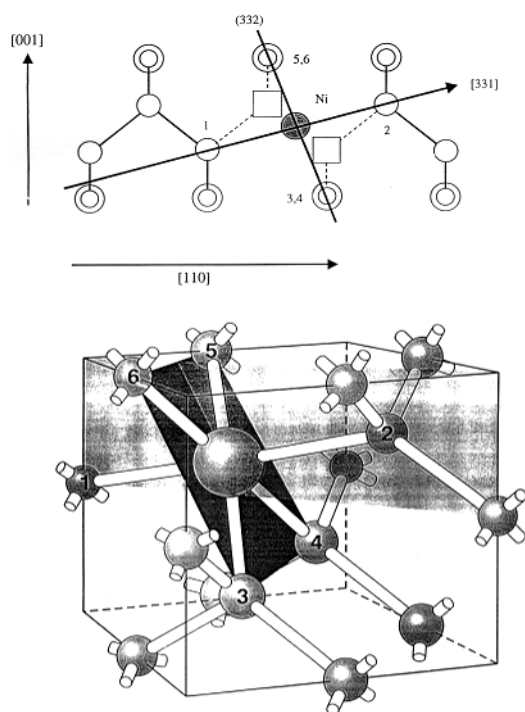
Figure 1. The basic structural fragment of the nickel–nitrogen containing centres in diamond: a plan view projected onto a $(1\bar{1}0)$ plane and a perspective view of a unit cell. In the plan, the vacant carbon sites are marked as squares. The nickel atom is between them and its six ligands are numbered 1 to 6. Single circles (and squares) lie in the plane of the page and double circles represent atoms a distance $a_0/2\sqrt{2}$ above and below the plane. The perspective shows two important planes in the structure: $(1\bar{1}0)$ which is lightly shaded and contains the central large Ni atom and ligands 1 and 2; and (332) which is heavily shaded and contains the Ni atom and ligands 3–6. The latter plane is shown in projection on the plan view, as well as the [331] direction which passes through the Ni atoms and ligands 1 and 2.

2. Experiment

2.1. Synthetic diamonds

The synthetic diamonds were grown on a seed in an Fe–Ni–C solvent/catalyst environment at 1650–1750 K and 5.5 GPa by the temperature gradient method in a poly-anvil split-sphere type of ultra-high-pressure apparatus [20]. Some experimental data were obtained on a suite of 40 synthetic diamonds grown without nitrogen getters with the natural abundance of ^{13}C, while four crystals were especially grown with source material containing 5% of ^{13}C. Measurements described in section 2.2 showed that the actual ^{13}C content was 4.6% in the synthetic diamonds. These diamonds were mainly of octahedral habit, and yellow in colour because of a high content of nitrogen incorporated as single substitutional atoms, N_s (labelled the P1 or the C centre in the EPR and optical literature, respectively). The P1 centre concentration was estimated from both the EPR intensity and the intensity of the 1135 cm^{-1} band and the 1344 cm^{-1} line in the one-phonon IR absorption region. Some of the nitrogen was present in the form of two nitrogen atoms occupying adjacent sites (A centre) identified by a 1282 cm^{-1} absorption band in the IR spectrum. The total nitrogen concentration in both of these forms in the natural diamonds

was about 200 ppm. For the ^{13}C enriched diamonds grown at 1750 K, a small intensity in an absorption line at 1332 cm^{-1} indicates that a few ppm of the single substitutional nitrogen may be present in the ionized form (as N_s^+) [21]. Some of the as-grown synthetic diamonds, including one enriched in ^{13}C, were annealed at 2300 K for 3 h at 5.5 GPa stabilizing pressure. When annealed, the initially yellow crystals became much paler and slightly greenish. Such annealing is known to stimulate diffusion of impurity atoms and their aggregation into complex defects [2, 3]. The EPR data after HPHT treatment showed that the P1 concentration decreased to 10 ppm while at the same time spectra from NE1, NE2, NE3 and NE5 defects appeared in the EPR [1, 13, 14, 22].

For comparison with the data for synthetic diamonds, a study was also made of the optical and EPR spectra of more than 100 specimens of natural diamond from the Yakutia deposits (from the collection of the Institute of Inorganic Chemistry, SB RAS, Novosibirsk), which were categorized by the intensity of the S2, S3 and 523 nm luminescence of the nickel-containing NE1–NE3 defects [13, 14, 22].

2.2. EPR spectra

The EPR spectra were recorded using a Bruker EPR ES 200 D spectrometer, operating at the X-band (~9.5 GHz), and EPR spectrometers designed in the Clarendon Laboratory, operating at the Q-band (~35 GHz) [23]. Experiments in the temperature range from 4.2 K to 300 K were made using an Oxford Instruments ESR 900 liquid helium continuous flow system and a goniometer specially designed for it, with two planes of rotation. Orientation of the diamonds studied was performed using the well documented EPR spectrum of P1 [1].

Since the EPR spectra from NE1, NE2, NE3 and NE5 centres overlap at the X-band as a result of their nearly equal g-values, the spectral resolution was improved by using the Q-band. This separated the groups of lines with different g-values so that the gaps between them were large enough to measure the HFS from ^{13}C. The EPR spectra for the annealed nickel-containing diamonds were measured at the Q-band for the applied magnetic field B parallel to $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$: see figure 2.
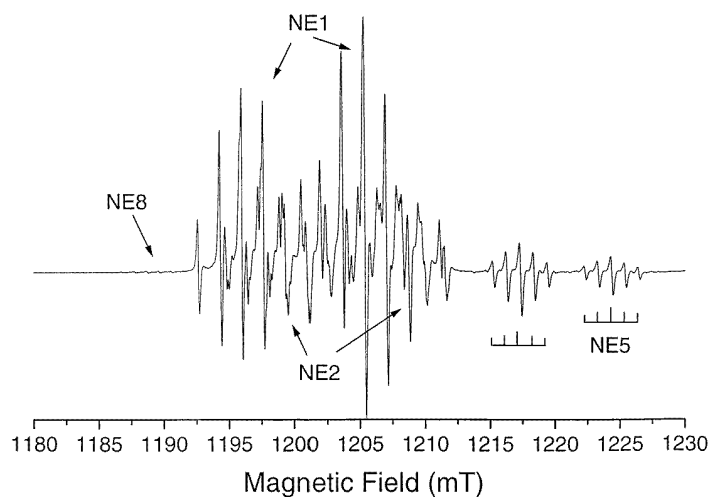

Figure 2. EPR spectra of P,T-treated nickel-containing synthetic diamonds for B parallel to $\langle 100 \rangle$ at the Q-band.
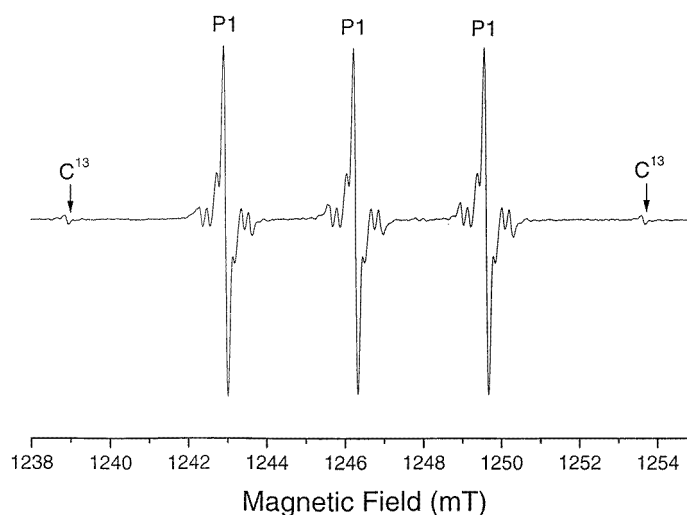
Figure 3. The EPR spectrum of the P1 centre for B parallel to $\langle 100 \rangle$ in as-grown synthetic diamond enriched in ^{13}C: the relative intensities of the lines shows that the abundance of ^{13}C is 4.6%.

To measure the actual abundance of ^{13}C in the diamonds grown from isotopically enriched carbon, the EPR spectrum for the P1 centre was recorded with 2 μW microwave power, to avoid microwave saturation. The ratio between intensities I of hyperfine lines shown in figure 3 for ^{13}C and one of the lines of the P1 centre, corresponding to a ^{12}C environment, $I(^{13}\text{C})/I(^{12}\text{C}) = 0.024(1)$, which corresponds to 4.6(2)% abundance of ^{13}C.

2.3. Optical measurements

2.3.1. The mid-IR region. The absorption spectra were measured with 1 cm^{-1} resolution at room temperature using a Perkin–Elmer 1710 IR Fourier transform spectrometer. The samples were pressed into an indium plate, the light beam being passed through opposite natural faces. The absorption spectra were calculated using the internal standard method in which the absorption of the diamond lattice at 1995 cm^{-1} is taken to be 12.3 cm^{-1} [3, 7, 24], and thus any complicated geometry of the samples and the beam path inside them are taken into account.

The spectra recorded were deconvoluted into three components related to the different nitrogen defects, P1 centres (with a main band at 1135 cm^{-1} and a sharp 1344 cm^{-1} line), A-centres (1282 cm^{-1} absorption band) and ionized P1 centres (sharp absorption line at 1332 cm^{-1}), using relations between absorption coefficients and concentrations given in the literature [21, 25].

2.3.2. The UV, visible and near IR regions. The absorption spectra in the 200 to 3200 nm region were measured using a Perkin–Elmer Lambda 19 spectrometer with an Oxford Instruments liquid nitrogen cryostat. The photoluminescence spectra were recorded using excitations at 360 nm and 430 nm (using an Oriel Xe 1 kW lamp through a Spex 1680 b 0.22 m monochromator) and at 514.5 nm and 632.8 nm using Ar and He–Ne lasers, respectively. Emission was measured using a Spex 1404 0.8 m monochromator with 1800 g nm^{-1} holographic gratings and a thermoelectrically cooled Hamamatsu R928 photomultiplier, which

was sensitive up to a wavelength of 900 nm. The crystal was mounted on a sample holder inside a DN 1704 Oxford Instruments liquid nitrogen cryostat of a reservoir type. When recording the luminescence excitation spectrum, the emission range was fixed while the wavelength of Xe exciting light was continuously scanned.

3. Results

3.1. Previous measurements

The EPR spectra for the centres discussed in this paper are described by the spin-Hamiltonian, with electron spin $S = \frac{1}{2}$

$$H = g_1\mu_B H_{z'} S_{z'} + g_2\mu_B H_{x'} S_{x'} + g_3\mu_B H_{y'} S_{y'} + \sum_i (A_1^i I_z^i S_z + A_2^i I_x^i S_x + A_3^i I_y^i S_y) \qquad (1)$$

where the summation of HFS terms is over all nuclei which interact with the electron spin, $I = 1$ for ^{14}N and $I = \frac{1}{2}$ for ^{13}C and the principal directions (x, y, z) may be different for each nucleus and different from (x', y', z'). The number of hyperfine terms varies from centre to centre.

Table 1 lists all of the spin-Hamiltonian parameters which have been measured for the new nickel-related centres, both previously measured and those reported in this paper, so that the information is readily comparable. The new measurements, described below, are those for C atoms, and all data for the NE8 centre. The g-tensors (for all except NE2) have monoclinic I symmetry (C_{2h}), where the principal direction 1 is normal to the {110} plane of reflection symmetry. In table 1, the principal directions have been listed for the centre with a $(1\bar{1}0)$ plane of reflection symmetry, so that it is clear how all principal directions are related to one another for one defect, but the crystal contains 12 equivalent sites related by the symmetry operations of the diamond structure. So principal direction 1 is along $[1\bar{1}0]$. α is the angle between principal direction 2 and [110]. Apart from g-values, the measured parameters in the table are the values of A_j, the principal directions of A_1, and the number of ^{14}N and ^{13}C nuclei involved. The assignment to particular labelled atoms, related to the numerical labelling in figure 1, is a deduction from the theoretical analysis in section 4, and is included here for easy reference.

For ligand nuclei 1 and 2, which lie in the $(1\bar{1}0)$ plane of symmetry, one principal value (A_3) lies along $[1\bar{1}0]$, and β is the angle between A_1 and [111], the direction appropriate to an undistorted sp^3 orbital on these ligands available to bond with nickel. Although, for opposite nuclei 1 and 2, the direction of the orbital available to bond with nickel lies along directions [111] and $[\bar{1}\bar{1}\bar{1}]$ respectively, related by inversion of the signs, these lead to identical principal values of A_i, so we have conventionally chosen the direction [111]. For the other ligand nuclei, again for opposite atoms, such as 3 and 5, for which the orbitals available to bond with nickel lies along directions $[\bar{1}11]$ and $[1\bar{1}\bar{1}]$ respectively, we have conventionally chosen the direction with two negative signs. For these nuclei, there is no symmetry requirement for the principal directions A_j of any of them, but those for identical nuclei are related to those for other nuclei by the symmetry operations of the site: γ is the angle between A_1 and $[\bar{1}\bar{1}1]$ or $[\bar{1}1\bar{1}]$, whichever is closer to the direction appropriate to an undistorted sp^3 orbital on these ligands available to bond with nickel.

3.2. The NE1 centre

Figure 4 shows the EPR spectra from the NE1 centre in the 4.6% ^{13}C enriched synthetic diamond. The experimental HFS parameters for ^{13}C and ^{14}N are given in table 1. To check these values of HFS-tensor parameters a simulation of the spectrum was matched to the experimental

Table 1. Measured values of spin-Hamiltonian parameters for the centres discussed in this paper. The values of A/h are given in MHz. The g-values for NE1–3 and HFS parameters for ^{14}N, except for those for NE8, are taken from [26]. The directions are for a site of C_{2h} symmetry, with $(1\bar{1}0)$ as its plane of reflection symmetry. g_1 corresponds to $[1\bar{1}0]$, and α is the angle between g_2 and $[110]$. NE2 has C_1 symmetry, and g_1 is $20°$ from $[1\bar{1}0]$. A column labelled $[i]$ means that the parameters are the same as for atom number i. β is the angle between A_1 and $[111]$. γ is the angle between A_1 and $[11\bar{1}]$ or $[\bar{1}11\bar{1}]$.

| | | Atom number: | 1 | 2 | 3 | 4 | 5 | 6 |
| | | Approx. dir^n of A_1: | [111] | [111] | [$\bar{1}$11$\bar{1}$] | [11$\bar{1}$1$\bar{1}$] | [$\bar{1}$11$\bar{1}$] | [11$\bar{1}$1$\bar{1}$] |
Centre	g-value	Atom	N	N	C	C	C	C
NE1	$g_1 = 2.1282$	A_1/h (MHz):	58.5		48.7			
	$g_2 = 2.007$	A_2/h (MHz):	40.0	[1]	31.4	[3]	[3]	[3]
	$g_3 = 2.0908$	A_3/h (MHz):	40.6		31.4			
	$\alpha = 14°$		$\beta = 5°$		$\gamma = 0.2°$			
		Atom:	N	N	N	C	C	C
NE2	$g_1 = 2.1301$	A_1/h (MHz):	58.8	52.4	4.9	31.4		
	$g_2 = 2.0100$	A_2/h (MHz):	39.8	33.0	9.8		[4]	[4]
	$g_3 = 2.0931$	A_3/h (MHz):	39.5	35.0	6.9	[100]		
	$\alpha = 14°$		$\beta = 3°$	$\beta = 0°$				
		Atom:	N	—	N	N	—	—
NE3	$g_1 = 2.0729$	A_1/h (MHz):	44.8		18.6			
	$g_2 = 2.0100$	A_2/h (MHz):	34.7		14.0	[3]		
	$g_3 = 2.0476$	A_3/h (MHz):	32.2		14.0			
	$\alpha = 14°$		$\beta = 4°$					
		Atom:	—	—	N	N	C	C
NE5	$g_1 = 2.0329$	A_1/h (MHz):			34.2		115.9	
	$g_2 = 2.0898$	A_2/h (MHz):			27.4	[3]	72.2	[5]
	$g_3 = 2.0476$	A_3/h (MHz):			25.0		69.7	
	$\alpha = 27.5°$				$\gamma = 3.8°$	$\gamma = 0.7°$		
		Atom:	—	—	N	N	N	N
NE8	$g_1 = 2.0439$	A_1/h (MHz):			31.9			
	$g_2 = 2.1722$	A_2/h (MHz):			21.8	[3]	[3]	[3]
	$g_3 = 2.0846$	A_3/h (MHz):			21.0			
	$\alpha = 29.7°$				$\gamma = 9.8°$			

spectrum. In figure 4 one can see that, in diamonds enriched in ^{13}C, there are two lines which are symmetrically located in the wings of the strong lines at the edge of the EPR spectrum of NE1. Simulation of the HFS spectrum for 4.6% ^{13}C shows that the observed ratio between the intensities of the lines corresponds to four equivalent ^{13}C atoms. Analysis of the HFS parameters for ^{13}C showed that the HFS-tensor for ^{13}C has axial symmetry with A_1 parallel to $\langle 111 \rangle$, the A_1 directions not being located in the plane containing the N–Ni–N axis: so $\gamma = 0$. The HFS parameters for ^{13}C are given in table 1.

3.3. The NE2 centre

The paramagnetic NE2 centre is formed at higher annealing temperature than NE1, $\sim$2000 K. This centre is similar to NE1 in the g-tensor (but has lower symmetry (C_1)) and HFS-tensor
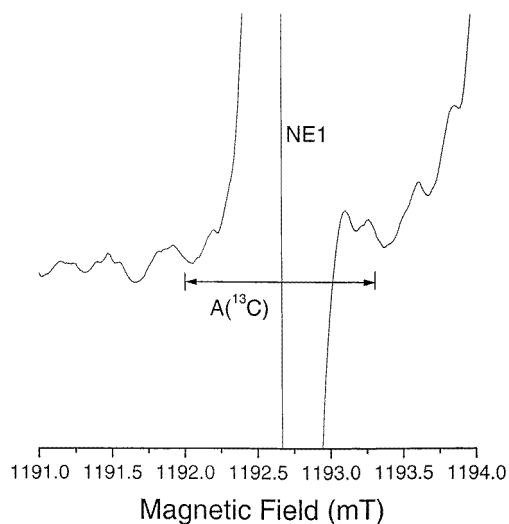
Figure 4. The ^{13}C hyperfine structure for the NE1 centre for B parallel to $\langle 100 \rangle$.

for two of the nitrogen atoms. The principal difference between NE2 and NE1 is additional HFS from a third nitrogen atom and a resulting lowering of symmetry. The NE2 centre is presumed to be formed from NE1 by capture of an additional nitrogen atom. Unfortunately, it was impossible to analyse the HFS from ^{13}C, because of the complicated and superimposed lines of the NE2 spectrum, and the low symmetry of the defect (24 magnetic nonequivalent position) which causes a decrease in the $I(^{13}\text{C})/I(^{12}\text{C})$ ratio.

Only the HFS from ^{13}C for B parallel to $\langle 100 \rangle$ was determined unambiguously for this centre. The value of the HFS parameter was found to be close to that of ^{13}C for the NE1 centre.

3.4. The NE5 centre

The nickel–nitrogen centre NE5, present in both annealed nickel-containing synthetic diamonds and in natural diamonds, had been tentatively assigned to a defect with an NE1-type of structure which had captured two vacancies [22]. Its EPR spectrum is difficult to analyse because its intensity is weak relative to those of NE1, NE2 and NE3. It was possible to resolve its EPR spectrum only for B along $\langle 100 \rangle$ at the X-band. At the Q-band the NE5 spectrum is also overlapped by the NE1 and NE2 spectra, but for B along $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$ it is possible to resolve clearly groups of lines related to the NE5 centre: see figure 5. The latter allowed not only analysis of the HFS from ^{13}C, but also more precise determination of the magnitudes and directions of the principal values of the g-tensor and the HFS-tensor for nitrogen atoms. Previously, based on the EPR spectra for only one orientation of B parallel to $\langle 100 \rangle$, the nitrogen atoms in the structure of the defect were thought to be magnetically equivalent, with identically oriented HFS-tensors [13]. The spectrum at Q-band for B parallel to $\langle 111 \rangle$, the direction of the maximum difference in the value of the HFS constants between the two nitrogen atoms, revealed that their HFS-tensors are differently oriented, although they have the same principal values.

The experimental values of the HFS- and g-tensors, obtained from measurements for three principal crystallographic directions are given in table 1. The experimental EPR spectra for B parallel to $\langle 100 \rangle$ are shown in figure 5.
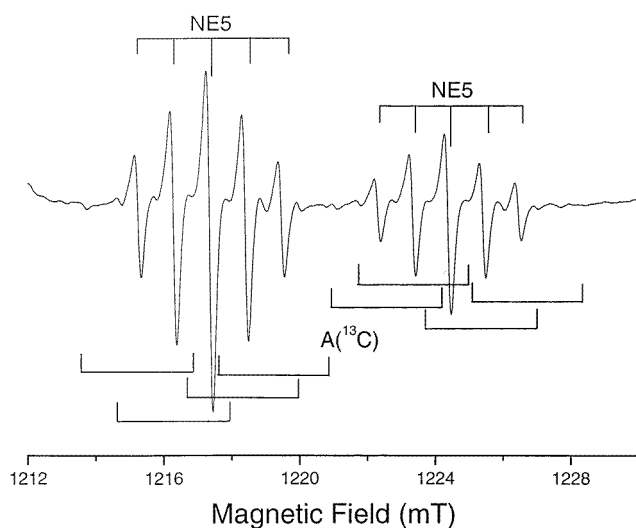
Figure 5. EPR spectra of the NE5 centre at the Q-band for B parallel to $\langle 100 \rangle$.
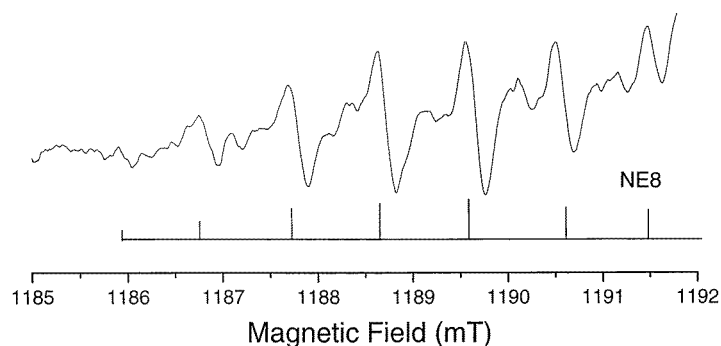

Figure 6. EPR spectra of the NE8 centre at the Q-band for B parallel to $\langle 100 \rangle$.

The principal directions of the component A_1 of the HFS-tensor for both nitrogen atoms are in a plane perpendicular to the $(1\bar{1}0)$ plane containing g_2 and g_3.

The ratio of intensities $I({}^{13}\mathrm{C})/I({}^{12}\mathrm{C})$ of the spectra shown in figure 5 is 0.05(1), which at 4.6% ${}^{13}\mathrm{C}$ corresponds to two equivalent ${}^{13}\mathrm{C}$ in the defect structure. Analysis of the angular dependence of the HFS from ${}^{13}\mathrm{C}$ showed that the directions of A_1 for these ${}^{13}\mathrm{C}$ atoms are parallel to $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$, respectively, and lie in the same $(1\bar{1}0)$ plane as the directions of A_1 for the two nitrogen atoms.

3.5. A new centre labelled NE8

When analysing the weak satellites related to HFS from ${}^{13}\mathrm{C}$ from the NE1, NE2 and NE5 centres in the EPR spectra of diamonds annealed at 2300 K, a new spectrum was found with HFS from four equivalent nitrogen atoms. Figure 6 shows the EPR spectra for the new centre for B parallel to $\langle 100 \rangle$. When the diamond is orientated so that the HFI-tensors of all four nitrogen atoms make the same angle with the magnetic field, the EPR spectrum consists of nine lines with intensity ratios 1:4:10:16:19:16:10:4:1.
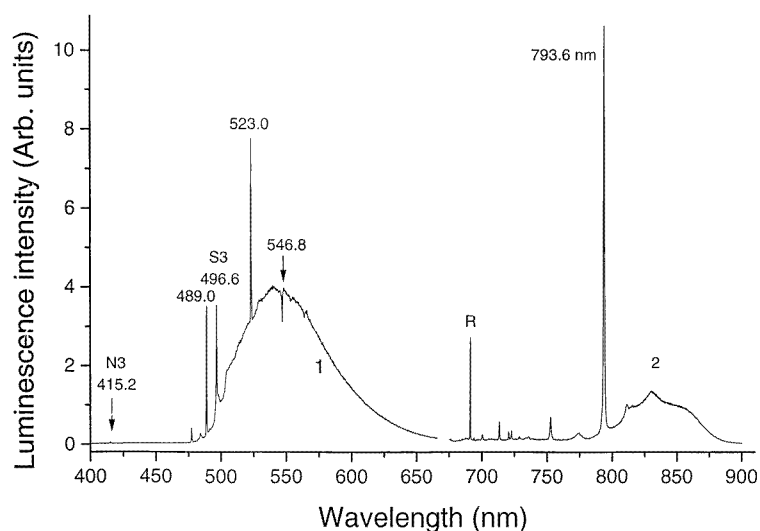
Figure 7. Photoluminescence spectra of annealed synthetic diamond recorded at 80 K for 365 nm (1) and 633 nm (2) excitation by Xe lamp and He–Ne laser, respectively.

Analysis of the angular dependence of the EPR spectrum for the NE8 centre showed that this centre has electronic spin $S = \frac{1}{2}$ and a g-value typical of a d ion with a more than half filled d shell. The g-tensor approximates to axial symmetry with g only 4.5° from [332]. The HFI-tensors for all four nitrogen atoms are also nearly axially symmetric and the principal directions corresponding to A_1 are at 9.8° to $\langle 111 \rangle$ directions (two are close to $[\bar{1}1\bar{1}]$ and two to $[\bar{1}\bar{1}1]$) all rotated towards $[1\bar{1}0]$ and lying in a (110) plane, which is perpendicular to the plane containing g_2 and g_3. A_2 for all ligands is along [110].

The NE8 centre has been found not only in HPHT treated synthetic diamonds but also in natural diamonds which contain the nickel–nitrogen NE1–NE3 centres.

3.6. Optical spectroscopy in the visible and near IR ranges

Absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded for as-grown and annealed synthetic diamonds, as well as for more than a hundred natural diamonds from the Yakutiyan deposits which exhibit yellow–green S2/S3 PL. The main purpose of the optical measurements was to find an optical analogue for the new NE8 paramagnetic defect. Since the centre corresponds to a high degree of aggregation, and includes four equivalent nitrogen atoms in its structure (section 3.5), most attention was paid to crystals with the complex nickel–nitrogen defects NE1, NE2 and NE3. These exhibit a yellow–green PL in vibronic systems with the zero phonon lines (ZPLs) at 488.9 nm (NE2), 496.7 (NE1) and 523.2 (NE3) (figure 7). The first and the last ZPLs were attributed for a long time to one defect, but careful spectroscopic study [13, 14, 26, 27] showed the existence of two separate defects. The identification of these three optically active defects was based on the correlation of their optical absorption with the intensity of the EPR spectra of the NE1–NE3 centres, and the systematics of the behaviour of corresponding optical and EPR features under different treatments, particularly on HPHT treatment and under x-ray irradiation or optical illumination. The former stimulates impurity diffusion and aggregation of defects [13, 14, 19, 26–28], while for the latter only a change of the charge state of the defect takes place [28, 29]. Among the
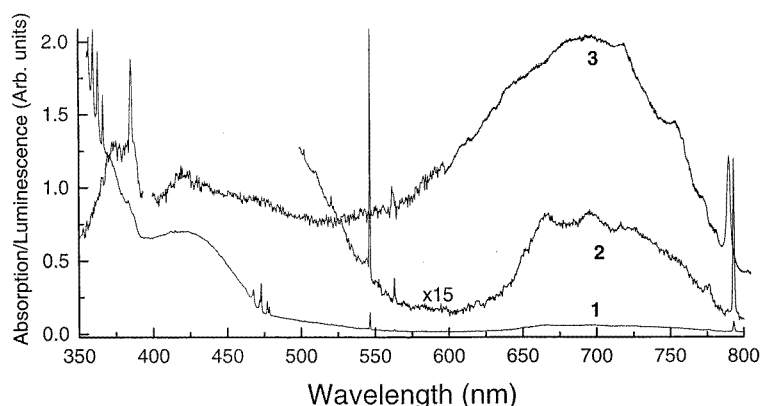
Figure 8. Absorption $(1, 2)$ and luminescence excitation (3) spectra for 830 nm emission in the 793.6 nm vibronic system, recorded with 0.5 nm resolution at 4.2 K $(1, 2)$ and 1.0 nm resolution at 80 K (3) for annealed synthetic diamond (C727).

synthetic diamonds, these complex defects are typical for samples which have been HPHT treated at $T \geqslant 1900$ K [13, 14, 20, 26, 27, 30], although in some cases such defects can be formed directly in some areas of the crystal during the crystal growth, together with nitrogen defects [30]. Both the results obtained and literature data [2, 3, 31] show that these defects are nearly always associated with another vibronic system with ZPL at 793.6 nm in absorption/PL and PLE spectra.

Figure 7 shows the PL spectra of synthetic diamonds annealed at 2200–2300 K, which are recorded with 360 nm Xe lamp excitation through a Spex monochromator, or at 632.8 nm excitation by an He–Ne 27 mW laser. The UV light excites emission in all three vibronic systems at 488.9, 496.7 and 523.2 nm as well as weak systems with ZPLs at 415.2 nm and 484.2 nm. The latter two correspond to the well known defects, N3 (three nitrogen atoms and a vacancy [3, 7, 24]) and Ni_s^- [24], respectively. The narrow dips at 546.8 nm and 552 nm in the background of the vibronic side band are a result of self-absorption in photoinduced centres also related to nickel–nitrogen defects [32]. Both UV, visible and near IR illumination were found to result in intense luminescence in the 793.6 nm vibronic system (figure 8) with well pronounced vibronic sidebands attributable to 40 ± 2 and 70 ± 2 meV phonons. The 40 meV vibration is typical of defects containing vacancies [3, 7, 21] and the 70 meV vibration can be associated with the $\Lambda 3$–(A) vibrational branch in the diamond lattice. Both of these vibrations have also been found in the luminescence spectrum for the S2 and S3 centres [21]. Analysis of PL spectra shows that the 793.6 nm centre has a moderate value of the electron–phonon coupling with a Huang–Rhys factor $S = 3.5$ [24]. There are several weaker narrow lines which can be seen between the S2/S3 and 793.6 systems in figure 8. The most intense line at 691.1 nm corresponds to the Raman line for excitation at 632.8 nm He–Ne. The lines at 693.7 nm, 700.2 nm and 703.4 nm, as well as the 720.6–722.6 doublet and the line at 752.8 nm, are found only in crystals grown in an Ni-containing environment, and thus are also associated with nickel defects. The latter two lines are accompanied by sidebands corresponding to 36 meV and 45 meV phonons, respectively and will be considered in detail elsewhere.

Figure 8 shows the absorption and PLE spectra recorded for 830 nm emission in the 793.6 system sideband for one of the annealed crystals. Thus the only resonant ZPL can be seen at 793.6 nm, both in luminescence and PLE spectra. The vibronic structure is somewhat different

in emission and PLE spectra. In the latter, there are well pronounced maxima at 722.2, 759.2, 777.3 and 785.2 nm as a result of interaction with phonons with energies 153(2), 71(2), 33(2) and 17(1) meV, respectively. The last three had been found earlier for other defects [27]. Only the 71 meV vibration can be seen in the luminescence spectrum (figure 7). Two bands at 666 and 695 nm were found only in absorption, and are likely to be due to other defects.

In the PLE spectrum there are broad bands at 370 and 430 nm, which have been assumed to be the only ones in the papers devoted to natural diamonds [3, 24, 31]. The 430 nm band begins at 540 nm and forms a well pronounced background for NE1–NE3 related absorption, from which it is well distinguished at wavelengths shorter than 480 nm (figure 8). The narrow line at 385.2 nm is well pronounced in PLE but is seen only weakly in absorption.

It is of note that the intensity of absorption related to the nickel-related defects is more than an order of magnitude weaker in natural diamonds than in synthetic diamonds, and as a result there was no evidence of them in the absorption spectra of natural diamonds, where they were found only in PL and PLE [3, 24, 31]. In annealed synthetic diamonds, broad absorption bands due to the NE1–NE3 centres and to the 793.6 system limit the transmission in the visible range from both short and long wavelength sides, and result in their greenish colour. The intense luminescence of the NE1–NE3 defects and in the 793.6 nm system, as well as the greenish colour exhibited after annealing of synthetic diamonds, are found in {111} growth sectors which were originally yellow due to absorption by P1 defects.

4. Analysis of the data

The principal reason for studying ^{13}C HFS in nickel-related centres was to obtain information to confirm, or indicate modifications of, the models of these centres, all of which are postulated to have a basic structural unit of an Ni atom at the centre of a double semivacancy. The divacancy has six dangling orbitals, which can bond in a distorted octahedral arrangement with the nickel ion at its centre. The nickel-related centres differ in the number of nitrogen atoms in the coordination shell (the ^{14}N HFS has been previously measured [26]).

The information about these centres, from which their structure can be inferred, is analysed as follows:

4.1. Calculation of spin densities from hyperfine structure parameters

As the unpaired electron density on both N and C atoms is presumed to be in 2s or 2p wavefunctions, the former giving an isotropic contribution and the latter a traceless contribution, one can decompose the measured HFS $\boldsymbol{S} \cdot \boldsymbol{A}^i \cdot \boldsymbol{I}^i$ for the ith atom to a good approximation to $A_s^i \boldsymbol{S} \cdot \boldsymbol{I}^i + A_p^i (3S_z I_z^i + \boldsymbol{S} \cdot \boldsymbol{I}^i)$. From these parameters, one may calculate the total spin density on the ith atom, ρ_i^2, and the proportions α_i^2 and β_i^2 in s and p states respectively ($\alpha_i^2 + \beta_i^2 = 1$) using the relations [33]:

$$A_s^i = 4\pi/3 \rho_i^2 \alpha_i^2 g_e g_N \mu_B \mu_N \langle |\Phi| \rangle_{2S}^2 \tag{2}$$

$$A_p^i = 1/5 \rho_i^2 \beta_i^2 g_e g_N \mu_B \mu_N \langle r^{-3} \rangle_{2p} \tag{3}$$

where $\langle |\Phi| \rangle_{2S}^2$ is the density of a 2s-electron at the nucleus, and $\langle r^{-3} \rangle_{2p}$ is averaged for a 2p-electron. The s/p ratio λ_i is β_i^2 / α_i^2. Table 2 lists the parameters derived in this way for the various centres measured.

This estimation ignores the small contribution to A_p due to dipolar interaction between the nuclear moment and the electronic magnetic moment on the nickel atom, which can be estimated only imprecisely because of lack of knowledge of their relative positions and the spin

Table 2. Spin density ρ and s–p hybridization parameter λ calculated from HFS parameters in table 1. N and C atoms are labelled with a subscript indicating the atom number in table 1 (and figure 1).

Atom	NE1		NE2			NE3		NE5		NE8
	$N_{1,2}$	C_{3-6}	N_1	N_2	N_3	N_1	$N_{4,6}$	$N_{4,6}$	$C_{3,5}$	N_{3-6}
ρ (%)	12.0	5.1	14.1	13.0	2.7	9.1	3.6	2.5	13.3	7.5
λ		4.2	5.3	4.3	5.0	5.9	3.4	3.3	2.9	5.5	4.6

density on the nickel atom. This means that the parameters β and λ may be slightly smaller that those given in table 2.

4.2. Deduction of the electronic state from the g-values

The g-values were found to be in general agreement with the proposed model, all except NE4 corresponding to a tetragonal distortion of the octahedral arrangement, caused by interaction with the ligands. Some appear to correspond to the unpaired electron being in the $d_{(3z^2-r^2)}$ orbital and others to its being in the $d_{(x^2-y^2)}$ orbital.

The g-values calculated for a tetragonally distorted $d_{(3z^2-r^2)}$ orbital are [34]:

$$g_{zz} = g_e \tag{4}$$
$$g_{xx} = g_{yy} = g_e + 6\lambda/\Delta_2 \tag{5}$$

where Δ_2 is the energy difference between $d_{(3z^2-r^2)}$ and $dz_{(x\pm iy)}$, and the spin–orbit coupling parameter λ is negative. Hence for $d_{(3z^2-r^2)}$

$$g_{xx} \sim g_{yy} > g_{zz} \sim g_e. \tag{6}$$

The g-values calculated for a tetragonally distorted $d_{(x^2-y^2)}$ orbital are [34]:

$$g_{zz} = g_e - 8\lambda/\Delta_0 \tag{7}$$
$$g_{xx} = g_{yy} = g_e - 2\lambda/\Delta_1 \tag{8}$$

where Δ_0 is the energy of dxy and Δ_1 is that of $dz_{(x\pm iy)}$, relative to the energy of $d_{(x^2-y^2)}$. Hence for $d_{(x^2-y^2)}$:

$$g_{zz} > g_{xx} \sim g_{yy} > g_e. \tag{9}$$

The extra positive charge on a nitrogen ligand means that its outer electrons are more tightly bound than those on a carbon ligand, and overlap less with the nickel wavefunctions. So, they start with lower energy and are less pushed down by bonding: the bonding orbital approximates to a lone pair on the nitrogen. In consequence the anti-bonding orbital has relatively small density on N, and tends to have lower energy than an anti-bonding orbital on C. This changes the relative energy of $d_{(3z^2-r^2)}$ and $d_{(x^2-y^2)}$ depending upon where the N atoms are in the coordination shell.

5. Discussion of the sites observed

5.1. The NE4 centre

When all six neighbours are carbon atoms, the site should have D_{3d} symmetry about the $\langle 111 \rangle$ direction of the VNiV unit. This is what is found for the simplest of the centres, NE4 [26], which is therefore postulated to be the simple double semivacancy, but unfortunately the EPR

lines are too wide for the observation of ^{13}C HFS, so we have no further information on this centre from our measurements.

If some ligands are replaced by nitrogen atoms, the symmetry will change, as will the amount of distortion from octahedral symmetry.

5.2. The NE1 and NE2 centres

In [17, 21] the NE1 and NE2 centres were postulated to have a common structural unit: an N_1–VNiV–N_2 chain, lying in a $(1\bar{1}0)$ plane (figure 1): so N_1 and N_2 are in diametrically opposite ligand positions, and they are assumed to dominate the crystal field. Since the spectrum of NE2 differs from that of NE1 by the addition of HFS from a third nitrogen atom, N_3, and only small differences in the HFS constants of N_1 and N_2, it was previously proposed that the third nitrogen atom was not in the first coordination shell, but captured in a site adjacent to either N_1 or N_2 in the first coordination shell of the double semi-vacancy, probably N_2 as it has the greater difference in HFS from NE1.

Both centres have g-values appropriate to the unpaired electron in a $d_{(3z^2-r^2)}$ orbital oriented along the N_1–Ni–N_2 chain, the direction of g_2 making an angle of $14°$ with [110], very close to the [331] direction which corresponds to $N_1 \ldots N_2$ in the undistorted structure. This structure leads to quite large HFS parameters for N_1 and N_2, the observed values in NE1 and NE2 being typical of octahedral complexes in the $d_{(3z^2-r^2)}$ state, when nitrogen atoms are located along the z-axis at a distance $\sim$0.2 nm [34]. The spin densities on the ligands for this orbital depends upon the angle ϕ between the z-axis and direction R to the ligand nucleus, at distance R, and on the angle θ between R and the direction of the p orbital on the ligand:

$$\rho^2 \sim \cos^2\phi(3\cos^2\theta - 1)/R^3 \qquad [34]. \qquad (10)$$

Wherever we have complete information, the ligand HFS parameters suggest that the unpaired p electron on the ligand is close to a $\langle 111 \rangle$ direction.

For NE1, the parameter λ of sp-hybridization for [13]C (5.31) is larger than the value for purely tetrahedral symmetry, which, according to the theory of valency, indicates an increase of the valent angle, and a slight outward shift of these carbon atoms from their normal lattice sites.

If the model for NE1 is correct, the four carbon ligands of Ni in the double semi-vacancy lie in a plane which is nearly normal to the $d_{(3z^2-r^2)}$ orbital ($\theta = 80°$). So, the spin density at the carbon atoms is expected to be about 50% of that on N_1 and N_2. The ^{13}C HFS parameters for four equivalent carbon atoms are in good accord with this expectation for NE1. There is no indication of ^{13}C HFS from any other atoms. This observation of HFS of the expected magnitude from just six ligand atoms is extremely strong confirmation of the double semivacancy model.

The total spin density in the first coordination shell is 44%, and that further away from Ni is expected to be small, so about 50% of the unpaired electron is presumed to be located on the Ni atom. It is interesting to compare this with Ni_s^- where 75% of the unpaired electron is located on the nickel ion and 24% in the four carbon ligands [11, 12].

A similar analysis cannot be made for NE2, because the greater complexity of its spectrum means that information about the ^{13}C HFS is much more limited. It is not even possible to confirm the number of equivalent (or near equivalent) carbon atoms in the coordination shell. We will argue later that evidence from NE5 suggests that the third nitrogen atom may be at one of the other sites in the coordination shell. This anyway seems more likely than at a neighbouring site to N_2, because at the latter site it would have to be N^+, otherwise it would set up a separate paramagnetic system with $S = \frac{1}{2}$, interacting with the nickel centre. But,

if the site were N^+, then like the N^+ component of W7 [35] and N1 [36], it would have a predominantly isotropic HFS. That $\lambda = 6.2$ strongly suggests that the spin density of this third nitrogen atom lies in the coordination shell. A rough estimate, based on the limited evidence, suggests that the spin density in the coordination shell is similar to that for NE1.

5.3. The NE5 centre

The new experimental data about the direction of A_1 for the two nitrogen atoms do not correspond to the previously suggested model of the NE5 centre. The present measurements show that the HFS for both two ^{13}C and for the two ^{14}N have A_1 close to $\langle 111 \rangle$ directions which do not lie in the $(1\bar{1}0)$ symmetry plane, and the pairs are related by reflection symmetry in this plane. So they could correspond to the four ligands in the plane almost normal to the direction of g_2: the angle of $27.5°$ is very close to normal to the (332) plane containing these four ligands, and the g-values are appropriate to a $d_{(x^2-y^2)}$ orbital. The bonding orbital has a strong lone pair character from the N atoms, so the unpaired antibonding orbital is distorted towards larger admixture with p orbitals on the two C atoms.

The parameter of s,p hybridization for the portion of the wavefunction located on the nitrogen atoms was calculated from the nitrogen HFS parameters to be $\lambda = 2.93$, while for the two ^{13}C atoms $\lambda = 5.35$. The values of λ indicate that the carbon atom has been displaced away from Ni: this is reminiscent of the situation in the P1 centre where the extra electron in the antibonding orbital pushes the C atom much more than the N atom [33]. The total spin density on these four ligands is 31.2%. One does not expect much spin density on the other two C atoms of the coordination shell and no other ^{13}C HFS is observed. Hence, here there appears to be over 60% of the spin density on the Ni atom.

The very small spin densities on the N atoms, relative to that on the C atoms diametrically opposite them in the complex, which indicates the way in which the unpaired electron wavefunction is biased toward the carbon, suggest that the smallest HFS parameter for ^{14}N in NE2 corresponds to an N atom in the first coordination shell.

The investigation of diamonds grown at 1600 K and annealed at 2200 K as well as those grown at 1750 K exhibited the appearance of NE5 after the annealing stage, simultaneously with the appearance of NE1. NE1 is probably a precursor for the formation of the more complicated defect NE2 by capturing an additional nitrogen atom. In the same way NE5 can be regarded as a precursor for the formation of NE3.

5.4. The NE8 centre

Many of the parameters of the newly discovered centre NE8 are similar to those of NE5. As for NE5, the g-values show that the unpaired electron is in a $d_{(x^2-y^2)}$ orbital. The ^{14}N HFS parameters indicate that NE8 is also based upon a VNiV unit which has captured four N atoms in the plane almost normal to the C–VNiV–C chain. The s/p-hybridization parameter indicates considerable outward shift of the four N atoms. The strong lone pair character of the bonding orbitals means that the spin density in the two C atoms is very low, and no ^{13}C HFS is observed. The spin density on the four nitrogen atoms is 24.4%. Hence the spin density on Ni is about 70%.

NE8 represents the highest coordination with nitrogen that we have observed.

6. Some comments on the nitrogen in nickel-nitrogen centres

It appears that, on annealing as grown nickel containing diamond, it first becomes possible for the large nickel atom to eject a neighbouring carbon atom into an interstitial position, to form the basic VNiV structure of the NE4 centre. At higher annealing temperatures, nitrogen atoms become mobile, possibly assisted by the carbon interstitials released by the formation of NE4. Although migrating N atoms in pure diamond can coalesce to form nearest neighbour pairs, A centres, they do not appear to form larger clusters without association with a vacancy, but then it is feasible for them to cluster around a vacancy to release the internal strain around N_s. In nickel-containing diamond it appears that the VNiV fragment also forms a nucleation centre for the condensation of migrating N atoms into its ligand shell.

For one N atom in the coordination shell, all sites would be equivalent. This must be a precursor of all of the centres observed. Its non-appearance must suggest that it is diamagnetic.

For two N atoms, of the two observed sites, one has inversion symmetry and the other reflection symmetry in $(1\bar{1}0)$: the third possible low symmetry site is not found.

For three N atoms, NE3 has reflection symmetry in $(1\bar{1}0)$. There are no other possible sites of high symmetry, so NE2 has lower symmetry; but the site where all three N atoms are at one end of the defect does not occur, presumably because it is too unbalanced.
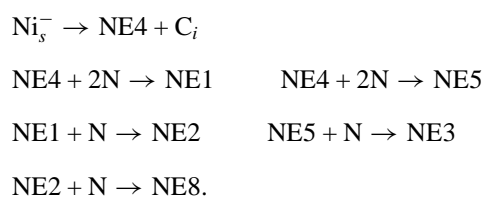
For four N atoms. NE8 is the only arrangement with reflection symmetry in $(1\bar{1}0)$, none of the possible low symmetry sites occur.

No site containing five N atoms is seen, maybe because that is too high an N coordination, maybe because it is diamagnetic or maybe because there is too small a residual concentration of donor nitrogen for its creation.

A neutral site containing six N atoms would be diamagnetic.

For a given number of N atoms the system seems to like to settle into as symmetric an arrangement as possible. How does it organize that? Do the diffusing nitrogen atoms sense this symmetry at a distance? Once they arrive in the wrong place, they would have to diffuse all round a 'chair' to exchange places with a neighbouring carbon ligand.

There seems to be a tendency towards symmetry, to even out the local strain. That NE2 and NE3 do not interconvert suggests that there is no migration of N from one site in the coordination shell to another, so that the migration of N towards the defect must be influenced by strain at a distance. If nitrogen atoms do not move about in the coordination shell once they have arrived, there ought to be clear pathways for the formation of the centres observed, which appear to be as follows:

$$Ni_s^- \rightarrow NE4 + C_i$$

$$NE4 + 2N \rightarrow NE1 \qquad NE4 + 2N \rightarrow NE5$$

$$NE1 + N \rightarrow NE2 \qquad NE5 + N \rightarrow NE3$$

$$NE2 + N \rightarrow NE8.$$

Note that although no stable EPR centre has been observed with only one N ligand, optical excitation with light of energy greater than 3.76 eV produces the photochromic centre NE7, which does have hfs from a single nitrogen atom, the values of the A-tensor lying between 17 and 25 MHz [26]. The increase in the concentration of NE7 is correlated with a decrease in concentration of N_s^0, and this apparent charge transfer is reversed by heating or by exposure to red light. There is too little evidence about NE7 to know whether it corresponds to a single nitrogen atom in the coordination shell of VNiV. We discuss this further in section 8.

7. The optical analogue for the paramagnetic NE8 centre

The most probable optical analogue for the NE8 defect in EPR is the vibronic system with a ZPL at 793.6 nm. Notwithstanding the variety of nickel-related defects, which includes more than ten centres for which the structure has been determined, and tens of Ni-related lines from defects of unknown structure, only a few are stable on high temperature annealing at $T \geqslant 2300$ K: the overwhelming majority of features in the optical spectra disappear as a result of defect aggregation or transformation. The 793.6 nm system is observed in the same samples as the nickel–nitrogen complex centres such as NE1–NE3, which contain two or three nitrogen atoms. This confirms the stability of the 793.6 nm defect as well as of high degree of participation of impurity aggregation. As for NE1–NE3, both the NE8 defect and the 793.6 nm system are found in natural diamonds. Their lower concentration in natural diamond is a result of lower transition metal content (up to 1% in the surrounding rocks), while for synthetic diamonds the Ni catalyst content in the original charge forms tens of per cent. If one supposes that the 793.6 nm system corresponds to the NE8 defect, one can understand the similarity of their optical properties, such as the same lattice vibrations (40, 70 meV) and a complex system of excited levels, which may be due to the common fragment of Ni in a divacancy position. Nevertheless, there are also some differences between vibronic systems with ZPLs at vibronic 488.9; 496.7; 523.2 nm and that with ZPL at 793.6 nm, which also needs explanation: the first three demonstrate a relatively long term PL decay time in the μs to ms range [37] as result of spin forbidden electronic transitions, while the 793.6 PL corresponds to an electric dipole transition with a dipole moment $d = 4 \times 10^{-30}$ Cm and PL decay time of $t = 2.7 \times 10^{-8}$ s [21]. None of the vibronic systems under consideration have been extensively investigated using the structure-sensitive methods of optical spectroscopy; and a detailed study of the Stark effect and uniaxial stress measurements are in progress. If the suggested correlation between the vibronic systems and the EPR spectra is correct, a quadratic Stark effect is expected for both NE1 and NE8 defects, because they have an inversion centre.

8. The electronic state of nickel in the nickel–nitrogen defects

The interpretation of paramagnetic resonance of transition metal ions in crystalline salts is based upon the well tested theory of the crystalline electric field [34]. Calculated EPR spectral parameters agree well with experiment for ionic crystals. However, it is difficult to take covalency into account. For semiconducting crystals, Ludwig and Woodbury [19] and Watkins [38] designed different empirical approaches using molecular orbital theory, which describe the experimental results well. Their approaches are based on the idea that the transition metal donates n electrons for the formation of n covalent bonds. The rest of the electrons, depending upon the symmetry of the site, fill the orbital doublet for a tetrahedral environment, or the orbital triplet for an octahedral environment. In the nickel–nitrogen complexes, the nickel is in a strong-bonding environment. Using the approach of Ludwig and Woodbury (LW), Ni should donate six of its ten electrons for the formation of bonds with the six neighbouring atoms (carbon atoms for NE4). The remaining electrons, in accordance with Hund's rule, should enter the lower orbital triplet. NE4 has electron spin $S = \frac{1}{2}$ and D$_{3d}$ symmetry, which requires five electrons, so we have to suppose that the defect is negatively charged. So it seems that the extra electron is retained when Ni$_s^-$ becomes NE4. The energy level scheme for this, and the other defects, is given in figure 9.

The transformation of the NE4 defect into NE5 and NE1 is associated with the capture of two nitrogen atoms: that no EPR is observed from a unit with only one N ligand suggests that

Centre	NE4	NE1	NE2	NE3	NE5	NE8
Structure	NiC_6^-	$NiC_4N_2^-$	$NiC_3N_3^0$	$NiC_3N_3^0$	NiC_4N^{2-}	$NiC_2N_4^+$
Config.	t_2^5	$t_6^2 e$	$t_6^2 e$	$t_6^2 e$	$t_6^2 e$	$t_6^2 e$
Spin	1/2	1/2	1/2	1/2	1/2	1/2

Figure 9. The energy level scheme of orbital levels for the nickel ion in the octahedral position of the proposed site in the diamond structure.

the extra electron from N completely fills the orbital triplet to give $S = 0$, again suggesting an overall negative state for the defect. The two nitrogen atoms in NE5 and NE1 replace two carbon atoms, and so bring two extra electrons into the system. These should completely fill the states of the lower orbital triplet to give $S = 0$. That NE1 and NE5 have $S = \frac{1}{2}$ means that they also are negatively charged, with one electron in the orbital doublet, and this electron corresponds to $d_{(3z^2-r^2)}$ or $d_{(x^2-y^2)}$ depending upon the relative positions of two N ligands.

One may speculate about whether the photochromic centre NE7 is formed by transfer of an electron from N_s^0 to non-paramagnetic $(NiNC_5)^-$, to form $(NiNC)^{2-}$, which has the same configuration as NE1, and the single N ligand would make the electron occupy $d_{(3z^2-r^2)}$. The orbital of this unpaired electron would be strongly polarized towards the C atom opposite N, as for the C atoms in NE5, so that one would expect considerably smaller spin density on the N atom than in NE1 (that observed in NE7 is about half of that in NE1).

The more complicated aggregation states NE2 and NE3 correspond to capture of an additional nitrogen atom by NE1 and NE5, respectively, thus adding an extra electron to the system. In the neutral state, six electrons would fill the lower orbital triplet, leaving one in the doublet. If these defects were also negatively charged, they would have $S = 1$, so the observed spin $S = \frac{1}{2}$ indicates that they are neutral. So, their electronic state seems exactly like those of NE1 and NE5, but there is a difference in that the change in the nitrogen coordination makes the $d_{(3z^2-r^2)}$ orbital lower for both NE2 and NE3.

It is found experimentally that the concentrations of NE1 and NE5 can be decreased by x-ray irradiation, whereas those of NE2 and NE3 cannot. The effect of x-ray irradiation is to transfer electrons from the nickel–nitrogen centres to N^+. This supports the conclusion that the atomic configurations of NE1 and NE5 correspond to a negative state. That NE2 and NE3 do not change electronic state on x-ray irradiation indicates that the equilibrium charge state of all of these defects is controlled by the position of the Fermi level, and that their energies are in nearly the same position in the energy gap, so they all end up in having the same electronic configuration.

The capture of a fourth N atom produces NE8. In the neutral state the eight electrons not required for bonding would fill the orbital triplet, and leave two electrons in the orbital doublet, which should give $S = 1$. That the centre is observed to have $S = \frac{1}{2}$ and to correspond to $d_{(x^2-y^2)}$, which would be lower in energy than $d_{(3z^2-r^2)}$ for the configuration with four N atoms in a plane, indicates that this centre must be positively charged. Again this corresponds to the same electronic configuration as the other centres, pointing to the importance of the position of the Fermi level.

We do not observe a centre with five N atoms. This corresponds to one C atom, which would delineate the z-direction, and in the orbital doublet $d_{(x^2-y^2)}$ would be lower in energy than $d_{(3z^2-r^2)}$. In the neutral state this would have $S = \frac{1}{2}$, with the electron in the latter state. That we do not observe it may indicate that it is not formed, or it may indicate that it is in negative charged state with $S = 0$. The latter might not be unexpected, as the lone pair character of most of the ligand bonding orbitals would lead to a general lowering of the antibonding orbitals in the energy gap.

A centre with six N atoms would revert to D_{3d} symmetry, which would also probably be neutral, because the d shell would be full and unable to accept more electrons.

9. Conclusions

The EPR study carried out of synthetic diamonds enriched in ^{13}C has confirmed the previously suggested model for the transformation of the as grown Ni_s^- defect by formation of a structure of double semivacancy type with nickel at its centre. The data on the HFS of ^{13}C ligands for the NE1 and NE2 centres is consistent with previously proposed models for these centres; the HFS constants are small because the carbon atoms are located in a plane normal to the unpaired $d_{(3z^2-r^2)}$ orbital of nickel ion.

For the NE5 centre, two equivalent ^{13}C atoms and two equivalent nitrogen atoms were found to be situated in one plane in the double semivacancy structure. Analysis of values and directions of the g- and HFI-tensors for ^{13}C and ^{14}N showed that the ground state for the nickel ion in the NE5 structure is $d_{(x^2-y^2)}$.

A new nickel–nitrogen defect, NE8, containing four equivalent nitrogen atoms, and corresponding to a further stage of the nitrogen aggregation process around the nickel ion, was found in both natural and synthetic diamonds. The centre appears together with the NE1–NE3 nickel–nitrogen defects, and is presumed to be formed from NE2 (NE3) when it captures an additional nitrogen atom, and correlates with a vibronic system with a zero phonon line at 793.6 nm in luminescence/absorption spectra.

The observed electronic states of nickel–nitrogen defects were found to be described well by the model of Ludwig and Woodbury of filling electronic levels for transition metal ions in the strong-bonding approximation.

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