Optical and EPR centres involving 3d metals in diamond

J.M. Baker*

Oxford Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK and
Department of Physics, King's College London, Strand, London WC2R 2LS, UK

ABSTRACT

Many fewer 3d ions are known to be incorporated at lattice sites (both substitutional and interstitial) in point defects in diamond than in silicon. In diamond, only nickel and cobalt have been positively identified. There appears to be a great variety of nickel-containing sites, and several different cobalt-containing sites, some of these also involving substitutional nitrogen. The evidence for incorporation of other 3d atoms is much less certain, but there is possibly some for Ti, Cr, Mn, Fe, Cu and Zn. Some general inferences may be drawn from these data.

Keywords: 3d transition ions, diamond, EPR centre, optical zero phonon lines,

1. INTRODUCTION

Point defects in diamond are interesting because of their potential to affect the optical absorption, electronic transport and mechanical properties of a material whose wide range of optical transparency gives it potential for opto-electronic applications. Transition metal impurities may make interesting defects because of the possibility of a range of readily changeable charge states.

Low levels of all of the 3d transition elements have been shown to be present in natural diamonds,[1] but very few natural diamonds contain 3d-related point defects. Although the control of diamond synthesis is improving rapidly, it is not as straightforward to prepare diamond with known dopants as silicon. Impurities are incorporated at different rates in different growth sectors [2] and at different temperatures [3], and only a few atomic species are known to diffuse in diamond. Natural diamonds are variable and inhomogeneous, so it is often difficult to characterise the defects they contain, and many of these defects have not been reproduced in synthetic diamond. Synthetic diamonds grown at high pressure and high temperature (HPHT) [4] have to be contained in a metal bomb using a solvent catalyst mixture containing several chemicals, so the growing specimens are exposed to many contaminants, including the impurities in the materials with which they come in contact. Most are grown using a 3d transition metal solvent catalyst, so it is in these diamonds that most 3d-related point defects have been found. The growth of a large HPHT single crystal requires maintenance of the growth conditions over a period of hours, for crystallisation onto a single seed crystal. It is also possible to produce a large number of spontaneous crystallites much more quickly (seconds to minutes), at lower P,T, which may contain different defects from single crystals, and which can be collected as a powder sample.[5] Growth by chemical vapour deposition (CVD) [6] at lower temperature may possibly allow more intimate dispersal of a dopant, but is also subject to contamination by impurities in gases and substrate (and possibly transport from the walls of the vessel), in addition to growth defects peculiar to CVD. Lack of diffusion may make it impossible to obtain a general dispersal of many impurities implanted into the surface of a pure specimen [7], but that may not matter for applications in a device which uses a thin surface layer. Although attempts have been made to implant ions of the whole of the 3d group, only Ti, Cr, Co, Ni and Zn have been shown to have produced point defects.[8]

Many fewer 3d transition metal atoms, indeed fewer atoms from throughout the periodic table, have been shown to be present as point defects in the crystal lattice of diamond than are found in silicon. In diamond, only nickel and cobalt have been positively identified, whereas all 3d elements have been found in silicon (with the curious exception of cobalt).[9,10] This reflects the much smaller space available in diamond with a 36 % smaller lattice constant (the covalent radius of C is 0.077 nm and that of Si is 0.118 nm). The other common impurity incorporated into the diamond lattice is nitrogen, either in single substitutional form N_s [11] (where subscript s is used to indicate a substitutional site) or in the form of aggregates such as the A-centre (N_s–N_s pairs).[12] Diamond containing > 1 ppm N is classified as type I (Ib if it is predominantly N_s, Ia if it is predominantly aggregated) and containing < 1 ppm N as type II.[13] The diamond lattice can also incorporate boron, and when the concentration of B_s exceeds that of N_s the diamond is classified as type IIb and is rendered semiconducting by B_s acting as an acceptor.[14] Otherwise, it is type IIa, which is relatively pure. Most synthetic HPHT diamond is type Ib, unless nitrogen getters are used.

---

*Email: m.baker1@physics.oxford.ac.uk

XI Feofilov Symposium on Spectroscopy of Crystals Activated by Rare-Earth and Transition
Metal Ions, Alexander A. Kaplyanskii, Boris Z. Malkin, Sergey I. Nikitin, Editors,
Proceedings of SPIE Vol. 4766 (2002) © 2002 SPIE · 0277-786X/02/$15.00

The defects discussed in the paper comprise isolated, or small clusters of, impurity atoms in diamond. The experimental methods for obtaining information about these defects are discussed in section 2. In sections 3 and 4 the types of sites for 3d ions, and the crystal fields at these sites are discussed respectively, using nickel-related sites for illustration. Sections 5, 6 and 7 discuss other sites related respectively to nickel, cobalt and other 3d ions.

2. EXPERIMENTAL

Two techniques have yielded most valuable information about point defects in diamond; optical absorption (A) and luminescence (L),[15] and electron paramagnetic resonance (EPR) spectroscopy.[16]

The optical spectra have broad features and narrow zero phonon lines (ZPL). Absorption must originate from the ground state, so ZPL in absorption spectra indicate the energies of excited states. Luminescence may be excited by incident light (photo-luminescence, PL) or by electron bombardment (cathodo-luminescence, CL); this corresponds to emissive transitions between any excited states of the defect, not necessarily to the ground state (an excited state may be able to return to the ground state by a non-radiative route). Photo-luminescence excitation (PLE) is a technique in which a particular luminescence ZPL is monitored as a function of the energy of the incident light, so it shows which absorbed energies lead to the chosen ZPL transition. This measures excited energy levels of the defect giving rise to the chosen ZPL, and by the onset of a continuum may indicate the depth of the ground state below the conduction band. By measuring the relative intensities of different ZPL for a range of samples one can determine whether they correspond to the same (or at least correlated) or different defects.

For 3d ions at sites of high symmetry, some electron states will still have some orbital degeneracy, and so should exhibit fine structure due to spin-orbit coupling, which could be up to several hundred meV for free ion magnitudes.[16] Sometimes ZPL are associated with somewhat broader phonon replicas, where one or more local mode phonons are emitted or absorbed to shift the energy for the ZPL.[17] Structure in the range 25 - 75 meV has usually been attributed to quasi-local vibration, and up to 170 meV as due to lattice phonons.[8] Many of the ZPL exhibit a small fine structure, typically between 1 - 10 meV. This is reminiscent of the fine structure due to spin-orbit coupling in free 3d ions, but it is much smaller, and it does not correlate with an interval rule. This suggests that the spin-orbit coupling parameters are reduced either by covalent bonding or by the Jahn-Teller [J-T] effect.[16] There is generally too little information about the states between which the transitions take place to construct a reliable theory. Only for a few cases has further discussion been attempted.

All of this determines some information about the level structure of different defects, but does not indicate what they are. Measurements of the splittings and shifts of ZPL produced by uniaxial stress along <100>, <111> and <110> may be used to determine the symmetry of the site and of the states between which the transition occurs.[18] In practice, few defects in diamond have given sufficiently satisfactory results under uniaxial stress for unambiguous assignment of a symmetry. The only direct indication of the atomic species involved would be given by a characteristic isotope shift, but measurement of that requires very narrow lines. Typically, ZPL have a line width of ~ 1 meV, compared with a range ~ 5.5 eV for possible transitions within the band gap of diamond. The 1.4 eV zero phonon line (ZPL), associated with the NIRIM-2 EPR centre,[19] had a line width of only 0.16 meV in PL, which allowed it to be shown to be due to nickel from isotope shifts.[20] It is possible to obtain an indication of the mass M' of an impurity ion (or strongly bound complex) if the frequency ω_R of its quasi-local mode of vibration can be obtained from phonon replicas near its ZPL. If it is assumed that the force constant is unchanged $\omega_R = \omega_D \surd\,(M/3(M'-M)$, where ω_D is the Debye frequency of diamond and M is the mass of the C atom.[8,21] This method suggests that some of the ZPL observed in implanted samples may correspond to strongly coupled pairs of the 3d ions.[8] Quite a number of narrow ZPL have been observed only in synthetic diamonds grown with nickel or cobalt solvent catalysts. Although iron, chromium and manganese have also been used as solvent catalysts, no ZPL have been correlated with these elements in HPHT single crystals.[22] When a defect has been produced uniquely by implantation with ions of a particular element, it has been assumed that the defect is related to that element.

EPR lines in diamond can also be very narrow, ultimately limited by magnetic interaction with the nuclear magnetic moments of the 1.1% abundant isotope ^{13}C to about 7 μT (~ 200 kHz),[23] or a resolving power of ~ 200,000 at 35 GHz. However, resolution can be made difficult by the crowding of lines into the region near $g = g_e$. Provided that it is possible to obtain a clear picture of the angular variation of the spectrum in a single crystal diamond, the symmetry and other properties of the defects are clear. In a powder, or polycrystalline CVD material, the angular variation is averaged and less information is found. The symmetry of the sites of isolated, or small clusters of, impurity atoms is provided by the parameters of the spin-hamiltonian describing EPR spectra,[16] and information about the number and disposition of surrounding carbon atoms may be provided by ^{13}C hyperfine structure (hfs) in the EPR spectrum.[24] Identification of the paramagnetic impurity atom is clear if it has a characteristic hfs (eg. nitrogen is ~ 100% ^{14}N with $I = 1$).

As EPR gives information about the ground state and optical spectra give information about excited states, most information will be provided if both can be observed in the same defect. In principle, any point defect has an optical spectrum, and any with a multiplet ground state might exhibit EPR. So all EPR defects should have an optical analogue, but not vice-versa. However, an optical spectrum may not contain narrow ZPL (so hardly any of the many 3d-related EPR defects in silicon [9] have optical ZPL), and an EPR spectrum may not be observed for selection-rule or technical reasons. Furthermore, as allowed optical transitions are so much stronger, an EPR analogue may have too weak a signal for detection. Correlation of EPR and optical spectra of the same defect has generally been done by comparing the spectral intensity for a range of samples covering a range of concentrations of the defect. In principle, connected spectral effects like optically detected magnetic resonance (ODMR)[25] or magnetic circular dichroism (MCD)[26] may be used to make the link, but there are only a few examples of their application to diamond which are mentioned below. Photo-EPR, a study of the change of intensity of an EPR spectrum produced by optical illumination with monochromatic light as a function of its photon energy, has been used to measure the energy separation from the valence or conduction bands. For example, the $Ni_s^{-/0}$ acceptor state (W8 EPR) is located 2.49(3) eV below the conduction band.[27] Similar measurements have been made for the EPR centres AB3, AB4 and AB5.[27,28] Implantation of some ions of the 3d group (Ti, Cr, Co, Ni and Zn) has produced optical ZPL. However, as the thickness of the implanted layer is very small, the concentration of such defects is far below the level detectable by EPR.

One difficulty in the identification of 3d atoms in diamond is to know whether a defect is due to a 3d atom and which the atom is. Many 3d ions in salts have g-values close to that of the free spin, g_e, because the orbital angular momentum is quenched by the crystal field.[16] However, there is usually a tell-tale indication of 3d character, in that matrix elements of spin-orbit coupling, $\lambda \mathbf{LS}$, between the ground state and an excited state at energy Δ lead to small departures Δg from g_e, $\Delta g \sim \lambda/\Delta$.[16] Most EPR defects in diamond have very small Δg,[29] because spin-orbit coupling is small and the band gap is large, so a larger than usual Δg can indicate a defect probably containing a 3d atom. For half of the 3d-group where the dominant nucleus has hfs, the identification of the atom should be clear, but for the others, even identifying the configuration does not identify the atom. Only three defects have been unambiguously related to 3d ions. The 1.4 eV ZPL associated with the NIRIM-2 EPR centre [19] has been mentioned above. The W8 EPR centre has been shown to be Ni_s^- by ^{61}Ni hfs.[30] The O4 EPR centre has been shown to be ^{59}Co by its hfs.[31] No hfs has been found in diamond attributable to ^{51}V or ^{45}Sc, but it is generally difficult to say whether lines without hfs belong to Ti, Cr, Fe or Ni (or Zn). One centre discussed below, W36, which was originally associated with B, because of the four line hfs attributed to ^{11}B,[32] may to be due to Cu.[33] A centre discussed below (KUL7) with a six-line hfs has been attributed to ^{55}Mn.[34]

3. SITES OF 3d IONS

Three types of site have been associated with 3d ions, all exemplified by nickel: (a) a substitutional site with T_d symmetry (Ni_s^-, $3d^7$, W8 EPR [35] and probably 2.51 eV ZPL [36]); (b) an interstitial site with T_d symmetry (Ni_i^+, $3d^9$, NIRIM-1 EPR)[19]; (subscript i has been used to indicate the T_d interstitial site); (c) a semi-vacancy site with D_{3d} symmetry (NE4 EPR, possibly Ni_{sv}^-, $3d^5$)[37]; (subscript sv has been used to indicate the semi-vacancy site, where the metal ion is situated at the centre of a nearest neighbour di-vacancy, alternatively written $(C_3VNiVC_3)^-$ to indicate the six ligands. In this site the metal ion is covalently bonded with these six, approximately octahedrally positioned ligands at 0.18 nm.). Other sites of lower symmetry may be formed by association of these basic sites with other point defects, most probably N_s (which is very common in diamond) and V (the symbol here used for the vacancy, as vanadium has never been found in diamond). The semi-vacancy site itself is an association of Ni_s and V, in which the site of Ni has been readjusted. Also, the semi-vacancy site is observed with from 1 – 4 ligands replaced by N (indicated by ^{14}N ligand hfs) (EPR defects NE1-3, 5, 8, 9), most having the $3d^7$, $S = ½$, configuration.[38,39]

W8 and NIRIM-1 are found in as-grown synthetic diamond grown in nickel-containing solvent catalyst, but post-growth annealing is usually required to form NE1-8 from samples containing W8.[37] The assignment of these EPR defects to nickel is indicated by their mode of production by annealing of synthetic diamonds containing Ni_s^-, which produces a decrease in the concentration of W8 while that of NE1-4 rises, suggesting the conversion from the substitutional to the semi-vacancy site. This indicates that substitutional nickel can create carbon interstitials and vacancies at the appropriate temperature through the reactions [40]:

$$Ni_s \Rightarrow NE4 + C_i \qquad\qquad NE4 \Rightarrow Ni_s + V.$$

Both C_i and V are mobile above about 750 [41] and 900 K [42] respectively. Nitrogen is also mobile above ~ 1800 K, in the presence of transition metals or V,[43] so there is a tendency for N to aggregate with other N, with V and with Ni. Hence, the temperature of growth, and subsequent thermal history, influences the centres present. The take-up of Ni and Co has been found to be dependent upon the growth sector, being almost exclusively in {111}.[2] In most diamonds as-grown, the nitrogen content is in the form of N_s, but after annneal at high enough temperature much of it is in the form of A-centres. Exceptionally, some aggregation may occur during growth. The relative concentration of A-centres and N_s is a good indication of the degree of aggregation.

The identification of Ni_s^- and the semi-vacancy sites NE1-9 are clear from hfs of neighbouring atoms. That NIRIM-2 is Ni_i^+ with a perturbing defect along <111> is indicated by analysis of fine structure and g-values of ground and excited states.[44] The identification of NIRIM-1 as Ni_i^+ at a T_d site is much less certain. Computed hfs parameters [45] for neighbouring atoms, suggest that lack of observable hfs favours Ni_i^+ over Ni_s^+ ($3d^5$). Also the positive sign of δg favours Ni_i^+ but its magnitude ($-4\lambda/\Delta$) is much smaller than one would expect for values of λ and Δ similar to those appropriate to NIRIM-2 (see section 4).

For many years it was thought that nickel was not present in natural diamond: W8 was first observed in synthetic diamond,[46] and was tentatively attributed to nickel as it appeared only in diamonds grown from nickel-containing solvent catalyst. However W8 and its derivatives NE1-3, have subsequently been found in natural diamonds from Yakutia and Argyle.[38,47,48] These diamonds exhibit other EPR centres, which may also be related to nickel.

It is not clear whether Ni_s and Ni_i are simultaneously present in the same diamond, because both Ni_s^0, $3d^6$, and Ni_i^0, $3d^{10}$, are EPR inactive. For Ni_s to become EPR observable as Ni_s^-, requires donor N_s,[49] whereas for Ni_i to become EPR observable as Ni_i^+, requires an acceptor B_s [19] so that these conditions are mutually exclusive. That Ni_s^- and Ni_i^+ have sometimes been observed in the same specimen may be due to inhomogeneity. Theoretical calculations of the stability of Ni_i and Ni_s in various charge states have shown a dependence upon the Fermi level.[45]

4. THE CRYSTAL FIELD

EPR of 3d ions at sites of T_d symmetry in silicon, both substitutional and interstitial, has shown that the crystal field acting on the 3d ion at a substitutional site is dominated by the four tetrahedrally placed ligands, but that at the interstitial site has the opposite sign, being dominated by the six octahedrally placed next nearest neighbours (nnn), and at both types of site the crystal field is smaller than the internal spin-spin exchange, so that Hund's rules apply.[9] Although the latter is true for the range of atoms observed, the general applicability of Hund's rules has been contradicted by computation using self-consistent linear muffin-tin-orbitals (LMTO) Greens functions for T_d sites of all possible charge states,[50] which indicate low-spin ground states for interstitial ions at the low-Z end and for substitutional ions at the high-Z end. The situation in diamond, where the much smaller lattice constant should make the crystal field much larger, is unclear because the known examples of substitutional and interstitial sites are $3d^7$ to $3d^9$, where the resultant spin is the same in both limits. Nickel, and probably cobalt, can occur in the semi-vacancy site. Nickel at this site appears mainly to correspond to $3d^7$ (or possibly $3d^5$ for NE4) with $S = ½$,[38] so even for these sites with ligands at 0.18 nm the crystal field dominates exchange. So, one would expect this also to be so for the covalently bonded substitutional site where the four tetrahedrally placed ligands lie at 0.154 nm. The crystal field for the interstitial site is complicated by the lack of covalent bonding with the tetragonally situated nearest neighbours (nn) and the opposing contribution from octahedrally placed nnn: the latter can dominate because of direct overlap with the e-orbitals.

Several, ab initio, computational techniques have been applied to calculate the stability, electronic state, local distortion and local phonon modes for point defects in diamond (local density functional (LDF) technique, applied to a cluster of C atoms around and centred on the impurity, or using a supercell method; or Green's function techniques[45, 51, 52]). LDF calculations for nickel and cobalt (and neighbouring 3d-atoms) suggest that all the sites (substitutional, interstitial and semi-vacancy) have crystal fields which dominate internal spin-spin exchange;[53,54] but cluster calculations give different results for Ni_i^+, some preserving the T_d symmetry [54,55] and some predicting a trigonal distortion.[53, 56]

There is no hard experimental evidence. In principle, it could be provided by $3d^6$. Apparently Ni_s^0, $3d^6$, is not observed by EPR, although it is known to be present because X-irradiation can stimulate the reaction $Ni_s^0 + N_s^0 \Rightarrow Ni_s^- + N_s^+$, leading to an equal rise and fall in the concentrations detected by EPR of Ni_s^- (W8 EPR[35]) and N_s^0 (P1 EPR[11]), respectively.[49] Co_s^-, $3d^6$, is not observed either, although by analogy with nickel one might expect Co_s^- to be present in as-grown type Ib diamond. $3d^6$ would be, for high spin $e^3t_2^3$, ^5E; and for low spin $e^4t_2^2$, $^3T_2$, $J' = 2$. In principle, EPR could be observed in either, but strong J-T effects on ^5E leave a system like Cr^{2+} in MgO, observed only by acoustic resonance;[57] and a combination of J-T effects and rapid spin-lattice relaxation might make the EPR of $^3T_2$ too wide to observe.

Any sustitutional defect with $S > 3/2$ would be a counter-indication. There are two such possibilities. One is the EPR defect W44, with $S = 5/2$, with very weak orthorhombic symmetry, which has been attributed to $3d^5$ at a distorted substitutional site,[58] but it is not yet clear that the site is 3d-related. Only two EPR defects with $S = 2$ have been observed in diamond. One is the optically excited $^5A_2$ state of the neutral vacancy, V^0, with $g = 2.0033$.[59] The other is the EPR centre W10 [60] which is trigonal, with $S = 2$, and has been attributed to $3d^6$ (Cr_i^0), but we show below that this is not correct. So, although these two examples leave a possibility of doubt, the likelihood is that at least for the substitutional and semi-vacancy sites the crystal field dominates inter-electron exchange.

There is an EPR defect E1, observed in powders of synthetic diamond grown from solvent catalysts containing cobalt, which has been attributed to Co_i^{2+} .[61] This centre has not been observed subsequently in any other synthetic diamond, so there must be a question about its authenticity. However, it remains an intriguing result, which needs explanation or refutation. If the attribution were correct, the g-values ($g_{\|} \sim g_{\perp} \sim 4.33$) corresponds to $3d^7$, $t_2^5e^2$, $^3T_1$ ($J' = ½$), which is the "high spin" state, showing that at least for the interstitial site internal exchange is larger than the crystal field.

A relevant discussion is given of a ZPL attributed to W_i^0, $5d^6$, in CVD diamond.[62] In ionic salts, the 4d and 5d groups are examples of "low spin" states, in contrast to the usual "high spin" states for the 3d group.[16] In contrast, the data for W_i^0 in diamond requires a high spin state ground state, $t_2^4e^2$, $^5T_2$. A 5-line multiplet structure of the ZPL arises from splittings in the ground state indicating a quenched spin-orbit coupling and a motional averaging between tetragonally J-T distorted states. This contrasts with interstitial $3d^6$ in silicon,[9] where the J-T effect is presumably weaker and so leaves J' as a good quantum number, but with significantly reduced effective spin-orbit coupling and almost completely quenches the orbital contribution to the g-values. The attribution of the ZPL to tungsten was because exposure to it was the common factor in all specimens, in which it was observed: the attribution to tungsten is supported by the frequency ω_R of the quasi-local vibration.[8] However, tungsten seems a remarkably large atom to be incorporated interstitially in diamond, it is also surprising that a 5d atom corresponds to "high spin" coupling: it may indicate association with vacancies. Other heavy ions [Ta and Tl] have been implanted to produce optical centres.[8]

Another unknown in diamond is the nature of the bonding and anti-bonding orbitals between 3d ions and the ligands. At an interstitial site, no bonds are formed between the 3d ion and its neighbours, but in a substitutional site or a semi-vacancy site, four or six covalent bonds respectively are formed with the ligands. Orbitals of particular symmetry on the 3d atom are admixed with linear combinations of the surrounding ligand orbitals with the same symmetry. In most compounds of 3d atoms, the ligand orbitals are more tightly bound than the 3d orbitals, so the full bonding orbitals are primarily located on the ligands, and partially filled anti-bonding orbitals are primarily located on the 3d atom (ion).[16] In contrast, in silicon, the 3d orbitals are more tightly bound than the dangling orbitals of the surroundings, so the available electrons tend to fill the 3d orbitals, leaving the unpaired electrons primarily on the ligands. This leads to the so-called "vacancy model" where the nature of the 3d atom is relatively unimportant, and merely acts as a sink for ten 3d electrons.[63] The properties of the defect are similar to those of the vacancy with the residual number of electrons. An alternative model proposed by Ludwig and Woodbury (L-W)[9] is analogous to the situation in salts: electrons are transferred from the 3d ion to fill the dangling bonds, equivalent to filling bonding orbitals primarily on the ligands, and the residue are regarded as associated with the 3d ion. These models are the extremes between which the true situation lies. In addition to affecting the energy ordering of the resultant molecular orbitals, the vacancy model increases the ligand hfs and decreases the spin-orbit coupling parameters for the unpaired electrons. It is not clear whether diamond is like silicon, LDF theory again gives different results; Ref.[51] suggests that the binding energy of the 3d electrons becomes higher towards the heavy end of the group, favouring the L-W model, but Ref.[54] confirms the vacancy model for Ni_s.

For Ni_s^- in diamond, two observed features suggest that the vacancy model may be appropriate: (a) ligand hfs for nn and nnn ^{13}C atoms correspond to about 40 % of the electron spin density,[35] and the ^{61}Ni hfs corresponds to 25-40 % of the electron spin density [30] (LDF theory of Ref.[54] predicts 21%), (b) the spin-orbit coupling parameter deduced from Δg of the ground state, corresponds to $\lambda \sim -9.3$ meV, much closer to the value for carbon (-6 meV) [64] than that of nickel (-60 meV).[16] In contrast, the analysis of the EPR of NIRIM-2 and the optical ZPL at 1.404 eV,[44] although not completely satisfactory in the context of a pure $3d^9$ configuration, appears to suggest a value of $\lambda \sim -56$ meV for the interstitial site.

In silicon, the EPR g-values for high symmetry interstitial sites of $3d^6$ and $3d^7$ show a J-T effect [9] via a reduction in the orbital contribution;[65] but such sites do not occur in diamond. In diamond, for Ni_s^-, $3d^7$ in T_d symmetry, the ground state ($^4A_2$) is not affected by the J-T effect, but the triplet ($^4T_2$) state at 2.51 eV shows very small fine structure.[66] The spin-orbit coupling appears to be quenched by a factor of ~ 0.04. For Ni_i^+, $3d^9$, the ^2E ground state appears to undergo a J-T distortion to rhombic symmetry at very low temperatures, but is motionally averaged at higher temperatures.[19]

5. OTHER POSSIBLY NICKEL-RELATED SITES

The NE1-3,5,8 sites are of low symmetry, C_2 or C_1; but, there are also many sites in diamond, probably nickel-related, which are of quite high symmetry. The principal signature is that they occur mostly in synthetic samples grown from nickel-containing solvent catalyst, and they have positive mean Δg. Definitive models for these sites have not been established. There are upwards of 20 EPR and 40 optical defects, which may be nickel-related.

Table 1. EPR centres in diamond which may be nickel-related.

Centre(S) D (GHz)	Sym.	g_1	g_2,g_3	g_{av}	$g_{\|} - g_{\perp}$	$g_{av} - g_e$	**[No. N]** Δν	model	Ref.
$W8^s$ (3/2)	Cub.	2.0319		2.0319	0	0.0296	1.8	Ni_s^-	35
NIRIM-1	Cub.	2.0112		2.0112	0	0.0089	45	Ni_i^+	19
$ME1^n$(3/2)	Cub.	2.02		2.02	0	0.0177	50 (a)		48
$W31^n$	Cub?	2.0020	2.0025	2.0023	-0.0005	0	0.8	? Ni_i^-	67
NIRIM-2	Trig.	2.3285	0				60	Ni_i^+- X	19
Pa1	Trig.	2.25	0				110		68
AB1	Trig.	2.0024	2.0920	2.0621	-0.0868	0.0598	5		69
AB2	Trig.	2.0072	2.0672	2.0472	-0.0600	0.0448	5		69
AB5(1) 31.72	Trig.	2.037	2.022	2.027	0.015	0.0247	200	$(Ni_s - N_s)^-$	70
NE4	Trig.	2.0227	2.0988	2.0734	-0.0761	0.0711	3	$(C_3VNiVC_3)^-$	37
NE9	Trig.	2.0921	2.1705	2.1444	-0.0784	0.1421	**[3]**	$(C_3VNiVN_3)^0$	71
NOL1(1) 171	Trig.	2.0235	2.002	2.0092	0.0215	0.0069	**[1 B]**	N_i^{2+}- B_s^-	72
Ro1	Tetr.	2.0151	2.2113	2.1456	-0.1962	0.1433	8		47
AB3	Orth.	2.1105	2.0663 2.0181	2.0650	0.0624*	0.0627	5		69
AB4	Orth.	2.0220	2.0094 2.0084	2.0133	0.0166*	0.0110	5		69
NE6	Orth.	2.0109	2.0207 1.995	2.0088	0.0030*	0.0065	5		37
AB7	Orth.	1.9910	2.0078 2.0046	2.0011	-0.0152*	-0.0012			28
$NE1^s$	Mon.	2.1282	2.007 2.0908	2.075	0.1212*	0.0727	**[2]**	$(C_2NVNiVNC_2)^-$	37
NE3	Mon.	2.0729	2.0085 2.0476	2.043	0.0644*	0.0407	**[3]**	$(C_2NVNiVN_2C)^0$	37
NE5	Mon.	2.0903	2.039 2.0044	2.0446	0.0859*	0.0423	**[2]**	$(C_3VNiVN_2C)^-$	37,38
NE8	Mon.	2.0439	2,1772 2.0846	2.1019	0.1333*	0.0996	**[4]**	$(CN_2VNiVN_2C)^+$	37,38
$NE2^s$	Tric.	2.1301	2.0100 2.0931	2.0777	0.1201*	0.0754	**[3]**	$(C_2NVNiVN_2C)^0$	37
AB6	Tric.	2.0742	2.0244 2.0185	2.0309	0.0528*	0.0367			28
NE7	?	>2					**[1]**	$(C_3VNiVNC_2)^{2-}$	37,38

$g_{av} = (g_1+g_2+g_3)/3$. * indicates average of g_2 and g_3. S = ½, if not stated otherwise. **No. N** corresponds to resolved hfs; Δν is line width in MHz when there is no resolved hfs. Most spectra occur in synthetic diamonds. ^{s} indicates sometimes in natural diamonds. ^{n} indicates only in natural diamonds. (a) ^{14}N ENDOR has been observed on this line (see text).

Table 2. Zero phonon lines related to 3d transition metals.

	Energy (eV)	method	Symm.	trans.	EPR centre	model	comment anneal temp (K)	Reference
Ti	1.249^{I}	C	$O\text{-}I^{P}$			$Ti\text{---}Ti^{P}$	I 1700	8, 74
Cr	1.673^{I}	C				$2Cr^{P}$	I 1100	8
Ni	$1.4008^{*}\{2.7\}^{g}$	P,C,A	Tr	$E - A_1$	NIRIM2	Ni_i^{+} (a)	low N	68, 75
	1.883	A	Rh-I	$A_1 - B_1$		? Ni-N	high N	75
	2.51	A	T_d	$^4A_2 - {}^4T_2$	W8*	Ni_s^{-}	high N	75
	2.534<*2.597, 3.142*> 2.595, 2.623, 2.634* 3.38-3.62 (S2)	P,A A			NE2	$(C_2NNi_{sv}N_2C)^0$ C_1 symmetry	high N 2200	76 77
	2.495<*2.621, 2.618, 2.468*>, 2.621* (S3)	P			NE1	$(C_2NNi_{sv}NC_2)^{-}$	high N 2200	76
	2.369<*2.591*> 2.582	P,A			NE3	$(C_2NNi_{sv}N_2C)^0$ C_{1h} symmetry	high N 2200	76
	1.563<*1.562, 3.219*>	P,C,A			NE8	$(CN_2Ni_{sv}N_2C)^{+}$	high N 2200	78, 79
	$2.5587\{1.5, 3.1, 4.7\}^{e}$	C			ODMR	$2Ni^{P}$		8,75,80,81
	3.065{11}	A				$2Ni^{P}$		8
	1.06	MCDA	Tr		Pa1			68
	1.72, 1.75	MCDA	Tr		AB1(b)			68
	2.292^{I}	C				$2Ni^{P}$	I 900	8
	1.83, 1.92, 2.02, 2.1, 2.2 (f)	P			correlated KUL1		CVD	82
Co	$2.3666\{11.8, 18.4\}^{e}$ <*3.085, cont 4.45*>	P,C	Tr	$E - A_1$		? $Co_s - N_s{}^{P}$	high N 2100	8,22,83, 84
	2.135{5}	C	M-I		? O4	$(C_3Co_{sv}C_2N)^{-}$		78, 83
	1.989	P				$2Co^{P}$		8, 83
	$2.2771\{6.0, 13.6\}^{e}$ <*3.004, 3.673,cont 4.3*>	P				$Co+N^{P}$		8,83,84
Zn	2.393^{I}	C				$2Zn^{P}$	I 1100	8

P indicates photoluminescence, C cathodoluminescence, A absorption, MCDA magnetic circular dichroism absorption; * sometimes observed in natural type Ib diamonds; ^{I} produced by implantation; ^{P} deduced from ω_R of phonon replica; { } denotes a multiplet with energy above the lowest state in meV, superscript ^{e} denotes that the splitting is in the excited state; <> denotes PL *excitation energy*, with excitation to the continuum marked *cont.* (a) Relaxed along <111>; (b) this was attributed to NE4 [44], but the g-values are much closer to those of the more recently discovered AB1; (f) fine structure ~ 9 meV on all lines.

Other ZPL for

Ni in low N diamonds 2.201A [79], 2.268A [79], 1.21148 $\{1.79, 4.06, 6.05, 7.7, 14.0, 16.5, 20.3\}^{?}$ A [85] {this has been attributed to another charge state of the 1.004 eV ZPL [85]}, 2.971 P [86]
Ni in high N diamonds as-grown at 1600 K [1.534, 1.715 $\{4.7\}^{e}$, 1.769, 1.950, 2.136, 2.407, 2.461] P [78]
Ni in high N diamonds after anneal 1950-2200 K 1.659 <*2.428*> PC [78,79], 1.693 AC [87] 1.704 <*2.403*> PC [78,79], 1.826 P [78], 1.939{13} AP [78], 2.071 <*2.298*> P [77,78], [2.156, 2.268, 2.306, 2.468, 2.481] P [77]
Ni in high N diamonds after anneal > 2200 K 2.654 AP [86], 1.660 <*2.427*> CP [79], 1,.646 <*1.929, 2.750*> P [77,78], [1.737, 1.770] P [78]
Co in high N diamonds after anneal > 1800-2100 K 1.363 A [79], 1.852 A [8,78], 1.9835 $\{3.1,7.1\}^{e}$ PC [83], 2.207 $\{4\}^{e}$ PC [79,83], 2.590 P [83] [2.379, 2.385, 2.556, 2.889] C [88].
Further references and comments for these centres and others are given by Zaitsev [73] and Field [88].

Table 1 lists these EPR sites. There is too little certainty to make detailed comment about all of them. In those with cubic symmetry, the inclusion of W31 is perhaps provocative, as its 4-line hfs has been attributed to ^{33}S on the basis of their intensity relative to the line for even isotopes,[67] but its acceptor-like properties are strangely at odds with the assignment to S^{+}, in contrast perhaps to Ni_i^{-}, $3d^{10}4s$. However, one theoretical computation predicts that this configuration is unstable.[45] It is unfortunate that the large line width of NIRIM-1 prevents its definite identification as a

T_d interstitial site by ^{13}C hfs. ^{13}C matrix ENDOR has been observed over the full width of the very wide line of ME1, suggesting that it is a genuine point defect. ^{14}N ENDOR has also been observed for a single N atom suggested to be a_0 distant along <100> from the unpaired electron ($S = 3/2$, $A_{||} = 1.336$ MHz and $P_{||} = 92$ kHz),[48] but a somewhat unconvincing case is made to reconcile several conflicting properties of this defect.

Table 2 lists the principal ZPL. It is not a complete list; some others are included in Zaitsev's catalogue,[73] but it indicates the very large number of different sites. Most ZPL appear to be associated with the low-symmetry semi-vacancy-related sites. They fall into four groups in diamond (a) as-grown with getters to keep the N content low, (b) as-grown without getters, so with high N content, (c) those with high N content modestly annealed between 1950-2200 K, and (d) those with high N content annealed above 2200 K. Those in group (b) decrease as those in group (c) increase, and these in turn decrease as those in group (d) anneal in. These processes appear to correspond to the gradual migration of N towards, and attachment to, the 3d ion in a semi-vacancy site. Those in group (c) which anneal in and out again before sites NE1-3 (which are known to involve 2 and 3 N ligands) anneal in, may be due to semi-vacancy sites with just one N ligand.[38] As these are not observed in EPR, it is assumed that they must de diamagnetic ($3d^6$) in the ground state. NE7 may correspond to a charge transfer state of one of these defects.[38]

The ZPL at 2.65 eV gives ODMR spectra characteristic of the ground states of both N_s^0 and Ni_s^-. Ni_s^- appears to be correlated with the fine structure, while N_s^0 is associated with a broader lower energy luminescence. So, the luminescence seems to arise from two overlapping bands, but the mechanism involved in the nickel-related band is not yet understood. ODMR[68] shows that NIRIM-2 [19] is associated with the 1.404 eV ZPL and that, in spite of very similar g-values, it is a separate defect from Pa1.

A remarkable feature of Table 1 is the large number of different sites with relatively high symmetry. Particularly intriguing is the large number of trigonal sites, as hole-like trigonal sites largely correspond to holes in the e-orbitals, which are not affected in first order by either spin-orbit coupling or a trigonal crystal field.[16] Eq (1) is the general spin hamiltonian for trigonal EPR centres

$$H = g_{||}\mu_B S_z B_z + g_{\perp}\mu_B(S_x B_x + S_y B_y) + D[S_z^2 - (1/3)S(S+1)], \tag{1}$$

where only the first two terms are required for the majority of the centres which have $S = ½$, but the third term is required for centres with $S > ½$. Of the trigonal centres, NIRIM-2 and Pa1 have the properties one would expect, as the degeneracy of the e-orbitals is split by the combined effect of the trigonal crystal field and spin-orbit coupling, leading to a very small or zero $g_{\perp}$. The departure from $g_{\perp} = 0$ is due to admixture of a_1-orbital, and for that to be large, as it is for many of the trigonal sites, requires the a_1 level to be very close to that of e. For example, one can account for the properties of NE4 in terms of $3d^5$, t_2^5, at a semi-vacancy site (as one can for the similar low-symmetry site of O4, which is cobalt related [30]), but that requires a very small trigonal splitting of the T_2 state. In contrast, LDF theory predicts a configuration $a_1^2e^3$,[53] whose g-values ought to be similar to NIRIM-2 (but for Cu_{sv}^0 it predicts a_1e^4).

If the trigonal component of the crystal field is small enough, one might expect (as for cubic symmetry) that the site would be subject to a J-T distortion of tetragonal or lower symmetry, which would separate the e-orbitals. The EPR line shape of NIRIM-1, and its temperature dependence, does suggest that there is J-T distortion at very low temperature, which is motionally averaged at higher temperature.[19] If a similar motional averaging occurred in sites where symmetry had been lowered from trigonal by J-T distortion, it might average only those sites distorted from a specific <111> direction, and so lead to an apparently trigonal site.

Another way to produce a trigonal site of apparently $S = ½$ is to place $3d^7$, $S = 3/2$, in a trigonal crystal field which is strong enough to give a fine structure parameter $D >> h\nu$, where ν is the microwave frequency. For $M = \pm ½$ lower, $g_{\perp eff}$ in $S = ½$ formalism would be changed from the true value of $g_{\perp}$ by an amount dependent upon $D/h\nu$; but asymptotic to $2g_{\perp}$ for $D >> h\nu$, so relatively easily recognisable. For $M = \pm 3/2$ lower, for which the transition has to be $\Delta M = 3$, the intensity would be zero for **B** parallel to the axis, but with increasing signal strength towards **B** perpendicular to the axis. The value of $g_{\perp}$ would be small, and also dependent upon ν, and $g_{||}$ would be close to 6.[89]

The trigonal EPR centre AB5 is an analogous site of $3d^8$, $S = 1$, except that as $D = 31.72(2)$ GHz measurements at $\nu \sim 35$ GHz showed both $\Delta M = 1$ and $\Delta M = 2$ transitions.[70] As this centre was found in diamond with high concentration of N_s (~ 90 ppm), it has been attributed to $(Ni_s - N_s)^-$, with a line width too great for the hfs of ^{14}N to be resolved (though a trigonally distorted site of Ni_i^{2+} cannot be ruled out). The newly discovered EPR centre NOL1 [72] is another site of this type for $3d^8$, $S = 1$, with $D >> h\nu$ ($D \sim 5.7$ cm^{-1}), where only the $\Delta M = 2$ transitions are observed. As this centre also occurs in synthetic diamonds grown from nickel solvent catalyst, but with nitrogen getters leaving its boron content uncompensated, and in addition it exhibits a 4 line hfs, it has been attributed to $(Ni_i \cdots B_s)^+$.[72] NOL1 is similar to $Fe_i^0 \cdot\cdot B_s^-$ in silicon,[90] but since there was no iron in the solvent catalyst it has been attributed to the nickel analogue.

Other sites, which are difficult to model, are those with D_{2d} (Ro1) or near D_{2d} (AB4) symmetry. A <100> split-interstuitial is unlikely for a 3d ion. A substitutional site would require 2 neighbours (most likely N_s^+) incorporated at ± a_o along <100> or 4 at ± $(\sqrt{½})a_o$ along <110> and <1$\underline{1}$0>, both unlikely. A T_d interstitial site requires 2 nnn at ± $½a_0$ along <100> or 4 nnn at ± $½a_0$ along <010> and <001>. The hfs predicted by LDF theory for ^{13}C at such a nnn site,[54] extrapolated to the g_N value of ^{14}N, would lie within the observed line width. As AB4 is C_{2v} (only nearly D_{2d}) it might correspond to one N_s^+ neighbour of Ni_i^+.

It is curious that a different set of EPR sites appears to occur in crystals grown by Feigelson (the NE1-9 centres) and at NIRIM (the AB1 - 5 centres); the growth temperatures of the latter are only slightly higher. There are not yet models for AB1- 4, but they do not seem to be related to a semi-vacancy site.

6. COBALT-RELATED SITES

Table 2 lists a number of optical centres, all observed in luminescence except for one weak absorption, which are observed only in diamonds grown with cobalt solvent catalyst.[83] As ^{59}Co is 100% abundant, the involvement of Co is not detectable by an isotope structure. Only one of the centres (1.985 eV) is observed in as-grown diamonds. The remainder appear only after anneal above the temperature at which N becomes mobile, and most N is in the form of A-centres, so are likely to be cobalt-nitrogen complexes; and they have been shown to correspond to different defects. As for nickel, these appear almost exclusively in {111} growth sectors. Their concentration is much lower than that for nickel complexes found under the same conditions. One optical ZPL has been shown by stress measurements to correspond to a trigonal site,[90] and LFD simulation[91] suggests that it corresponds to $(Co_s - N_s)^0$, $3d^6$, $a_1^2e^2$, $S = 0$.

Only the EPR centre O4 is proven to be cobalt related by its ^{59}Co hfs[31] (there is also another similar, as yet unidentified, site in the same diamond with similar hfs).[92] O4 has C_{2h} or C_{1h} symmetry with g-values like $3d^5$ in a distorted octahedral crystal field.[16] It has been proposed to be Co_{sv}^{2-}, with one N_s^+ ligand to lower the symmetry and give the large line width through unresolved ^{14}N hfs. The parameters for O4 (and for other EPR centres discussed below) are listed in table 3. It is possible but not proven, that the ZPL at 2.135 eV, which has monoclinic I symmetry, corresponds to O4.

Table 3. Parameters for EPR centres discussed in the text which are not Ni-related.

EPR centre	Diamond type	S	g-value	D (MHz)	other factors	symm.	model	Ref.
O4	synth. Ib	1/2	1.8438 1.7045 2.3463			C_{2h} or C_{1h}	$(C_3VCoVC_2N)^-$	31
W15	Ib	1	2.0028	2874	$I = 1^+$, $A_s = 2.2$ $A_p = 0.07$, $P = -5.04$	C_{3v}	$(N\text{-}V)^-$	93
W36	nat. IIb	1	2.002	155.4	$I = 3/2^+$, $A_s = 6.9$ $A_p = 0.9$, $P = -5.4$	Trig	? Cu-related	32,33
W32	nat. IIb	1	2.002	204.9		Trig	see text	32
R4/W6	IIa	1	2.002*	390*		Trig*	$(V\text{-}V)^0$	94
W10	nat. IIa brown	2	2.001	154.4		Trig	see text	60
W44	nat. Ia	5/2	2.0025	62 <110> -56 - 6 <001>		C_{2v}	? $3d^5$	58
KUL7	powder	1	~2		$I = 5/2$ $A = 118$		Mn-related	34

* Parameters for 440K where C_{2h} symmetry approximates to axial about <111>.

$^+$ Additional terms in the spin hamiltonian for W15 and W36 $A_s(\mathbf{S{\cdot}I}) + A_p(3S_zI_z - \mathbf{S{\cdot}I}) + P[I_z^2 - (1/3)I(I+1)]$; A_s, A_p and P in MHz.

7. OTHER POSSIBLY 3d-RELATED SITES

An EPR centre (KUL7) with S = 1 and a six-line hfs, corresponding to an isotope with 100% natural abundance with

I = 5/2, has been observed in HTP powders as ΔM = 2 transitions, and has been attributed to either Mn_S^+, $3d^2$, or Mn_i^-, $3d^8$.[34] This is surprising, as no Mn-related site has been found in HPHT single crystals grown from manganese solvent catalyst. The only likely alternative isotope, ^{27}Al, discounted as KUL7 is not found in diamonds grown with Al, but is found only with Ni-Mn solvent catalyst.

We have mentioned above the EPR centre W44, found in natural, plastically deformed, type Ia diamond, with S = 5/2 at an almost cubic site, with very small orthorhombic distortion (see table 3). If this is due to 3d electrons it must correspond to $3d^5$, probably at an interstitial site, but what very small perturbation would lead to a fine structure parameter D at least an order of magnitude smaller than that recorded for any ionic crystal? In principle, it could be a site with ferro-magnetically coupled constituents $S_1 = 3/2$ (Ni_s^-) and $S_2 = 1$ (Ni_i^{2+}), similar to $Fe_i^0Al_s^-Fe_i^+$ in silicon,[95] but it is unlikely that isotropic exchange would be large enough for $S_1 + S_2 = 3/2$ to be not populated, and yet the anisotropic interaction small enough to give the very small D. It is not proven that W44 is transition metal related, but it is very difficult to construct a model for any nearly cubic centre with at least five unpaired electrons; the negative vacancy, V^-, for example has configuration $a_1^2t_2^3$ S = 3/2 [96], and does not have a nearby excited state with S = 5/2.[97] Hence, by default one has to take $3d^5$ seriously.

We have also mentioned above the EPR centre W10, found in natural type IIa brown diamond, which has S = 2, trigonal symmetry and a very small fine structure splitting D (see table 3).[60] It has been attributed to $3d^6$ (Cr_i^0) [60] at a site with a strong trigonal component to the crystal field which leaves a doubly occupied lowest a_1 state and single occupancy of the upper two pairs of e states, $a_1^2e^2e^2$. The system of 6 electrons corresponds to a ^5D state which is split by the crystal field into a singlet ground state, a doublet at energy K, of the order of the trigonal component of the crystal field, and another doublet at much higher energy Δ. The orbital angular momentum is quenched, but spin-orbit coupling mixes the two excited states. The admixture with the lower doublet dominates, as K << Δ. The leads to $\delta g \sim \lambda/K$ and $D \sim \lambda^2/K$. The measured δg is very small, showing that the angular momentum is highly quenched. However, this analysis leading to a small value of D is flawed, as it ignores a large contribution to D from spin-spin interaction (parameter ρ) [16], which makes $D \sim (\rho+\lambda^2/K)$, and ρ is expected to have a magnitude similar to that for Fe^{2+}, $3d^6$ ($\rho \sim 0.9\ cm^{-1}$).[98] This critical analysis casts doubt on the original interpretation of W10. It is much more difficult to make constructive comments about alternatives. Two possibilities have been suggested without much conviction [33]: (a) substitutional Zn_s^{2+} might behave like $3d^{10}$ at the centre of V^0 for which the ground state of the "vacancy" model has become $^5A_2$ (but why should that show weak trigonal distortion?); (b) Zn_{sv}^{2+}, $3d^{10}$, at the centre of a semi-vacancy site $(V_2)^{2-}$ for a vacancy model state $a_{1g}^2a_{1u}^2e_g^2e_u^2$, S = 2 (but no EPR has been observed attributable to $(V_2)^{2-}$ without a central atom for a comparative value of D; but this is similar to the model suggested below for W36). There are no helpful clues from silicon where there are only two defects with S = 2 [10]: $3d^6$ at the T_d interstitial site where because of orbital degeneracy the g-value is very different from g_e [9] and a strange site involving a tetrahedral arrangement of four Mn_i^0.[99] It is not clear that W10 does involve a transition metal, but it is also difficult to devise a model for a site with S = 2 and a very small trigonal D value.

The trigonal EPR defect W36, with S = 1 and I = 3/2, has been attributed to a boron-related defect both because it is found in type IIb diamond, and because the dominant isotope, ^{11}B, has I = 3/2.[32] W36 also has very small Δg (see table 3), suggestive of a defect associated with a vacancy or an interstitial, rather than a transition metal. The other notable features are a relatively large quadrupole parameter P, small hyperfine parameters A_s and A_p and a small D (103 MHz). The former three parameters match quite closely those of ^{14}N in the EPR defect W15, with S = 1, which is known to be $(N - V)^-$ (see table 3), but the value of D for the latter is 2874 MHz: this shows that W36 cannot be related to B - V. It seems impossible to model (at least simply) a trigonal B-related defect with the observed parameters. It has been suggested [33] that the site could correspond to Cu^+ in a semi-vacancy site; provided that the "vacancy" model is applicable, so that the defect is like $3d^{10}$ in $(V_2)^0$. Cu^+ is smaller than Ni^- which fits in the semi-vacancy site. The magnitude of D for the EPR centre R4/W6, identified as $(V_2)^0$, is similar to that of W36 (see table 3), and the small Δg is also consistent with the vacancy model. The positive charge state of the defect would arise from charge transfer to B_s acceptors in the type IIb diamond. This identification is speculation. W36 is a rare centre found in some natural type IIb diamonds. But, if it is Cu at a semi-vacancy site, it should be possible to fabricate this site in synthetic diamond following a similar recipe as used for NE1-8.

There is an EPR defect W32,[32] with very similar parameters to W36, but without hfs (see table 3), also found in type IIb diamond, which could be Ni^0, $3d^{10}$, in $(V_2)^0$, the nickel analogue of W36. This, in disagreement with the prediction of LDF calculations for this site, which give a ground state $a_1^2e^2$, S = 0.[51] However, similar calculations for the same number of electrons, but replacing Ni by Co gives S = 1 and S = 0 states very close in energy.[53] The use of the vacancy model for W32 contrasts with the properties of NE4, suggested to be Ni^0, $3d^{10}$, in $(V_2)^-$, which occurs in type Ib diamond, where δg suggests a much larger amplitude of unpaired electron on the Ni atom.

ZPL have been observed for implanted Ti, Cr and Zn, each corresponding to a strongly coupled pair of atoms.[8]

8. DISCUSSION

Much remains to be established about those defects in diamond which may be related to 3d atoms. Although the data discussed above shown that there might be at least one defect related to each of the 3d atoms, except vanadium, the most reliable and extensive are related to nickel and cobalt. Of these two, nickel is found in greater concentration and at more different sites than cobalt. This correlates with the results of LDF calculations of the stability of the 3d-atoms in the three principal sites, where Ni has the lowest (or next lowest) energy.[51] The latter suggests that it might be much more difficult to incorporate the larger 3d atoms. Very few of the many optical and EPR spectra linked with nickel or cobalt have been associated with a molecular model. Only the EPR centres W8 and O4, and the ZPL at 1.404 eV, are proved to be 3d-related by hfs and isotope structure respectively. For the majority of the rest the assignment relies on the occurrence of the defect only in synthetic diamond grown from nickel or cobalt solvent catalyst. A surprising feature of the data is the very large number of different nickel (and cobalt)-related sites. Not many of the EPR and optical centres have been linked. Finding models for all of these nickel-related centres, especially the large number of trigonal centres, presents a challenge, as the symmetry lowering constituent (probably N_s, B_s or V) must lie on the <111> axis through the nickel atom, or be present in groups of 3 corresponding to C_3 symmetry about a <111> axis (see NE4 & 9 in table 1). The nickel atom is probably incorporated in either a T_d substitutional, a T_d intersitial or a D_{3d} semi-vacancy site. So far, ligand hfs has been observed for very few of the centres. so there is insufficient information for proper characterisation. For the defects found in synthetic diamond, further evidence might be obtained, particularly by using diamond isotopically enriched in ^{13}C, to make ligand hfs more easily measurable. Identification is much more difficult for those found only in natural diamonds, for which the only solution may be to discover ways of making them artificially.

The tenuous evidence for other 3d-related centres, coupled with the high energy calculated using LDF,[53] may mean that it will be difficult to induce larger 3d atoms into point defects. However, Ti, Cr and Zn have been implanted into a surface layer, and have formed a point defect on annealing. It will be very important to find out what sort of defect, as that may guide the strategy for incorporating the larger ions. In this context, it would be useful also to characterise properly the proposed W_i^0 defect (section 3).

The EPR centres discussed fall into two clear categories, those with significant departure of g-value from g_e, and those with g-values close to g_e. The latter can be attributed to 3d atoms, only if an extreme form of the "vacancy" model is applicable, and so far there is no clear evidence that it is: the closest one can come is the interpretation of Δg for Ni_s^- which suggest a spin-orbit coupling parameter λ much closer to that for carbon than for nickel, supporting the validity of a moderate vacancy model.

It is not even clear whether the crystal field is larger or smaller than internal electron-electron exchange, though it seems likely that it is larger for substitutional and semi-vacancy sites: the few "high spin" centres found in diamond have not yet been proved to be associated with transition metals.

REFERENCES

1. J. P. F. Sellschop, in *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, chap 3.
2. A. T. Collins et al., *Phil. Mag.* **B** 61 (1990) 797.
3. H. Kanda and S. C. Lawson, *Industrial Diamond Review* **2** (1995) 56.
4. R. C. Burns and G. J. Davies, in *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, chap 10.
5. R. J. Wedlake, in *Properties of Diamond, Ed J.E. Field, Acadmic Press 1979*, chap 16.
6. Y. Sato and M. Kamo, in *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, chap 11.
7. J. F. Prins, in *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, chap 8.
8. A. M. Zaitsev, *Phys. Rev. B* **61** (2000) 12909.
9. G. W. Ludwig and H. H. Woodbury, *Solid State Physics* **13** (1962) 223.
10. C. A. J. Ammerlaan, *Paramagnetic Centres in Silicon, Landolt-Bornstein,* in press.

11. W. V. Smith et al., *Phys. Rev.* **115** (1959) 1546.
12. G. Davies, *J. Phys. C* **9** (1967) L537.
13. W. Kaiser and W. L. Bond, *Phys. Rev.* **115** (1959) 857.
14. R. M. Chrenko, *Phys. Rev. B*7 (1973) 4560; E. C. Lightowlers and A. T. Collins, *Diamond Research 1976*, Industrial Diamond information Bureau, London p 21.
15. C. D. Clark et al., in *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, chap 2.
16. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions, Oxford University Press,* Oxford 1970.
17. G. Davies, *Phys. Chem. Carbon* **13** (1977) 1.
18. A. A. Kaplyanskii, *Optics and Spectroscopy* (1963) 329 & 557.
19. J. Isoya et al.., *Phys. Rev.* **B** 42 (1990) 9843.
20. G. Davies et al., *Europhys. Lett.* **9** (1989) 47.
21. J. W. Steeds et al., *POLYSE* **95** (1995) 11.
22. A. T. Collins, *Diam. Relat. Mater.* **9** (2000) 417.
23. J. A. van Wyk et al., *J. Phys. D: Appl. Phys.* **30** (1997) 1790.
24. J. M. Baker et al., *Hyperfine Interactions* **120/121** (1999) 377.
25. S. Geschwind, in *Electron Paramagnetic Resonance*, Ed S. Geshwind (Plenum, New York NY 1972) chap 5.
26. J. M. Spaeth et al., *Structural Analysius of Point defects in Solids* (Springer Verlag, New York, 1972) p 87.
27. R. N. Pereira et al., *J. Phys. Condens. Matter* **13** (2001) 8957.
28. R. N. Pereira, private communication (2001).
29. C. A. J. Ammerlaan, *Paramagnetic Centres in Diamond, Landolt-Bornstein,* in press.
30. M. I. Samoilovich et al., *JETP Lett.* **14** (1971) 379.
31. D. J. Twitchen et al., *Phys. Rev. B* **61** (2000) 9.
32. J. H. N. Loubser and J. A. van Wyk, *S. Afr. J. Phys.* **10** (1987) 165.
33. J. M. Baker, *J. Phys.: Condens. Matter* **13** 92001) 2053.
34. K. Iakoubovskii and A. Stesmans, *Phys. Stat. Sol. (a)* **186** (2001) 199.
35. J. Isoya et al., *Phys. Rev. B* **41** (1990) 3905.
36. A. T. Collins et al., *Diam. Relat. Mater.* **7** (1998) 333.
37. V. A. Nadolinny et al., *Appl. Mag, Res.* **12** (1997) 543.
38. V. A. Nadolinny et al., *J. Phys. Condens. Matter* **11** (1999) 7357.
39. V. A. Nadolinny et al., private communication, 2001.
40. V. A. Nadolinny et al., *Diam. Relat. Mater.* **9** (2000) 883.
41. D. C. Hunt et al., *Phys. Rev. B* **61** (2000) 3863.
42. G. Davies et al., *Phys. Rev. B* **46** (1992) 13157.
43. D. Fisher and S. C. Lawson., *Diam. Relat. Mater.* **7** (1998) 266; I. Kiflawi et al., *Diam. Relat. Mater.* **7** (1998) 327.
44. P. W. Mason et al., *Phys. Rev. B* **60** (1999) 5417.
45. U. Gerstmann et al., *Phys. Stat. Sol. (b)* **217** (2000) 665.
46. J. H. N. Loubser and P. Van Ryneveld, *Nature* **211** (1966) 517.
47.. R. M. Mineeva et al., Dokl. Akad. Nauk **334** (1994) 755.
48. C. Noble et al., *J. Phys. Condens. Matter* **10** (1998) 11781.
49. S. C. Lawson et al., *J. Phys. C,* **10** (1998) 6171.
50. F. Beeler et al., *Phys. Rev. Lett.* **55** (1985) 1498 and *Phys. Rev. B* **41** (1990) 1603.
51. R. Jones and P. R. *Briddon, The ab initio cluster method and the dynamics of defects in semiconductors, Identification of defects in Semiconductors,* Ed M. Staviola, (Academic Press, 1998).
52. A. Zunger, *Phys. Rev. B* **28** (1983) 3628; *Solid State Phys.* **39** (1986) 276; *Phys. Rev. B* **11** (1975) 849.
53. K. Johnston, private communication, 2001.
54. U. Gerstmann et al., *Physica B* **273-274** (1999) 632.
55. J. Goss et al., *Mater. Sci. Forum* **196-201** (1995) 67.
56. Y. Jinlong et al., *Phys. Rev. B* **49** (1994) 15525.
57. J. R. Fletcher and K. W. H. Stevens, *J. Phys. C* **2** (1969) 444; F. G. Marshall and V. W. Rampton, *J. Phys. C* **1** (1968) 594.
58. J. A. van Wyk et al., private communication 1998.
59. J. A. van Wyk et al., *Phys. Rev. B* **52** (1995) 12657.

60. J. H. N. Loubser and J. A. van Wyk, *Rep. Prog. Phys.* **41** (1978) 1201.
61. V. S. Bagdasaryan et al., *Sov. Phys. Solid State* **17** (1975) 991.
62. S. Lal et al., *Phys. Rev . B* **54** (1996) 13428; F. G. Anderson et al., *Solid State Comm.* **102** (1997) 867.
63. G. D. Watkins, Physica B + C **117B-118B** (1983) 9.
64. P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals* (Elsevier Publ. Co., Amsterdam 1967).
65. F. S. Ham, in *Electron Paramagnetic Resonance*, Ed. S. Geschwind, (Plenum Press, New York 1972) chap 1.
66. N. H. Nazare et al., *Mat. Res. Soc. Symp. Proc.* **339** (1994) 625.
67. J. A. van Wyk and J. H. N. Loubser, *Mater. Sci. Forum* **10-12** (1986) 923.
68. Th. Pawlik et al., *J. Phys. Condens. Matter* **10** (1998) 9833.
69. A. J. Neves et al., *Physica B* **273-274** (1999) 651.
70. A. J. Neves et al., *Diam. Relat. Mater.* **9** (2000) 1057.
71. V. A. Nadolinny, private communication, 2001.
72. V. A. Nadolinny et al., private communication, 2001.
73. A. M. Zaitsev, *Collection of Optical Data on Superhard Semiconductors. Part 1, Diamond, ISTOK* (1998) .
74. A. A. Gippius and A. T. Collins, *Solid State Commun.* **88** (1993) 637.
75. A. T. Collins and P. M. Spear, *J. Phys. C* **19** (1983) 6845.
76. V. A. Nadolinny and A. P. Yelliseyev, *Diam. Relat. Mater.* **3** (1994) 17.
77. S. C. Lawson and H. Kanda, *J. Appl. Phys.* **73** (1993) 3967.
78. A. P. Yelisseyev et al., private communication, 1998.
79. I. N. Kupriyanov et al., *Diam. Relat. Mater.* **8** (1999) 1301.
80. E. Pereira et al., *Diam. Relat. Mater.* **4** (1994) 53.
81. M. H. Nazare et al., *Phys. Rev. B* **51** (1995) 16741.
82. K. Iakoubovskii et al., *Phys. Rev. B* **62** (2000) 16587.
83. S. C. Lawson et al., *J. Appl. Phys.* **79** (1996) 4348.
84. I. N. Kupriyanov et al., *Diam. Relat. Mater.* **10** (2001) 59.
85. S. C. Lawson et al., *Phil. Mag.* **68** (1993) 39.
86. H. Kanda and K. Watanabe, *Proc. ICNDST6* (1998) Pretoria.
87. A. T. Collins and S. Tanley, *J. Phys. D* **18** (1985) 2537.
88. *The Properties of Natural and Synthetic Diamond, Ed J.E. Field, Academic Press 1992*, appendix H.
89. K. Irmscher et al., *Phys. Rev. B* **49** (1994) 7964.
90. W. Gehlhoff and K. H. Segsa, *Phys. Stat. Sol. (b)* **115** (1983) 443.
91. K. Johnston et al., *Physica B* **273-274** (1999) 647.
92. V. A. Nadolinny, private communication, 2001.
93. see entry for W15 in reference [29] and references therein.
94. D. J. Twitchen et al., *Phys. Rev. B* **59** (1999) 12900.
95. A. A. Ezhevskii et al., *Solid. State. Comm.* **81** (1992) 955.
96. J. Isoya et al., *Phys. Rev. B* **42** (1992) 1436.
97. C. A. Coulson and F. P. Larkins, *J. Phys. Chem. Solids* **30** (1969) 1963.
98. M. H. L. Pryce, *Phys. Rev.* **80** (1950) 1107.
99. G. W. Ludwig et al., *J. Phys. Chem. Solids* **8** (1959) 490.