Do isolated interstitial nickel atoms occur in diamond? A re-examination of the electron paramagnetic resonance defects NIRIM-1 and NIRIM-2

Do isolated interstitial nickel atoms occur in diamond? A re-examination of the electron paramagnetic resonance defects NIRIM-1 and NIRIM-2

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Abstract

All of the electron paramagnetic resonance (EPR) and optical data relating to some of the basic nickel-related defects in diamond have been compared, as well as previously little considered information about the effects of spin–orbit coupling and the magnitude of the crystal field. New models are proposed for the EPR defects, which are found in synthetic diamond grown at high pressure and high temperature with getters to reduce the content of nitrogen impurity: NIRIM-1 and NIRIM-2, which some authors have attributed to isolated interstitial nickel at an undistorted, or distorted, T_d site, respectively. It is suggested that NIRIM-1 is more likely to be substitutional Ni_s^+, $3d^5$, at a T_d site, than the previously suggested interstitial Ni_i^+, $3d^9$, and that NIRIM-2 is Ni_i^+, $3d^9$, pinned at a site 0.308 nm along $\langle 111 \rangle$ from a B_s^- impurity, beyond one of its nearest C neighbours. This supports the suggestion that isolated interstitial Ni_i is mobile.

1. Introduction

Recent advances in the production of synthetic diamond by high pressure and high temperature (HPHT) growth from a solvent–catalyst, or chemical vapour deposition (CVD), have made it realistic to envisage new technical applications of diamond. As point defects profoundly affect both the properties and the growth of the material, there has been interest in methods for their characterization, of which electron paramagnetic resonance (EPR) and optical absorption and fluorescence have been most informative. Point defects involving transition metals attract attention both because of their likely presence in HPHT diamond grown from transition metal solvent–catalyst, and because they may have several charge states which may be exploited in charge transfer and photochromic processes.

Although many optical and EPR spectral features have been attributed to transition metal defects, most of them to nickel, because they are unique to HPHT diamonds grown from

transition metal solvent–catalyst [1, 2], only a handful of transition metal sites have been fully characterized in diamond. There are several steps in the characterization process, to establish (a) the electronic configuration, (b) the transition metal element involved, (c) the symmetry of the site, (d) the nature of the ligand nuclei and the unpaired spin density on them and (e) the overall charge of the defect. Several of these are interrelated and difficult to establish in isolation.

Signatures which establish the element involved are

 (a) the nuclear mass, which affects the local phonon modes,
 (b) the distribution of stable isotopes, which gives isotope shifts to optical zero phonon lines (ZPL) and
 (c) the nuclear spins and magnetic moments of isotopes, which give a characteristic pattern to hyperfine structure (HFS) in the EPR.

Substitution of isotopically enriched constituents may be necessary to obtain these effects. So, e.g., the EPR centre W8 has been shown to be Ni-related from ^{61}Ni HFS [3]. The ZPL at 1.404 eV has been shown to be Ni-related through an isotope shift in the 1.404 eV lines [4]. These are the only two defects which have been proved to be nickel-related. Attempts to establish the mass of a heavy impurity from the frequency of quasi-local phonon modes [5], measured from phonon replicas of ZPL, are made uncertain by the unknown difference in local force constants around an impurity.

In single crystals, the symmetry of the site is clearly determined for defects with effective spin quantum number $S > 0$ from the angular variation of the EPR. For defects where the ground state has $S = 0$, which therefore do not exhibit EPR, there may be a narrow ZPL whose splitting under uniaxial stress along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ reveals both the symmetry of the site and the initial and final states of the transition [6].

As most transition metal-related sites have been attributed to nickel, from now on we concentrate on nickel-related sites. Section 2 discusses previously identified sites. Subsequent sections re-examine the data for three basic sites, and suggest new models for two of them, and section 6 does the same for the trigonal EPR defect NOL1.

2. Previously identified nickel-related sites

The most elementary basic sites for a transition metal such as nickel are the substitutional T_d site (Ni_s) and the interstitial T_d site (Ni_i). The Ni atom is too large to be incorporated at the hexagonal interstitial site, or as a split interstitial. More complex sites, of lower symmetry, are formed by annealing as-grown material [2], either due to accretion of diffusing vacancies or N_s; or by ejection of a carbon atom, to become C_i, to leave Ni at a so called paired or double-semivacancy (which we abbreviate as semivacancy) site [7]: the Ni atom sits at the centre of a divacancy. There is no evidence that Ni_s can jump into an interstitial site, and no mechanism for Ni_i to become Ni_s: probably the capture by Ni_i of a diffusing vacancy would cause conversion to Ni_s, but no observation of such a change has been reported.

It is a curious feature of the incorporation of nickel in HPHT diamond grown from nickel-containing solvent–catalyst that in type Ib diamond, where [N] > [Ni] ([X] represents the concentration of species X), the principal nickel-containing defect observed is substitutional nickel, Ni_s^-; whereas in type IIb diamond, where [B] > [N], the principal nickel-related defects observed have been attributed to interstitial nickel, Ni_i^+. The comments, based on theoretical modelling calculations, of Gerstmann *et al* [8] about the stability of various charge states of Ni_s and Ni_i as a function of the value of the Fermi energy E_F (determined principally by [N] and [B]) seem to imply that the *incorporation* of Ni as either Ni_s or Ni_i depends upon the value

of E_F, although this is not explicitly stated. For example, they say that for very low E_F, as Ni_s^{2+} is more stable than Ni_i^+, the latter does not exist in the material, even though it is the most stable state of Ni_i. As there is no mechanism for Ni_i to convert to Ni_s, this statement suggests that Ni is not incorporated as Ni_i in material with that E_F. The mechanism of incorporation of Ni as Ni_s or Ni_i has never been discussed. The discussion in [8] implies the validity of E_F at the growth surface. As discussed below in section 3.1, it is not even clear that the concept of general thermal equilibrium is valid in the bulk material. It is not clear experimentally whether Ni_s and Ni_i are both incorporated in the same crystal, or growth sector, and are made EPR active by electron donors or acceptors respectively. That both Ni_s^- and Ni_i^+ have sometimes been observed in the same sample [9] may be because they occur in different growth sectors. A recent modelling calculation has suggested that Ni_i is mobile in all charge states, and so would be expected to be present only when trapped by another defect [10]. There is no definite experimental evidence that Ni_i at a T_d site exists.

The EPR centre W8, has been shown beyond doubt to be Ni_s^-, $3d^7$. ^{61}Ni HFS has shown that it is nickel [3]; ^{13}C HFS from four nearest neighbours (nn) and twelve next nearest neighbours (nnn) shows that it is a substitutional site with T_d symmetry [11]; electron spin echo envelope modulation (ESEEM) has shown that $S = 3/2$ [11]. The only configuration to give this must be $3d^7$, which must correspond to Ni_s^-, $e^4t_2^3$, $^4A_2$.

To confirm the existence of Ni_i in a similar way using ^{13}C HFS would show four nn and six nnn, but no such HFS pattern has so far been observed.

Many other EPR spectra and optical ZPL have been attributed to nickel, as they occur only in HPHT diamonds grown from nickel-containing solvent–catalyst [1, 2]. Some of them have high symmetry and so may have a relatively simple structure. Some of them have been tentatively assigned to models.

The W8 defect occurs in type Ib diamond, in which the charge compensation for Ni_s^- is provided by the ionization of donor N_s^0 to form N_s^+. Correlated changes in opposite directions in the concentrations of Ni_s^+ and N_s^0 (P1 EPR centre) have been shown to be produced by x-ray- or photo-induced charge transfer [12, 13] (see below). This observation incidentally indicates the presence of EPR-inactive or invisible Ni_s^0, $3d^6$, in the material.

In type IIb diamond, the principal EPR centres are NIRIM-1, which in the 10 K range appears to have T_d symmetry, and somewhat less abundant NIRIM-2 which has C_{3v} symmetry [9]. The latter EPR spectrum has been correlated with the 1.404 eV ZPL [14]. A comprehensive theory of this defect has been developed [15]. It is shown to be trigonally distorted Ni_i^+, $3d^9$. That paper [15] did not speculate on the reason for the trigonal distortion, but it has been variously attributed to a vacancy or impurity [9] and a nn B_s^0 [16]. The more abundant EPR defect NIRIM-1 has been attributed to the T_d site of Ni_i^+, $3d^9$ [9]. This would be expected to show Jahn–Teller distortion to a lower symmetry [17], and there is indication of that at very low temperature, and even in the linewidth at 10 K where tunnelling between equivalent distortions leads to a pseudo-T_d symmetry [9]. The charge compensator giving Ni_i^+ in these two sites is probably B_s^0, which accepts an electron to form B_s^-. It is not clear whether Ni_s and Ni_i are simultaneously present in HPHT diamond, but observable by means of EPR only in the presence of donor N_s or acceptor B_s. (Ni_i^0, $3d^{10}$, would be EPR inactive.)

A trigonal defect NOL1, probably the same as NIRIM-5 [18], also found in heavily B-doped type IIb diamond, has been attributed to Ni_i^{2+}–B_s^- [16].

In this paper we suggest alternative models for NIRIM-1 and NIRIM-2. No new experimental data are presented in the paper; it merely draws together previously published data, and analyses all data for each defect, and considers the set of defects rather than each in isolation. It also considers in more detail than earlier discussion the effect of spin–orbit coupling, $\lambda L \cdot S$, where hL and hS are the orbital and spin angular momenta respectively of

the $3d^n$ configuration, and λ is the spin–orbit coupling parameter. In principle, this has three effects;

(a) it produces a fine structure splitting of the ZPL corresponding to transitions between states which have some residual orbital angular momentum,
(b) it produces a considerable departure of the g-values from the free spin g-value g_e for states which have some residual orbital angular momentum,
(c) even for states with quenched orbital angular momentum, its off-diagonal elements produce a shift of g-value, $\Delta g = g - g_e$.

Apart from the values of Δg for the Ni-related EPR centres, there is very little evidence of the effects of spin–orbit coupling. Fine structure observed on ZPL, other than phonon replicas, is typically <10 meV, suggestive of strong quenching effects such as covalency or the Jahn–Teller effect. The two examples discussed below are the only at best partially analysed systems.

3. A re-examination of the EPR centre W8, Ni_s^-, $3d^7$

There is no doubt that W8 is the best characterized nickel-related centre in diamond. From the EPR alone it is clear that the electronic configuration is $e^4 t_2^3$, as one would expect for a site of T_d symmetry, where e states have lower energy than t_2 states. The spin of this d^7 configuration would be the same for both high spin and low spin coupling, so it does not indicate which is appropriate for Ni_s^- in diamond.

The ground state is $^4A_2$, and one expects excited states $^4T_2$ at $10Dq$ and $^4T_1$ at $18Dq$: Dq is a measure of the cubic crystal field (CF). The energy of other states of d^7 (^4P and doublet states) depend upon the coupling scheme, but there is no information about them.

A ZPL at 2.51 eV is correlated with W8 [19], and its splitting under uniaxial stress is consistent with its corresponding to the transition $^4A_2 \Leftrightarrow {}^4T_2$ [20]; i.e. $10Dq = 2.51$ eV. Optically detected EPR of $^4A_2$ shows that it lies about 2.5 eV below the conduction band (CB) [13], so $^4T_1$ must lie in the CB.

The fine structure of the ZPL arises from a splitting of the $^4T_2$ excited state, which splits into $2 \times \Gamma_8 + \Gamma_7 + \Gamma_6$. The overall splitting is about 1 meV [20], very much smaller than the spin–orbit parameter of the free Ni^{3+}, $3d^7$, ion ($\lambda \sim 30$ meV) [17]. Nor does the fine structure splitting correspond to a simple interval rule for $J' = 5/2$ ($\Gamma_8 + \Gamma_6$), $3/2$ (Γ_8) and $1/2$ (Γ_7). However, this merely indicates that there is a large Ham factor [21], reducing the effects of spin–orbit coupling within the $^4T_2$ states, due to a dynamic Jahn–Teller effect.

The spin–orbit coupling also makes a contribution to the g-value of the $^4A_2$ state, which is close to g_e as the $^4A_2$ state has zero angular momentum, through matrix elements of $(\lambda \boldsymbol{L} \cdot \boldsymbol{S} + \mu_B \boldsymbol{L} \cdot \boldsymbol{B})$ between the $^4A_2$ and $^4T_2$ states, separated by $\Delta = 2.51$ eV:

$$g = g_e - 4\lambda/\Delta.$$

Here $\boldsymbol{B}$ is the applied magnetic field and μ_B is the Bohr magneton. So from the measured value of $(g - g_e) = 0.0296$ and $\Delta = 2.51$ eV, one can deduce that $\lambda = -9$ meV.

The off-diagonal effects of $\lambda \boldsymbol{L} \cdot \boldsymbol{S}$ are not reduced by the Jahn–Teller effect, so there must be some other reason that the deduced value of λ is also much smaller than 30 meV. None of the parameters fits comfortably into the standard CF theory for ionic salts. The ionic parallel would be Ni^{3+} in a tetrahedron of C^- ions. There are no examples of Ni^{3+}, but extrapolation from Ni^{2+} salts suggests that $10Dq \sim 2.5$ eV [17]. However, for covalently bonded systems the value of $10Dq$ is typically three times larger [17]. In contrast, local density functional (LDF) calculations, which do not do a very good job of predicting excited states [22], indicate

that the first excited state for Ni_s^- in diamond is at around 2 eV. The (extrapolated) value of λ for Ni^{3+} in ionic salts ($\sim$31 meV) will be reduced by covalent bonding [17].

The effect of overlap between Ni and its ligands is unclear. In ionic salts the closed ligand orbitals lie lower in energy than the 3d orbitals, so overlap between them produces mixed orbitals, the (full) bonding orbitals having mainly ligand character and the (open) antibonding orbitals having mainly 3d character. The situation in silicon [23], and possibly in diamond, is the reverse, so the orbitals of primarily 3d character are full, and the open antibonding orbitals have primarily ligand character: viewing this from the extreme, the ten 3d orbitals of the TM are full and the paramagnetism arises from the dangling bonds of the surrounding 'vacancy'. This is called the *vacancy* model [24]. This should lead to a value of λ intermediate between the value for Ni^{3+} and that for C ($\sim$3.6 meV) [25]. That the measured value from Δg ($\sim$9 meV) is much closer to that for C than Ni^{3+} shows that the wavefunction is primarily centred on the ligands. This corresponds to the *vacancy* model. This could also account for the relatively small value of Δ, as the paramagnetic ground state corresponds to the lowest state of V^-, $^4A_2$, and the first excited state of V^-, $^4T_1$, is at 3.15 eV for the empty V^- [26]. The *vacancy* model corresponds to the states 3d in the free Ni^{3+} ion lying below the ligand dangling bond, so admixture between them will push 3d down and the vacancy orbitals up. In T_d symmetry, this effect will be larger for t_2 orbitals than for e orbitals on the 3d ion; so it will be larger for the t_2^3, $^4A_2$ ground state than for the t_2^2e, $^4T_2$ excited state. So, that the measured value of Δ (2.5 eV) is somewhat smaller than the energy splitting of 3.1 eV for unoccupied V^- is in accordance with the *vacancy* model.

In addition to the unusually small value of the effective spin–orbit coupling parameter, the ligand HFS would be unusually large. The ^{13}C HFS parameters measured for W8 are also in reasonable agreement with the *vacancy* model [11].

The measurements of optically excited EPR [13] show that the energy $E(Ni_s^{-/0})$ lies at $E_{CB} - 2.5$ eV, where E_{CB} is the energy of the bottom of the CB or

$$Ni_s^- + h\nu(2.5 \text{ eV}) \Rightarrow Ni_s^0 + e_{CB},$$

where e_{CB} represents an electron at the bottom of the CB, and $h\nu$ is the absorbed photon. e_{CB} is captured by N_s^+:

$$N_s^+ + e_{CB} \Rightarrow N_s^0,$$

so the decrease in $[Ni_s^-]$, [W8], is matched by an increase in $[N_s^0]$, [P1]. Subsequent increase in the energy $h\nu$ produces another change at 3.0 eV corresponding to energy $E(Ni_s^{-/0})$ lying at $E_{VB} + 3.0$ eV, where E_{VB} is the energy of the top of the valence band (VB), or

$$Ni_s^0 + h\nu(3.0 \text{ eV}) \Rightarrow Ni_s^- + h_{VB},$$

where h_{VB} is a hole at the top of the VB. h_{VB} is captured by N_s^0:

$$N_s^0 + h_{VB} \Rightarrow N_s^+$$

so the increase in $[Ni_s^-]$, [W8], is matched by a decrease in $[N_s^0]$, [P1].

Theoretical estimates of $E(Ni_s^{-/0})$ using cluster modelling by Gerstmann *et al* [8] and by Goss *et al* [10] give $E_{VB} + 3.5$ and $E_{VB} + 2.9$ respectively, in good agreement with experiment, bearing in mind the considerable uncertainty of this type of calculation.

Hence, for appropriate assumed conditions, the parameters of W8/2.51 eV are in reasonable accord with expectation for Ni_s^-.

3.1. A comment on thermal equilibrium

The W8 defect occurs in type Ib diamond, in which the charge compensation for Ni_s^- is provided by N_s^+. This is to be expected, as the energy $E(Ni_s^{-/0})$ lies below $E(N_s^{0/+})$. As N_s^0 has local

C_{3v} distortion and N_s^+ has full T_d symmetry, there is a change in local coordinates between the equilibrium state of the two charge states. Thermal excitation of N_s^0 requires 1.7 eV [27]. For optical excitation there is no change of local coordinates, so this requires greater energy, 2.2 eV [28]. Hence, if there were complete thermal equilibrium in a crystal where $[N_s] > [Ni_s]$, one would have $[Ni_s^0] = 0$. $[Ni_s^-] = [Ni_s] = [N_s^+]$, $[N_s^0] = [N_s] - [N_s^+] = [N_s] - [Ni_s]$. In the optically excited EPR measurements described above, for $h\nu > 2.5$ eV electrons are transferred from Ni_s^- to N_s^+ via the CB. In principle, electrons could be transferred from N_s^0 to Ni_s^0 via the CB at $h\nu > 2.2$ eV. That this is not observed is what one would expect for complete thermal equilibrium, because although e_{CB} can be excited from the excess N_s^0, there is no residual Ni_s^0 to capture them, so they are recaptured by N_s^+. However, that it is possible to increase [W8], with a corresponding decrease in [P1], by x-irradiation [12] shows that there must be some $[Ni_s^0]$ remaining in the sample. As suggested by Collins [29] for another example, this is probably because there is no general thermal equilibrium. Charge transfer between N_s^0 and Ni_s^0 occurs relatively locally, so Ni_s^0 which are relatively distant from N_s^0 remain as Ni_s^0. Any e_{CB} excited optically from N_s^0 are recaptured locally, rather than diffusing through to compensate Ni_s^0. X-ray excitation is different, in that it excites electron–hole pairs, $e_{CB} + h_{VB}$, throughout the material. e_{CB} created close to Ni_s^0 can be captured, leaving h_{VB} to diffuse away to be captured by the majority N_s^0.

Hence, this experiment suggests that there is no general large scale thermal equilibrium.

4. A re-examination of the EPR centre NIRIM-2 and ZPL at 1.404 eV

As mentioned above the EPR centre NIRIM-2 [9] has been proved to correspond to nickel by an isotope shift observed on the ZPL at 1.404 eV [4], which has been shown to be correlated with NIRIM-2 [14]. Measured g-values for the Zeeman effect of the ZPL are also in agreement with those from EPR for the ground state [15]. The proposed model for this system, which has $S = 1/2$, is a trigonal site of $3d^9$, taken to be Ni^+ with no covalent bonds, i.e. in an interstitial site [15]. The ZPL has a 2.8 meV fine structure splitting into two lines, which arises from a doublet splitting of the ground state [14]. The NIRIM-2 EPR is observable only at very low temperatures ($\sim$4 K), so even at the highest temperature there should not be enough population of the excited state at 2.8 meV for it to be observed as an additional EPR line.

A crucial piece of evidence, which strongly constrains the model, is a measured value of $g_\perp = 2.5$ for the excited state [15]. In a trigonal CF, $3d^9$ has a lowest ^2E state and excited states ^2E and $^2A_1$. In first order the ^2E states have $g_\perp = 0$, and for the $^2A_1$ state $g_\perp = g_e$. The huge difference between the experimental value of $g_\perp$ and these predicted values indicates that there is appreciable mixing of ^2E and $^2A_1$ by spin–orbit coupling. This means that the spin–orbit coupling parameter λ is similar to the energy separation between ^2E and $^2A_1$. This energy separation must therefore be much smaller than the separation of the ground ^2E state from these two excited states, which shows that the CF is dominated by a cubic term. Pure cubic symmetry would lead to two states, $^2T_2$ and ^2E separated by $\Delta = 10Dq$ (1.4 eV). That ^2E is the lower state shows that the cubic term is octahedral, appropriate to a T_d interstitial site where the octahedrally arranged nnn dominate. A trigonal component K separates $^2T_2$ into ^2E and $^2A_1$ separated by $3K$, but it does not split the ^2E state. However, when taken together with spin–orbit coupling, there is a second order splitting of both ^2E states by $4K'\lambda'/\Delta$. This splitting in the ground state gives the fine structure of the ZPL of 2.8 meV; hence $K'\lambda' = +988$ meV^2. The measured value of $g_\perp$ of the upper state of the ZPL transition requires a specific value of $\lambda/K \sim 3.1$. The values of K' and λ' may not be the same as K and λ, as they may be affected by covalency, but on the assumption that they are the same, $K \sim -18$ meV and $\lambda \sim -55$ meV. The latter value is reasonably close to $\lambda \sim -76$ meV appropriate to a Ni^+ ion in ionic salts.

These numbers give for the g-value of the ground state (measured as $g_\parallel = 2.3285$ by means of EPR) $g_\parallel = g_e - 4k'\lambda'/\Delta - 8k'K'/\Delta = 2.26$, taking the orbital reduction factor $k' = 1$.

The extrapolated value of $10Dq$ for octahedral ionic salts of Ni^+ is ~ 0.5 eV, but that is for a typical ligand separation of ~ 0.22 nm. In diamond, the dominant nnn lie 0.18 nm distant, for which the CF would be much larger; so $10Dq = 1.4$ eV is not unreasonable.

The value of K seems small, showing that the trigonal distortion of the interstitial site is small. We have calculated [30] the value for K for a nn vacancy, on the assumption that as V^0 it has $S = 0$ like an isolated V^0 ($a_1^2 t_2^2$) (for trigonal symmetry this is not unreasonable as the configuration is probably $a_1^2 a_1^2$), and for a nn B^- or N^+. For a nn vacancy, $3K$ is probably greater than 1 eV, and is positive, which rules out the nn V model. This is anyway improbable, as the arrangement would be unstable against Ni_i moving into the adjacent vacancy. For a nn charged atom such as N^+ and B^-, the purely electrostatic effect of the point charge also gives $|3K| \sim 0.5$ eV, the sign depending upon the sign of the charge, negative K being associated with B^-, but the magnitude is likely to be increased considerably by changed overlap of the wavefunctions. Hence, it seems very improbable that the symmetry-lowering element is a nn vacancy or impurity. Gerstmann *et al* [8] have theoretically modelled the nn site in Ni_i–B_s, and find that it is more likely to exist as $(Ni_i$–$B_s)^+$, Ni_i^{2+}–B_s^-, which has a ground state $^3A_2$, so $S = 1$: this system is discussed further in section 6. A more distant vacancy or impurity along $\langle 111 \rangle$ would give a smaller value of $3K$. For, example for B^-, at a site beyond a nn C atom, or one completely opposite a nn C atom, both 0.308 nm distant from Ni_i^+, the contribution would be purely electrostatic, and reduced by a factor of 8 to 3 K ~ -63 meV, remarkably close to the measured value. However, one has to explain why either of these sites for B^- is more probable than other neighbouring sites, which would give rise to defects of lower symmetry, which are not observed. If NIRIM-2 were Ni_i^+, with B^- at a site distant 0.308 nm on the opposite side of Ni_i^+ from a C nn, electrostatic attraction could pull Ni_i^+ through the hexagonal interstitial site into the T_d site adjacent to B_s^-. That suggests that the site 0.308 nm from Ni_i^+, beyond a nn C, is the more likely.

The detailed CF theory of NIRIM-2 does not give complete accord with experiment, but it is close enough to indicate that a trigonally distorted T_d interstitial site is the likely model of NIRIM-2 [15]. This interpretation of NIRIM-2 is critically dependent on the value of $g_\perp$ for the excited state. If the trigonal CF, K, were much larger, the same fine structure of the ZPL could be accounted for by much smaller λ, but the value of $g_\perp$ for the excited state would be close to zero.

Another possible interpretation of the small trigonal distortion is offered by the indication of some, but not all, cluster calculations for the interstitial site having a spontaneous trigonal distortion [31, 32]. For example, Johnson and Mainwood [32] calculated $3K \sim 370$ meV. This might provide an explanation of NIRIM-2 as a self-distorted T_d interstitial site.

Before leaving the discussion of NIRIM-2, we should examine whether Ni_i^+ is the only nickel-related system which could explain the data. The salient features are $S = 1/2$, a ^2E ground state and a ^2T excited state with a trigonal distortion. Apart from $3d^9$ ($t_2^6 e^3$) in an octahedral CF, these parameters would be satisfied by $3d^1$ (e^1) in a tetrahedral CF (Ni_s^{5+}), and for low spin by $3d^7$ ($t_2^6 e^1$) in an octahedral CF (Ni_i^{3+}) or $3d^3$ (e^3) in a tetrahedral CF (Ni_s^{3+}); and even by $3d^7$ in a semivacancy site [7] (Ni_{sv}^{3-}). All of these possibilities are extremely unlikely charge states, so the Ni_i^+ model seems the most likely.

5. A re-examination of the EPR centre NIRIM-1

The NIRIM-1 EPR spectrum is exhibited by the diamonds which exhibit NIRIM-2, and it is present in greater concentration [9]. This suggests that it may be the undistorted T_d site of Ni_i^+.

NIRIM-1 has cubic symmetry at higher temperature ($\sim$77 K) but shows anisotropic line broadening at low temperature ($\sim$4 K) indicative of Jahn–Teller distortion, which becomes averaged at higher temperature. No ^{13}C HFS is observed, even for the minimum linewidth of $\Delta B_{pp} \sim 0.2$ mT at $10 K$. The ^{2}E ground state for Ni_i^+, 3d^9, would be expected to show Jahn–Teller distortion, like the many ionic salts of Cu^{2+} [16]. If the interpretation of NIRIM-2 is correct, the value of $10Dq$ for NIRIM-1 should also be close to 1.4 eV; but no ZPL has been associated with NIRIM-1, which is surprising.

Optically detected EPR has been observed for NIRIM-1 [33]. A marked increase in [NIRIM-1] with a threshold at 1.98 eV is interpreted as strong evidence that $E(Ni_i^{0/+})$ lies at $E_{CB} - 1.98$ eV:

$$Ni_i^0 + h\nu(1.98 \text{ eV}) \Rightarrow Ni_i^+ + e_{CB}.$$

That this excitation involves promotion of an electron to the CB, rather than from the VB, is said to be shown by the changes produced for $1.8 < h\nu < 2.0$, where a marked increase in [P1] is interpreted as capture of e_{CB} by N_s^+:

$$N_s^+ + e_{CB} \Rightarrow N_s^0,$$

e_{CB} having been produced by optical excitation with a threshold of 1.8 eV from some unidentified electron trap

$$X^- + h\nu(1.8 \text{ eV}) \Rightarrow X^0 + e_{CB}.$$

The simultaneous slight decrease in [NIRIM-1] in the presence of e_{CB} is taken to arise from

$$Ni_i^+ + e_{CB} \Rightarrow Ni_i^0,$$

so confirming the assignment of Ni_i^+ for NIRIM-1.

This measurement of the energy $E(Ni_i^{0/+})$ is in marked contrast to the theoretical estimates using cluster models at $E_{CB} - 3.3$ eV [8] and $E_{CB} - 3.8$ eV [10] respectively.

A further contrast with the prediction of one of the cluster models is that Ni_i is found to be extremely mobile in all charge states [10], so one would not expect to find isolated Ni_i^+. However, it could be stabilized by association with some nearby atom pinning defect (as for instance in NIRIM-2).

There is another major problem with this interpretation of NIRIM-1. The value of Δg ($=-4\lambda/\Delta$) is measured as 0.0089, which if Δ is assumed to be $\sim$1.4 eV leads to $\lambda \sim -3$ meV. This is completely incompatible with the value of λ indicated by the closely similar site of NIRIM-2 ($\sim$−55 meV).

The absence of resolved ^{13}C HFS for NIRIM-1 [9] is argued [31] to indicate Ni_i^+ as LDF theory indicates a very small HFS for the nn atoms, $A \sim 1$ MHz for nn and $\sim$9 MHz for nnn. This contrasts with the other possible cubic model for NIRIM-1, Ni_s^+, 3d^5, for which the theory shows that ^{13}C HFS would have been well resolved, $A \sim 35$ MHz for nn [31]. In contrast to Mn_s^{2-}, 3d^5, in silicon, which is high spin, $S = 5/2$ (t$_2^3$e^2), LDF theory predicts that Ni_s^+, 3d^5, in diamond is low spin, $S = 1/2$ (e^{4}t$_2$) [31]. The value of Δg for NIRIM-1 is much like that for 3d^5, Mn_i^{2+} and Mn_s^{2-}, in silicon in the high spin state. But this $S = 5/2$ state shows a cubic field splitting of the sextet into $\Gamma_8 + \Gamma_7$, which gives a well resolved structure in the EPR spectrum [34]. No such structure is observed for NIRIM-1. The ^{2}T$_1$ ground state for low spin would be subject to Jahn–Teller distortion, and also to splitting by spin–orbit coupling into $J' = 3/2$ (Γ_8) and $J' = 1/2$ (Γ_7) states such as Ir^{4+} in $(NH_4)_2PtCl_6$ for which the g-value of the lower $J' = 1/2$ state is given by $-(1/3)g_e - (4/3)k$, where k is an orbital reduction factor $1 \geqslant k$. Hence, for this first order theory, the numerical value of $|g|$ must be less than g_e, $\Delta g < 0$. However, Thornley [35] has shown that spin–orbit admixture of the excited t$_2^4$e state contributes $\sim$+8$\lambda/3\Delta$, which as g is negative increases its magnitude; this would indicate for

the observed Δg a value for $|\lambda|$ in excess of about 5 meV, not unreasonable in comparison with Ni_s^- ($\sim$3 meV). So, it is only the absence of ^{13}C HFS that makes the NIRIM-1 EPR spectrum inconsistent with Ni_s^+. It is not clear how definitely a HFS of this magnitude can be ruled out by the measurements so far made on a wide and weak EPR line.

As a model for NIRIM-1, Ni_s^+ has the advantage over Ni_i^+ that it is not predicted to be mobile by the cluster model calculations.

How does the possible assignment of Ni_s^+ as NIRIM-1 fit with the optically excited EPR at 1.98 eV? The cluster model calculation puts the energy of $Ni_s^{2+/+}$ at $E_{VB} + 1.6$ eV [8, 10]. This suggest that one should examine the possibility that the excitation at 1.89 eV corresponds to

$$Ni_s^{2+} + h\nu(1.98\ eV) \Rightarrow Ni_s^+ + h_{VB}.$$

Ni_s^{2+}, $3d^4$, would for low spin coupling correspond to e^4, $S = 0$, and so would be unobservable by means of EPR.

The main reason for rejecting this possibility is the optically excited changes observed between 1.8 and 2.0 eV, as explained above. One uncertainty about this explanation is the necessity to invoke an unidentified electron trap X^-: one would expect this species to be detectable by means of EPR as either X^- or X^0. No defect is known with an energy $E_{CB} - 1.8$ eV. However, the cluster model calculations put several nickel-related defects near to $E_{VB} + 1.8$ eV. If we assume $E(Ni_s^{2+/+})$ to be $E_{VB} + 1.98$ eV, the threshold at 1.80 eV could correspond to $E(Ni_i^{0/+})$ or $E(Ni_i^{+/2+})$: to fit with other aspects of the cluster model these defects would have to be trapped by another nearby defect. If the process at 1.80 eV generates h_{VB}, rather than e_{CB}, the change in the concentration [P1] could not correspond to

$$N_s^0 + h_{VB} \Rightarrow N_s^+ \tag{1}$$

as that takes [P1] in the wrong direction. In contrast, the reaction

$$Ni_s^- + h_{VB} \Rightarrow Ni_s^0$$

takes [W8] in the direction observed, which is difficult to explain on the supposition of excess e_{CB}.

There is a possible model for h_{VB} increasing the P1 EPR. This is based upon the discovery of Nadolinny [36] that in some Ni-containing type Ib diamond, pairs of associated Ni and N atoms are incorporated (Ni_s–N_s) sufficiently close together that dipolar interaction between the two paramagnetic species in the form (Ni_s^-–N_s^0) shifts and broadens the EPR of both species with the result that neither is observed. If such a species absorbed h_{VB},

$$(Ni_s^-\!-\!N_s^0) + h_{VB} \Rightarrow (Ni_s^0\!-\!N_s^0). \tag{2}$$

The removal of the paramagnetic Ni neighbour would allow the N_s^0 component to contribute to the P1 EPR: hence the concentration [P1] would appear to be increased by the absorption of h_{VB}.

This model could be confirmed if it were possible to monitor the change of [N_s^+] which accompanies that of [P1]. For process (a) these would change equally in opposite directions, whereas for process (b) the apparent change of [P1] would give rise to no change of [N_s^+]. However, it is experimentally difficult to monitor the changes of far IR absorption of [N_s^+] produced by optical illumination in the near IR/visible regions.

A confirmation of the model of NIRIM-1 as Ni_s^+ would be produced by observation of ^{13}C HFS in the EPR spectrum, which would probably require a sample isotopically enriched in ^{13}C.

Note that the interpretation of NIRIM-2 as a self-distorted T_d interstitial site would be incompatible with NIRIM-1 as the undistorted T_d interstitial site, but not with NIRIM-1 as Ni_s^+.

6. A re-examination of the EPR of NOL1

Nadolinny *et al* [16] have speculated that the EPR centre NOL1 is axially distorted Ni_i^{2+}, $3d^8$, with B_s^- along $\langle 111 \rangle$ at an unspecified distance. The ^{11}B HFS is very small suggesting little unpaired spin density on B.

The salient properties of NOL1 are that $S = 1$, $\Delta g_\parallel = +0.022$ and $\Delta g_\perp \sim 0$. The measured value of D (5.7 cm^{-1}, 171 MHz) is of little help in interpreting a model as there are probably large third order contributions. The accuracy of the determination of $\Delta g_\perp \sim 0$ is probably quite low.

Gerstmann *et al* [8] have theoretically modelled Ni_i^{2+}–B_s^-, and find it to be stable, but they do not estimate g-values, or D, or the spin density on B^-.

For Ni_i^{2+} in T_d symmetry, one can extrapolate from NIRIM-2 to get $\Delta \sim 0.8$ eV and $\lambda \sim -30$ meV: this would give $\Delta g = -8\lambda/\Delta = 0.3$. An axial perturbation would separate the first excited T_2 state into E and A_2 separated by K giving $g_\parallel - g_\perp = 8\lambda K/\Delta^2$, with a mean Δg equal to that for cubic symmetry. This immediately shows up two problems: (a) the measured Δg_{av} is much smaller; and (b) $g_\parallel - g_\perp \sim \Delta g_{av}$, showing that $K \sim \Delta$, a very large trigonal perturbation.

Nadolinny *et al* [15] noted parallels between the properties of NOL1 and the centres in silicon, $Fe_i^0 B_s^-$ and $Fe_i^0 Al_s^-$ [37–40]. However, there are notable differences:

(a) the ^{11}B and ^{27}Al HFS indicates much larger spin density, indicating greater overlap of the 3d wavefunction onto the adjacent impurity,

(b) $|g_\parallel - g_\perp| \ll |\Delta g_{av}|$, showing that the trigonal component of the CF is at least an order of magnitude smaller than the cubic component,

(c) $\Delta g_{av} \sim 0.07$, so $\lambda/\Delta \sim 10^{-2}$.

For the free Fe_i^0 ion $\lambda \sim 14$ meV; so for the interstitial in silicon $\lambda \sim 10$ meV and $\Delta \sim 1$ eV seem reasonable values. Hence, the parallel drawn by Nadolinny *et al* is dubious.

Returning to considering Δg_{av} for NOL1, taking $\Delta \sim 1$ eV, requires $\lambda \sim -3$ meV. This is incompatible with Ni_i, and much more like the case for Ni_s^- or Ni_s^+. As the trigonal perturbation is large, it is likely that the perturbing atom is in a nn position. Gerstmann *et al* [8] have theoretically modelled Ni_s^{2+}–B_s^-, which they claim to have an $S = 0$ ground state. If there were a covalent bond between Ni_s and B_s in a paramagnetic defect, the ^{11}B HFS would be very large, similar to that of ^{14}N in the EPR centre P1 (N_s^0–C_s^0). The small ^{11}B HFS suggests that the boron is in the form B_s^0, sp^2 bonded with three C ligands. The B_s^0 atom would relax back into the plane of these three ligands, so there is little overlap of the unpaired electron on the nickel atom. The lack of a covalent bond between Ni_s and B_s leaves Ni_s covalently bonded to its three C ligands. In heavily B-doped type IIb material the charge of Ni_s is likely to be positive. Even spin requires an even number of unpaired electrons, suggesting Ni_s^+, $3d^6$. We have seen that in T_d symmetry with four covalent bonds, $3d^6$, Ni_s^{2+}, is t_2^6, $S = 0$. But, in the very strong axial CF, the single electron states are a_1, e' and e''. That $S = 1$ suggests a ground state $(e')^4 (e'')^2$, $^3A_1$.

Such a defect, $C_3 Ni_s^+ B_s^0 C_3$, would have λ appropriate to a covalently bonded system, a very strong axial component of the CF and very weak ^{11}B HFS, as found experimentally.

This suggests that the stable state of Ni_s^{2+}, in the presence of large [B_s], becomes unstable when B_s^- is a nn. Ni_s^{2+}–B_s^-, $3d^6$, breaks up by transferring the electrons from the Ni_s–B_s bond, one to nickel and one to a distant B_s^0. Note that this is at variance with the predictions of the theoretical modelling mentioned above [8].

How could one confirm this speculative model of NOL1? One would expect strong ^{13}C HFS from the three ligands of Ni_s^+. This would probably be difficult to observe on the $\Delta M_s = 2$

transitions, which are the only ones so far to have been observed for NOL1. As $D = 171$ GHz, one would need to observe EPR near $h\nu = 170$ GHz to find the $\Delta M_s = 1$ transitions, preferably in a sample enriched in ^{13}C.

7. Conclusions

This paper has sought to contribute to the debate about the atomic models for some of the more basic nickel-related defects in diamond, and about whether interstitial nickel occurs in isolation from some pinning defect. It relies on comparison between different measurements and modelling calculations for different defects to get a mutually consistent interpretation. It uses pieces of evidence which have been only sketchily considered before, the effect of spin–orbit coupling, for which the most valuable contribution considered is that to Δg, and the magnitude of the CF.

This re-analysis suggests that the interpretation of NIRIM-1 as Ni_i^+, 3d^9, at a T_d site is less likely than that as Ni_s^+, 3d^5; and that NIRIM-2 is probably Ni_i^+, 3d^9, with the nearest C–C bond directed away from the Ni atom replaced by C–B$^-$, with B$^-$ further away from Ni.

The latter model suggests that Ni_i has to be captured by another point defect to be held in a static defect, in agreement with recent modelling calculations [10].

Re-analysis of the trigonal, boron-related defect NOL1, suggests that $\text{Ni}_\text{s}^+\text{B}_\text{s}^0$, a nn configuration with no connecting covalent bond, is more likely than the previously suggested Ni_i^{2+}–B_s^-.

The proof of the correctness of these new models is not easy, but methods of obtaining proof have been suggested.

Acknowledgments

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