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# Optical Centers Related to 3d Transition Metals in Diamond

Alexander Yelisseyev\* and Hisao Kanda<sup>1</sup>

Institute of Geology and Mineralogy, Russian Academy of Sciences, Siberian Branch, 3 Ac. Koptyug Avenue, Novosibirsk 630090, Russia <sup>1</sup>National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

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In the last three decades, extensive experimental studies have revealed numerable optical systems related to 3d transition metal (TM) ions in synthetic high-pressure, high-temperature (HPHT) and natural diamonds. Most of them were associated with nickel and cobalt and only a few are due to other TMs. A lot of structure-sensitive physical techniques including electron paramagnetic resonance (EPR) have been used to determine the structure of the centers in as-grown HPHT diamonds and the main trends in impurity transformation upon annealing have been established. The defects ranged from the simplest such as TM in substitutional, interstitial and double semivacancy sites to complicated TM-nitrogen complexes. Unfortunately, only for very few TM centers the optics-to-EPR correlations have been proved reliably; on the other hand, many of the TM defects are nonparamagnetic. Spectroscopic data concerning TM centers in diamond is summarized, defect structure is discussed and some applications are considered.

#### 1. Introduction

Of all minerals, diamond is relatively impurity free. This is a consequence of its short, strong C-C bonds, which offer a large barrier against impurity bonding to the lattice. Nevertheless, most of the elements within the periodic table have been found as impurities in diamond using different analytical techniques.<sup>(1,2)</sup> By now, at least the following impurities have been introduced into diamond during its growth or by ion implantation with the aim of creating the defects: H, He, Li, Be, C, B, N, O, F, Ne, Na, Al, S, Si, P, Ar, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Y, Zr, Nb, Mo, Pd, Ag, Cd, Sb, Xe, Ta, W, Pt, Au, Tl, and Er.<sup>(3)</sup> Those in bold face have been found to form optical centers.<sup>(3)</sup> Thus, they were positively identified as being atomically bonded to the diamond lattice. The other impurities may be associated with inclusions. Optical spectroscopy in absorption, luminescence and its other versions is a powerful tool when

<sup>\*</sup>Corresponding author: e-mail: elis@mail.nsk.ru

investigating point defects in crystals, and several hundreds of different features related to point defects have been revealed in optical spectra during the period of their intensive study since the middle of the last century: Most of them are cited in a recent handbook.<sup>(4)</sup> Over 100 vibronic systems appear due to few impurities from those mentioned above, namely due to nitrogen (as the most common impurity), boron and silicon. This variety arises from different structural arrangements of these impurities, the number of which increases significantly due to their combination with radiation damage products, such as vacancies, and their aggregation caused by defect migration after high-temperature annealing.

Concerning transition metals (TMs), nickel and cobalt were shown recently to produce numerous optical centers under certain doping, implanting and annealing conditions. Other TM ions give rise, as a rule, to only one characteristic center each.

TMs are an important component of the medium where a diamond is grown in most commercial high-pressure, high-temperature (HPHT) diamond syntheses. Only small crystals are produced unless a solvent catalyst is used. Many substances can be used, but those that allow the largest single-crystal diamonds to be grown are generally transition metals.<sup>(5)</sup> The ability of a TM to react with carbon increases with the number of electron vacancies in its d-orbitals: TM elements such as Cu and Zn with no d-vacancies are inert and do not bond with carbon whereas Ti and V with many d-vacancies are carbide formers.<sup>(5)</sup> Elements such as Cr, Mn, Fe, Co and Ni with few d-vacancies are effective carbon solvents. TMs with intermediate reactivity attract carbon atoms in graphite without forming carbide: such a moderate interaction may catalyze the graphite→diamond transition in the diamond stability field. The capabilities of a catalyst to nucleate and grow diamonds under a high pressure may be modeled by its atomic size and electronic configuration. This model suggests that the most powerful elemental catalysts are Co, Fe, Mn, Ni and Cr.<sup>(5)</sup> These TMs are the most commonly used catalyst components for the commercial production of synthetic diamond under a high pressure. Surprisingly, despite the covalence radius of TM ions being more than 1.5 times larger than that of carbon (0.077 nm),<sup>(6)</sup> dispersed nickel and cobalt atoms are efficiently incorporated into a diamond producing a number of optical and paramagnetic centers. In silicon crystals with much larger space available in the lattice due to a larger Si covalent radius (0.118 nm), all 3d elements with the exception of Co have been found as point defects.<sup>(7)</sup> Nickel- and cobalt-related defects that form in a diamond during its growth are strongly affected by the presence of other impurities, particularly nitrogen and boron. Understanding their properties is important for science and technology. It is very important to know the structural form in which TM ions get incorporated into the diamond lattice and the properties of diamonds changed by them. On the other hand, TMs are usually the components of rocks surrounding a diamond in the natural environment and may be captured from the melt when a diamond grows. Thus, any information about TM states in natural diamonds helps in the reconstruction of their growth conditions as well as the postgrowth history.

Considerable experimental work on the investigation of the TM-ion-containing defects in diamonds using different optical spectroscopy techniques has been carried out in the last three decades. The correlations between optical and electron paramagnetic

resonance (EPR) systems have been established, a theoretical study has been made by several groups of researchers, and a general understanding of the TM behavior in diamond has been reached. Our task in the present paper is to summarize the spectroscopic data concerning optically active TM-related defects with particular attention to their structure, properties, relationship with other impurities (N, B), and the regularities of the mutual transformation of defects during annealing. This information is mainly scattered in the literature although it is necessary to take into consideration the recent short reviews by Collins, 2000<sup>(8)</sup> and Baker, 2002<sup>(6)</sup> as well as those by Neves and Lopes, 2001 and Nazare, 2004 included in refs. 9 and 10, respectively. At least some specific applications of diamonds containing TM ions are considered.

# 2. Experimental Techniques

Two experimental techniques give the most valuable information about point defects in diamond: optical spectroscopy and EPR spectroscopy. Diamond is transparent in a wide spectral range from far IR to 5.5 eV in UV. As a purely covalent crystal, the ideal diamond possesses no dipole moment and there is no absorption in the one-phonon spectral region (73-165 meV).<sup>(4)</sup> The intrinsic absorption (A) is observed only in the two- and three-phonon regions spreading from single to triple Raman frequencies (165–495 meV). Some absorption in the one-phonon region is related to vibrations of nitrogen defects-single substitutional atoms (C-centers), pairs (A-centers) and complicated nitrogen-vacancy complexes B; the latter contain supposedly four nitrogen atoms and a vacancy.<sup>(4)</sup> Absorption related to quasi-local modes of heavy atoms with a mass M>40 u is expected at lower energies, supposedly in the 15 to 70 meV region. Beginning from 0.3 eV, one can find absorption due to electronic transitions between defect levels: the most well known example is boron absorption. At photon energies hv > 0.5 eV, the electronic transitions in the defects dominate in absorption spectra. The optical features are usually narrow zero phonon lines (ZPLs) with structured vibronic sidebands at higher energies in absorption spectra or at lower ones in photoluminescence (PL) and cathodoluminescence (CL) spectra, which are a result of electron-phonon interaction. The absorption originates from the ground state, so ZPLs in the absorption spectra indicate the energies of the excited states. The luminescence corresponds to radiative transitions downwards from the excited state, although the center may return to the ground state via a nonradiative route. The luminescence covers a wide spectral range from ~5.24 eV (excitonic processes) to ~1 eV,<sup>(4)</sup> the latter value being close to the limit for radiative transitions, ~0.85 eV, established by the "rule-of-thumb".<sup>(11)</sup> At lower photon energies, the probability of multiphonon nonradiative transition becomes considerable and the luminescence is quenched in the diamond. For oxides or sulfides with heavier atoms in the lattice, the maximum phonon energy is lower ( $\sim 60 \text{ meV}$ ) and the transitions remain radiative to lower photon energies,  $hv \sim 0.3$  eV, which corresponds to 4 µm in the wavelength scale. Photoluminescence 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 what absorbed energies lead to the chosen ZPL transition. In this way, we obtain a diagram of excited energy levels of the defect that gives rise to the chosen ZPL.

Essentially, a vibrational sideband of an impurity-related optical center is formed due to the interaction with intrinsic lattice phonons as well as with local vibrations (the energy of local vibrations  $h\omega_L$  is above the energy range of matrix phonons) and quasilocal vibrations (the energy of quasilocal vibrations  $h\omega_{QL}$  is within the energy range of the matrix phonons) that are localized at atom fragments of the corresponding defect. The energy values and type of the local and quasilocal vibrations are determined by the masses of the vibrating atoms inside defects and the interatomic forces driving these vibrations. Several common peculiarities have been noticed in vibrational sidebands of vibronic spectra when studying the spectra of the optical centers associated with heavy impurity atoms:

- relatively low electron-phonon coupling (the Huang-Rhys factor  $S \le 1$ );
- relatively narrow lines (with spectral width ranging from 5 to 15 meV);

• low phonon energies ranging from 20 to 40 meV in the vibrational sideband.<sup>(3)</sup> Simple expressions were given to calculate the energy  $h\omega_{\rm QL}$  and the width of specific quasilocal vibrations  $\Delta h\omega_{\rm OL}$ :<sup>(3)</sup>

$$h\omega_{\rm QL} = h\omega_{\rm D} \sqrt{M_{\rm C}/3(nM_{\rm I} - M_{\rm C})},$$
  
$$\Delta h\omega_{\rm QL} = \pi/6 \times h\omega_{\rm D} \times (M_{\rm C}/(nM_{\rm I} - M_{\rm C})),$$
(1)

where  $M_{\rm I}$  and  $M_{\rm C}$  are the masses of a heavy impurity atom and of the host carbon atom,  $h\omega_{\rm D}=150$  meV is the Debye frequency of the diamond lattice, and *n* is the number of impurity atoms involved in the quasilocal vibration.

Thermal activation spectroscopy is used in the case of defects with shallow levels in the forbidden band, which are located near the valence or conduction bands in a semiconductor model: in this case, a free charge carrier is generated upon band-to-band excitation using ionizing irradiation (electron beam, X-rays or VUV-UV photoexcitation with a photon energy of  $hv>E_g=5.5$  eV) or at the photoionization of a deep center, and afterwards, the released carrier is captured by a trap. The trap parameters can be estimated when analyzing the shape of the glow curve, which is recorded with sample heating at a constant rate.

For 3d ions at sites of high symmetry, some electron states will still have orbital degeneracy, and so they should exhibit a fine structure due to spin-orbit coupling, which should be up to several meV for free ion magnitudes.<sup>(6)</sup> Many of the ZPLs exhibit a fine low-energy structure, typically between 1–10 meV because the spin-orbit coupling parameters are reduced by the covalent bonding or by the Jahn-Teller (J-T) effect.<sup>(6)</sup> Valuable information concerning the structure of the defects, namely, the symmetry of the site, and electronic states between which the transition occurs can be obtained from the analysis of splittings and shifts of the ZPL produced by the uniaxial stress along <100>, <111> and <110>.<sup>(12)</sup> The symmetry of the defect, spin and *g*-factor values can be deduced from the analysis of the ZPL behavior under a magnetic field effect (the Zeeman effect and magnetic circular dichroism).<sup>(13)</sup> The only direct indication of the atomic species involved may be given by a characteristic isotope shift (most of the TM ions, apart from Mn and Co, have several stable isotopes) but such measurement requires

very narrow lines. Typically, ZPLs have a linewidth of ~1 meV and only in one case, for the 1.40 eV system in low-nitrogen diamonds, the linewidth is ~0.16 meV, which allows one to associate it with Ni from isotope shifts.<sup>(14)</sup> The presence of a TM ion in the defect structure also follows from the low-energy quasi-local modes  $\omega_{QL}$  in the phonon replica in a vibronic system.<sup>(3)</sup> The implantation of some ions of the 3d group (Ti, Cr, Co, Ni and Zn) has produced specific optical vibronic spectra.<sup>(3)</sup>

EPR lines in diamond can also be very narrow, ultimately limited by the magnetic interaction with the nuclear magnetic moments of the 1.1% abundant <sup>13</sup>C isotope. 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.<sup>(15)</sup> The number and position of surrounding carbon atoms may be determined by the <sup>13</sup>C hyperfine structure (HFS) in the EPR spectrum. The identification of a paramagnetic impurity atom is obvious if it has a characteristic HFS (e.g., nitrogen is ~100% <sup>14</sup>N with I=1). For half of the 3d ions where the dominant nucleus has HFS, the impurity atom identification should be obvious, but for the other half, even the configuration identification does not identify the atom. To date, only 3d ions of four defects have been unambiguously identified by EPR spectroscopy: the W8 paramagnetic center has been shown to be Ni<sup>-</sup> by  $^{61}$ Ni (*I*=3/2) HFS<sup>(16)</sup> and the O4, NLO2 and NWO1 paramagnetic centers have been shown to be <sup>59</sup>Co (I=7/2) by its HFS.<sup>(17)</sup> In most cases it is difficult to understand whether a paramagnetic defect is due to a 3d atom and what atom it is. However, there is a tell-tale indication of 3d character on the basis of the fact that most defects in diamond have g-values close to that of the free electron,  $g_e$ , and a departure  $\Delta g$  from  $g_e$ ,  $\Delta g \sim \lambda/\Delta$ , is very small because of the small spin-orbit coupling  $\lambda$  and large distance between excited and ground states  $\Delta$ .<sup>(15)</sup> Thus, a larger than usual  $\Delta g$  can indicate a defect probably containing a 3d atom.

EPR gives information about the ground state whereas optical spectra contain that about both ground and excited states; most information will be obtained if both methods are used to observe the same defect. In principle, any point defect has an optical absorption and any with a multiplet ground state might exhibit EPR. Thus, all paramagnetic defects should have an optical analogue, but not vice versa. However, an optical spectrum may not contain a narrow ZPL as it occurs with most 3d-related defects in silicon,<sup>(7)</sup> and both optical and EPR spectra may be weak enough because of selectionrule or technical reasons. In most cases, the correlation of optical and EPR spectra of the same defect has been performed by comparing intensities of corresponding signals for a range of samples covering a wide range of defect concentrations. In principle, connected spectral effects such as optically detected magnetic resonance (ODMR)<sup>(13,18)</sup> or magnetic circular dichroism (MCD)<sup>(13)</sup> may be used to make the link, but there are only a few examples for diamond. The ionizing irradiation or illumination may be used to bring a defect to another charge state and make it paramagnetic. Photo-EPR, a study of the change in EPR intensity produced by monochromatic light illumination as a function of its photon energy, has been used in several cases to estimate the position of the defect level in the forbidden band.

# 3. Nickel in Diamond

#### 3.1 As-grown diamonds: optical measurements

Along with a well-known spectrum from the  $N_s^0$  donor nitrogen, a set of broad bands was found in the 50-to-125 meV range in the absorption spectra of synthetic type Ib diamonds, which were synthesized in short-term experiments. The set and position of these bands depended on the metal catalyst used.<sup>(19-21)</sup> These bands were located at 62, 108–114, 132, 160 and 165 meV (close to the Raman frequency) for the Ni-Mn-C growth system,<sup>(21)</sup> at 62.6, 88, 116.5 and 122 meV for Co-Fe-C, and at 62.6 and 75.5 meV for Ni-Fe-C.<sup>(20)</sup> They were associated with the formation of stable chemical Me-C bonds: Two degenerate vibrations,  $h\omega_3$  and  $h\omega_4$  (62 and 111.6 meV, respectively), were expected for the T<sub>d</sub> symmetry of the substitutional impurity ion whereas they could be split because of symmetry lowering. The new bands agree well with the vibrational spectra of cyanocomplexes of the corresponding metals.<sup>(20)</sup>

A spectrum containing a sharp peak at 165 meV, the Raman frequency of diamond, and additional bands in the 111-to-136 meV range with the most specific bands at 117 and 129.5 meV was related to a new, X, center typical of octahedral sectors of synthetic diamonds from Ni alloys.<sup>(22)</sup> The analysis of the recharge processes after irradiation/ illumination showed that the X center is a positively charged donor nitrogen N<sub>s</sub><sup>+</sup> that usually accompanies the nickel incorporation: the 1 cm<sup>-1</sup> absorption in the 165 meV line is produced by (5.5±1) ppm N<sub>s</sub><sup>+</sup> centers.<sup>(23)</sup>

In the region of electronic transitions, absorption spectra of abrasive grits obtained with Ni catalysts consist of two vibronic systems with 1.883 and 2.51 eV ZPLs, a broad featureless band centered at ~1.4 eV combined with the typical absorption of donor nitrogen at hv>2.4 eV.<sup>(24)</sup> The details of nickel-related absorption and PL spectra are shown in Table 1. The absorption spectra had a well-pronounced minimum at ~2.2 eV, which accounted for the green color of these diamonds.<sup>(25)</sup> This fact was in agreement with the observations of a green coloration reported in a thin near-surface layer, ~5 µm thick, of natural diamonds after Ni diffusion<sup>(25)</sup> and around nickel inclusions in synthetic diamonds. The features in the visible and mid-IR region correlate with each other.

Optical properties of synthetic diamonds (SDs) with different nitrogen contents and their variation within samples were described in ref. 22 and a stringent correlation between nickel and nitrogen-related defects/systems was observed. The 1.883 and 2.51 eV absorption bands were found to be dominant, and the 1.4 eV band was very weak in the samples with a high nitrogen content, ~250 ppm (Fig. 1(a)). At the average nitrogen concentration (~30 ppm), the 1.4 eV band dominates (Fig. 1(b)), whereas at lower nitrogen concentrations (5 to 10 ppm), the 1.40 eV vibronic system is strong and the 1.883 and 2.51 eV systems are weak (Fig. 1(c)). A broad absorption band centered at 1.40 eV dominates in (b) and (c). A structured absorption band at 1.8 eV in (c) is related to the 1.40 eV vibronic system; an additional series of lines was found near 3.1 eV. The absorption in the 2 to 5.5 eV range is due to donor nitrogen (C: center) as is seen in typical natural type Ib diamonds. A crystal grown from Ni exhibits a yellow color, although it has a slightly brownish tinge, as well as green and brown. With the addition of nitrogen getters to Ni, the color changes from green to brown as the concentration of the getter is increased.

Photolun	ninescenc	e spectra (P)	С)		PL excit:	ation (PLF	3) and absorption spectra				
ZPL	ZPL	Phonon	S	Symmetry	ZPL	ZPL	Phonon energies hw (meV)	S	Symmetry	Group	ESR
(eV)	(uu)	energy hou (meV	_	(uniaxial etress)	(eV)	(uu)	and hroad hand nositions (AV)		(uniaxial etress)		
				(007110			(1.0) enomiend minn more		(cente		
2.6668	464.8			$T_{d}$	3.120	397.3				Ι	W8 <sup>(57)</sup>
2.5634	483.5				3.104	399.3					
2.5618	483.8				3.093	400.8					
2.5602	484.1				3.078	402.7					
2.5587	484.4	21			3.065	404.4	79				
					2.510	494.0	16.5		$T_d$	I	
1.9143	647.5			$C_{2v}$						I	
1.9063	650.2										
1.8843	657.8	65			1.8843	657.8	61				
1.4035	883.1			$C_{3v}$					$C_{3v}$	[ ]	NIRIM2 <sup>(52)</sup>
1.4008	884.8	63, 160		i	1.4008	884.8	63, 160		i		(NE4 <sup>(32)</sup> ?)
					1.220	1016	64, 113, 152, 164			I	
2.971	417.1	108 or	3.7				Broad band at $E>3.0 \text{ eV}$ ,			II	
2.962	418.5	91, 135(34)					with a maximum at 3.7 eV				
2.468	502.2	43	1.9							II	
2.071	598.6	54	0.8		2.298	539.5	31, 50	1.6		II	
1.990	622.8	59			1.990	622.8	50 meV, band 2.18 eV			II	
1.939	639.4	59								II	
1.720	720.7	31	1.2		1.720	720.7	29	0.7		Π	NE4 <sup>(65)</sup>
1.715	722.7				1.715	722.7					
					1.693	732.2	50		Rhombic I, C <sub>2</sub> ,	Π	
1.704	727.4	58	0.4	Triclinic	2.532	489.6	65	6.0		II	
					2.404	515.5	35 meV, band 2.65 eV	2.5			

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Photolum	inescence	spectra (PI			PL excita	tion (PLE)	and absorption spectra				
ZPL	ZPL	Phonon	S	Symmetry	ZPL	ZPL	Phonon energies $h\omega$ (meV)	S	Symmetry	Group	ESR
(eV)	(uu)	energy ha (meV)		(uniaxial stress)	(eV)	(uu)	and broad band positions (eV)		(uniaxial stress)		
1.660	746.9	58	1.7	Monoclinic I	2.428	510.6	50	2.5	Triclinic or monoclinic	П	
1.578	785.7	57	0.6		2.009 1.987	617.1 623.8	48	2.3		Π	
1.534 1.508	807.8 821.8	65	2.1		1.864 1.693	665 732	No phonons, bands at 2.1, 2.32 and 2.36 eV			Π	
1.413	877.2	54	б		1.941 1.685	638.5 735.4	55 meV, band at 2.13 eV 39 meV, band at 1.85 eV	3.7 2.7		Π	
1.276	971.4	47	1.3				Broad bands at 1.90 and 2.21 eV			Π	
2.596 2.535	477.5 488.9	33, 74 36	5.7	Triclinic	3.380 2.596	366.7 477.5	32 meV, band at 3.5 eV 28 meV, band at 2.8 eV	3.5 4.0		III	NE2 <sup>(69,70)</sup>
2.495	496.7	41, 72	4.8		2.618	473.4	28 meV, bands at 2.9, 3.65 and 3.8 eV	4.5		III	NE1 <sup>(69,70)</sup>
2.369	523.2	40, 72	4.4	Triclinic	3.610 2.589	343.3 478.8	100, 191 meV, bands at 3.4 and 3.8 eV 29 meV, band at 2.78 eV	2.6 2.9		Ш	NE3 <sup>(69,70)</sup>
2.243	552.7	33	1.0							III	
1.921	645.1	40								III	
$\begin{array}{c} 1.882, \\ 1.854, \\ 1.800 \end{array}$	658.6, 668.7, 688.8				2.427	510.8	88 meV, band at 2.65 eV	3.1		III	
1.770	700.3	40, 62	1.1							H	
1.738	713.4	37								Π	
1.647	752.7	45			2.749 1.928	450.9 642.8	42 meV, band at 3.0 eV 42 meV, band at 2.19 eV			Ш	
1.562	793.6	40, 70	3.3	Monoclinic II, C <sub>2</sub>	3.219 1.562	385 793.6	Bands at 1.77, 3.0 and 3.3 eV 33, 71, 155 meV	3.0		Η	NE8 <sup>(88)</sup>

Wavelength increases and photon energy decreases within each group (I, II and III).



Fig. 1. Absorption spectra of synthetic diamonds from NIRIM, Japan, obtained using Ni catalyst: (a) a yellow-brown SD with  $\sim$ 250 ppm nitrogen, (b) a bright yellow-green SD with  $\sim$ 30 ppm nitrogen and (c) a green SD with low nitrogen content.<sup>(22)</sup>

In nitrogen-containing diamonds grown with the Ni catalyst, the 1.40 and 2.56 eV vibronic systems were observed both in  $CL^{(26)}$  and PL spectra.<sup>(27)</sup> Both 1.40 eV<sup>(28)</sup> and 2.56 eV<sup>(29)</sup> systems were reported previously in the CL of some natural type Ib diamonds with an intensity much lower than in the case of synthetic diamonds. However, at that time it was not recognized that these systems were not associated with nickel. Luminescence decay times of ~33 and 10.5 ns for 1.40 and 2.56 eV systems, respectively, were measured as reported in ref. 30. The 2.56 eV CL is quenched at ~200 K, whereas the 1.40 eV emission is practically insensitive to the temperature up to room temperature.<sup>(22)</sup>

During the ion implantation experiments, the nickel origin of the 1.40 and 2.56 eV systems was confirmed: these systems as well as lines at 2.059, 2.292, 2.431 and 2.632 eV in CL were produced after the Ni<sup>+</sup> implantation into natural type IIa diamonds with the subsequent annealing at 1650 K.<sup>(31)</sup> The analysis of the implantation depth and softness

*s* relative to the uniaxial stress effect allowed one to relate the 1.40 and 2.56 eV centers with  $s\sim1$  Pa<sup>-1</sup> and  $s\sim3$  Pa<sup>-1</sup>, respectively, to soft defects (supposedly vacancy-containing ones). The 2.059, 2.292 and 2.632 eV centers with s<0.2 Pa<sup>-1</sup> correspond to hard, maybe interstitial-type defects.<sup>(4)</sup>

The 1.40 eV ZPL is a doublet with components at 1.4008 and 1.4035 eV.<sup>(26)</sup> The vibronic structure is different in absorption and CL; only two phonon sidebands at 50 and 160 meV were identified.<sup>(32)</sup> Temperature-dependent measurements confirm that the 1.40 eV ZPL doublet is due to a split ground state.<sup>(14,24)</sup> In the samples with low nitrogen content, a fine structure related to natural nickel isotopes was revealed in the absorption/PL spectra: each of the doublet components had a fine structure due to five natural nickel isotopes with abundance ratios of [<sup>58</sup>Ni] : [<sup>60</sup>Ni] : [<sup>61</sup>Ni] : [<sup>62</sup>Ni] : [<sup>64</sup>Ni] = 67.76 : 26.16 : 1.25 : 3.65 : 1.16 (Fig. 2), and this confirmed unambiguously nickel incorporation in the 1.40 eV defect.<sup>(14)</sup>

All spectroscopic features associated with Ni and green coloration were typical only of the {111} growth sectors<sup>(22,33–35)</sup> in synthetic diamonds. The 1.40 eV system in absorption and CL was found to be polarized with a maximum intensity for the E vector parallel to the (111) growth plane and a minimum one for the E vector perpendicular to (111).<sup>(33,34)</sup> There is some difference in the polarization degree of the ZPL doublet components: ~100% and 30% degrees were determined for high-energy and low-energy components, respectively<sup>(34)</sup> (Fig. 3). Thus, the observed 1.40 eV system can be produced by a defect with two dipole moments oriented at angles  $\varphi$ =13.17 and 31.5° to the {111} growth planes (Fig. 3).<sup>(34)</sup> The 1.40 eV system remains polarized after annealing up to temperatures of ~2000 K, which suggests a substantial barrier (>5 eV) to the defect reorientation.<sup>(22,34)</sup>



Fig. 2. PL spectrum of a synthetic diamond recorded at 2 K showing the 1.40 eV zero-phonon doublet with a fine structure related to nickel isotopes.<sup>(14)</sup>



Fig. 3. Comparison of polarization behavior of the 1.40 eV (a) and 1.22 eV (b) ZPLs: (1) for  $E \parallel (111)$  growth plane and (2) for  $E^{\perp}(111)$ .<sup>(35)</sup>

A further decrease in nitrogen concentration (<5 ppm) results in an increase in absorption in both the continuous background at hv>2 eV and the 1.40 eV system with the appearance of a new vibronic system with a group of eight ZPLs near  $\sim 1.22 \text{ eV}^{(35)}$ : such diamonds demonstrate a strong brown color. For this system, the broad highenergy feature consisting of three components appears to be polarized at right angles to the broad low-energy feature (2 components), and the central 3-component feature exhibits very minor polarization effects (Fig. 3(a)).<sup>(35)</sup> For the 1.22 eV system, when the broad low-energy feature is at its most intense value, the broad high-energy feature is at its weakest intensity value, and this result suggests that two mutually perpendicular dipole moments exist at the 1.22 eV center.<sup>(35)</sup> When illuminated with hv < 1.7 eV light, the 1.22 eV system disappeared but it could be made to reappear using the full spectrum of a halogen lamp or 488/514 nm lines of an Ar<sup>+</sup> laser. Simultaneously, the 1.40 eV absorption demonstrated changes in the opposite direction so that its intensity decreases as that of the 1.22 eV line increases and vice versa. The 1.40 eV intensity plotted against the 1.22 eV intensity gives a straight line: thus, the 1.22 eV center was proposed to be a different charge state of the 1.40 eV defect.(35)

The uniaxial stress and Zeeman measurements showed the trigonal symmetry and S=1/2 spin of the 1.40 eV center; thus, the center was considered to be an interstitial Ni<sup>+</sup> atom in a 3d<sup>9</sup> state.<sup>(36)</sup> A high-resolution magnetic circular dichroism study of the 1.404 eV ZPL confirmed the spin values (1/2) and g-values for the ground ( $g_{\parallel}\sim 2.32$ ,  $g_{\perp}\sim 0$ ) and excited ( $g_{\parallel}\sim 0$ ) states.<sup>(37)</sup> The comparison of vibronic structures in absorption/photoluminescence excitation (PLE) and PL spectra and analysis of temperature and isotopic effects revealed a localized vibration mode (LVM) with  $h\omega\sim 165$  meV and determined the position of higher excited states at 1.501 and 1.513 eV. These states together with the 1.404 eV level are the components of the excited <sup>2</sup>T<sub>2</sub> state (split under the effect of the trigonal crystalline field and spin-orbital coupling).<sup>(32)</sup>

The CL measurements<sup>(26)</sup> of the 2.56 eV system at 50 K showed four closely spaced ZPLs that are about 1.6 meV apart and localized at 2.5634 eV (line b), 2.5618 eV (c), 2.5602 eV (d) and 2.5587 eV (e). The lines thermalized according to a simple Boltzmann

rule<sup>(26)</sup> and, at the lowest temperatures (<9 K), an additional feature at ~2.6668 eV emerged, although the authors did not comment on this. At high temperatures (50 to 200 K) a broad peak (a) at ~2.588 eV due to transitions from a higher excited state could be observed, and again thermalized according to a simple Boltzmann rule.<sup>(26)</sup> Later CL measurements on a large, high-quality, low-nitrogen synthetic diamond at about 8 K, showed that each of the lines (c), (d) and (e) was split into a doublet (line (b) could not be observed at this temperature) whereas the lowest energy feature was not split.<sup>(22)</sup> Measurements in ref. 22 indicate that this lowest-energy component is at 2.5568 eV and that the splitting of the lines is approximately 0.4 meV for (d) and (e), and approximately 0.3 meV for (c).

A similar picture was obtained from PL measurements, although the 0.4 and 0.3 meV splittings were not resolved.<sup>(27,38)</sup> Unfortunately, the labeling of the peaks reversed the notification used in ref. 26, and the energies of the components at 20 K were quoted as 2.5585 eV (line (b)), 2.5600 eV (c), 2.5615 eV (d) and 2.5631 eV (e). Below 5 K, an additional line, labeled (a) was observed at 2.5569 eV and was the dominant feature at this temperature. An intense narrow line at 2.536 eV was related to a local mode with an energy of 21 meV, that is supposedly associated with a heavy (Ni) ion.<sup>(38)</sup> According to uniaxial stress measurements, the 2.56 eV PL is associated with the electric dipole transitions from five excited states ( $\Gamma 6 + \Gamma 8$ ) to a common split ground state ( $\Gamma 8 + \Gamma 7$ ) in the center of the tetrahedral (T<sub>d</sub>) symmetry.<sup>(39)</sup> The PLE spectrum for the 2.56 eV emission consists of two broad bands, peaking at 4.8 and 3.65  $eV^{(40)}$  with a fine structure as a quintet of equidistant lines between 3.06 and 3.12 eV, with the most intense line being 3.065 eV.<sup>(41)</sup> This fine structure has been found in the absorption spectra.<sup>(22)</sup> Both CL and PL quench as the temperature increases to 200 K.<sup>(22,41)</sup> PL decay is nearly exponential with  $\tau$ =140 us at 2.3 K. Decay time  $\tau$  decreases along with the increasing temperature as expected by the population of the higher-energy sublevels (b-e) that have a higher transition probability,  $\sim 40$  times higher than level (a). At  $T \sim 8$  K, a slow component with  $\tau = 1.5$  ms appears:  $\tau$  decreases as the temperature grows and reaches a constant value (0.8 ms) at 20 K.(38)

The 1.883 eV absorption system consists of three ZPLs with one-phonon replicas peaking at 61 meV from them.<sup>(42)</sup> One should note that the ZPL position varies from paper to paper and sometimes the same authors give different values. For example, 1.883, 1.905 and 1.913 eV were given in ref. 42, but one can find 1.885, 1.907 and 1.915 eV in ref. 43, whereas most of the authors indicate 1.883 eV for the longwave component. Our precise measurements gave 657.8, 650.2 and 647.5 nm values in wavelengths, which correspond to 1.8843, 1.9063 and 1.9143 eV in photon energies (Table 1), but we shall continue referring to this system as the 1.883 eV system following most of the researchers.<sup>(22,24)</sup> Only the longwave ZPL component is present in the PL spectrum at 15 K; the other two lines appear at temperatures higher than 110 K, with a one-phonon side band peaking at 65 meV.<sup>(42)</sup> Thus, the excited state is split into three levels. The uniaxial stress measurements show the rhombic I symmetry (C<sub>2v</sub> point group) with an optical transition between the A<sub>1</sub> ground state and three excited states (B<sub>1</sub>).<sup>(43)</sup> AZPL at 1.891 eV (B<sub>2</sub>) was related to a transition from the ground state to a higher-lying excited state.<sup>(43)</sup>

The 2.51 eV center has a ZPL of a complicated structure spanning about 1.5 meV at 4.2 K with phonon replicas at ~16.5 meV from it.<sup>(44)</sup> The uniaxial stress measurements show that in absorption, there is a transition from the  ${}^{4}A_{2}$  ground state to the  ${}^{4}T_{2}$  excited state in the center of tetrahedral symmetry,<sup>(45)</sup> which coincides with Ni<sub>s</sub><sup>-</sup>. The excited state is split into a quartet by the second-order spin-orbit interaction. Both the 2.51 and 1.883 eV absorption systems are typical of nitrogen-rich diamonds.<sup>(22)</sup> These two systems are observed to anneal out at the same temperature range, a range that is associated with nitrogen aggregation.<sup>(35)</sup> The different symmetry of these two spectroscopic features indicates that they are related to different nickel defects.

A PL system with a ZPL doublet at 1.720/1.715 eV (720.7/722.7 nm) was observed in as-grown HPHT diamonds or after HPHT annealing at 1950 K.<sup>(46)</sup> This system is approximately symmetric in low-temperature PL and PLE spectra, with low-energy phonons being at 31 and 29 meV and the Huang-Rhys factors being S~1.2 and 0.7, respectively (Table 1).

A PL system with a ZPL doublet at 2.962/2.971 eV usually referred to as the 2.96 eV system, with  $S \sim 3.7 - 4.0$  and phonon energies  $h\omega \sim 91$  and 135 meV, was found in both synthetic diamonds as-grown from nickel alloys and natural diamonds (NDs). In synthetic diamonds this system was observed along with the 2.56 eV system<sup>(47)</sup> or S2 and S3 systems,<sup>(48)</sup> whereas in natural samples, it usually accompanied the N3 system. This PL can be excited in a broad band at hv > 3.0 eV with a maximum at  $\sim 3.7$  eV. The excited state is split into two sublevels and the decay time varies from 40 µs below 15 K to 135 µs between 30 and 150 K.<sup>(47)</sup>

#### 3.2 EPR and related optical/EPR phenomena in as-grown diamonds

Three types of site have been associated with 3d ions, all exemplified by nickel: substitutional, interstitial and double semivacancy sites. The theory proposed by Ludwig and Woodbury (LW)<sup>(7)</sup> suggests that substitutional and interstitial TM species can be understood on the basis of 3d electrons, split into e and t<sub>2</sub> states by the T<sub>d</sub> crystal field of the host. For Ni<sub>s</sub>, four electrons go into bonding combinations with the four neighbors leaving 3d<sup>6</sup>, whereas Ni<sub>i</sub> retains all ten electrons. The crystal field splitting acts in opposite senses for Ni<sub>s</sub> and Ni<sub>i</sub>, leading to  $e^4t_2^2$  and  $t_2^{-6}e^4$  configurations for Ni<sub>s</sub> and Ni<sub>i</sub>, respectively. A different view is when a substitutional nickel defect is seen as a vacancy weakly bonded to nickel, only altering the occupancy of the dangling bond orbitals.<sup>(49)</sup> In the negative charge state, nickel is weakly bonded to the surrounding carbons via 4s electrons. The d and s shells of nickel are then full and three out of four electrons are left in the dangling bond orbitals resulting in a *S*=3/2 spin state. Both theories are in agreement on the charge and position of nickel ions that give rise to the *S*=1/2 and *S*=3/2 spin states.

An EPR signal, referred to as W8, was observed three decades ago for the first time in a synthetic diamond grown in the nickel-containing system:  $g=2.0310\pm0.0005^{(50)}$  (Table 2). The Ni involvement in W8 was confirmed in ref. 51: a  $0.65\pm0.005$  mT hyperfine splitting from <sup>61</sup>Ni was observed in powdered specimens with 86% content of this isotope in comparison with its 1.2% natural abundance.<sup>(16)</sup> This center was studied in detail using the pulsed Fourier transform EPR technique later when large synthetic diamonds became

Center	Spin	Symmetry	$g_1$	$g_2, g_3$	Number	Model	Diamond	Refr.:	Phototransition
	S				[N]		type	struc-	energy, eV
								ture	
W8	3/2	Cub.	2.0310				SD/ND	(50)	$\downarrow hv > 2.5$ (59,109)
			2.0319			Ni <sub>s</sub> <sup>0</sup>		(51)	$\uparrow hv > 3.0$
									$\uparrow X, \downarrow hv < 2.1^{(69)}$
NIRIM1	1/2	Cub.	2.0112			$Ni_i^+$	SD	(64)	$\downarrow hv > 1.98^{(59)}$
		at T>25K							
		C <sub>3v</sub>							
		at T=4 K							
ME1	3/2	Cub.	2.02	2.02	6	$Ni_s$ 6 $N_s$ (in 4nn)	ND	(104)	
W31	1/2	Cub?	2.0020	2.0025		Ni <sub>s</sub> <sup>-</sup> ?	ND		
NIRIM2	1/2	Trig.	2.3285	0		Ni <sub>i</sub> <sup>+</sup> -X (V ?)	SD	(64)	
						$C_3 Ni_{v-v} + C_3 ?$		(68)	
Pal	1/2	Trig?	~2.25	0			ND	(65)	
NE4	1/2	Trig.	2.0227	2.0988		(C <sub>3</sub> Ni <sub>v-v</sub> C <sub>3</sub> )-	SD	(69,70)	
(AB1)			(2.0027)	2.0923				(73)	No PT effect <sup>(59)</sup>
AB2	1/2	Trig.	2.0072	2.0672			SD	(99)	$\downarrow hv > 1.67^{(59)}$
AB5	1	Trig.	2.037	2.022		Ni <sup>2–</sup> -N <sub>s</sub>	SD	(102)	$\downarrow hv > 1.88^{(59,109)}$
									↑ <i>hv</i> >2.49
NE9	1/2	Trig.	2.0910	2.1670	3	(C3 Niv-v N3)0	SD	(17)	
				2.0910					
NOL1	1	Trig.	2.0235	2.002		$Ni_{i}^{2+} -B_{s}^{-}$	SD	(67)	$hv > 1.6^{(32)}$
(NIRIM5)						C <sub>3</sub> Ni <sub>v-v</sub> <sup>2+</sup> C <sub>3</sub> ?		(68)	
Ro1	1/2	Tetr.	2.0151	2.2113		$Ni_i^+$ ?	ND	(103)	
AB3	1/2	Orth.	2.1105	2.0663			SD	(99)	$\downarrow hv > 2.26^{(59)}$
				2.0181					
AB4	1/2	Orth.	2.0220	2.0094			SD	(99)	$\downarrow hv > 2.06^{(59)}$
				2.0084					
NE6*	1/2	Orth.	2.0109	2,0207			SD	(69)	$hv > 3.44^{(69)}$
				1.995					$\downarrow hv < 2.2$
AB7	1/2	Orth.	1.9910	2.0078			SD	(104)	
				2.0046					
NE1	1/2	Mon.	2.1282	2.007	2	$(C_2 N Ni_{v-v} NC_2)^-$	SD	(87)	$\downarrow X,\uparrow hv>3.1^{(69)}$
				2.0908			ND		
NE3	1/2	Mon.	2.0729	2.0085	3	$(C_2 N Ni_{v-v} N_2 C)^0$	SD	(87)	
				2.0476			ND		
NE5*	1/2	Mon.	2.0903	2.039	2	N-C- Ni <sub>v-v</sub> -C-N	SD,	(70)	$hv > 3.44^{(69)}$
				2.0044		N-V- Ni <sub>v-v</sub> -V-N	ND	(69)	$\downarrow hv < 2.2$
						(C3 Niv-v N2C)-		(6,17)	
NE8	1/2	Mon.	2.0439	2.1772	4	$(CN_2 Ni_{v-v} N_2C)^+$	SD	(88)	
				2.0846			ND		
NE2	1/2	Tric.	2.1301	2.0100	3	$(C_2 N Ni_{v-v} N_2 C)^0$	SD	(87)	
				2.0931			ND		
AB6	1/2	Tric.	2.0742	2.0244			SD	(102)	No PT effect(59)
				2.0185					
NE7*	1/2	?	>2		1	(C3 Niv-v NC2)2-	SD	(69,88)	$hv > 3.44^{(69)}$
						· · · · -			$\downarrow hv \leq 2.2$

Table 2Paramagnetic centers related to Ni in diamonds.

\*:centers, which are nonparamagnetic in usual conditions and can be observed only after preliminary X-ray irradiation or photoexcitation.<sup>(69,70)</sup>

î intensity increase and ↓:intensity decrease under X-ray irradiation/illumination.

available. The T<sub>d</sub> symmetry was established and the g=2.0319 signal was shown to be due to substitutional Ni<sub>s</sub><sup>-</sup> with an effective spin of S=3/2.<sup>(51)</sup> The length of the C-Ni bond is 0.204 nm, which is a typical metal-ligand distance for other metal organic compounds. This means that there exists a lot of stress around this defect. The structure identification was possible thanks to a successful observation of the EPR hyperfine structure, which revealed three atomic shells of one Ni site, four and 12 equivalent carbon sites in the W8 center. These carbon sites are classified as nearest neighbor (n) and next-nearest neighbor (nn) sets of equivalent carbon sites around Ni<sub>s</sub>, respectively. W8 requires the presence of donors. Indeed, Ni<sub>s</sub><sup>-</sup> is observed in material containing substitutional nitrogen N<sub>s</sub>. Cluster calculations confirmed the stability of the center, its electronic and spin states (3d<sup>7</sup>, S=3/2 for N<sub>s</sub><sup>-</sup>) and its T<sub>d</sub> symmetry.<sup>(52-55)</sup>

Although both the EPR  $Ni_{s}^{-}$  (W8) signal and the strengths of the 1.883 and 2.51 eV absorption bands demonstrate a tendency to increase simultaneously and all signals were related tentatively to one defect, the ratio of the intensities of the 1.883 and 2.51 eV bands was not constant and was generally lower for diamonds with low  $Ni_{s}^{-}$  absorption.<sup>(56)</sup> A better correlation was obtained between the  $Ni_{s}^{-}$  and 2.51 eV absorption than with the 1.883 eV absorption. The concentrations of  $Ni_{s}^{-}$  up to 70 ppm were detected and a relatively weak absorption in the 2.51 eV system suggests that either the oscillator strength is very low or optical transitions occur at a minor defect with a concentration that increases approximately in direct proportion to the W8 concentration.<sup>(56)</sup>

The ODMR experiments showed that UV excited luminescence in the 2.8–2.6 eV range arises from two overlapping bands. One results from a localized transition with specific ZPLs near 2.56 eV in the Ni<sub>s</sub><sup>-</sup> (W8) center<sup>(27,57)</sup> and the other, being structureless and centered at  $\sim 2.15$  eV, is due to a transition from a distant deep nitrogen donor  $N_{e}^{0}$  to a shallow acceptor at 0.37 eV above the valence band.<sup>(57)</sup> Another example of a close relationship between substitutional nickel  $Ni_s^-$  and donor nitrogen  $N_s^0$  is that these signals demonstrate correlated changes in the opposite directions in EPR upon illumination<sup>(58,59)</sup> or X-ray irradiation.<sup>(60,61)</sup> This means that Ni<sub>s</sub> is present in a different charge state (Ni<sub>s</sub>, Ni<sub>s</sub>) in diamond and donor nitrogen serves as a charge compensator for it. The considerable decrease in the intensity of the Nis- signal upon illumination with two well-pronounced thresholds at 2.47 and  $\sim$ 3.0 eV is related to the transitions to the bottom of the conduction band and to the  $\Gamma$  point conduction band, respectively.<sup>(58)</sup> Electrons from Nis are captured by some defects with shallow levels, which operate as traps of the charge carriers: as a result, a signal appears in the curves of thermostimulated luminescence (TSL).<sup>(62)</sup> The return process proceeds by following a tunnel mechanism when an electron goes directly from the trap level to a deep center or by following a thermostimulated mechanism when an electron becomes free upon heating, after which it recombines with an ionized luminescence center. In both cases, the transition via an excited state of the Ni<sub>s</sub> center takes place.<sup>(63)</sup> The illumination with hv > 2.47 eV reduces considerably the intensities of the 1.88 and 2.51 eV absorption lines and this may indicate that some of these defects are also ionized upon illumination.<sup>(58)</sup>

Two other EPR signals in synthetic diamonds with low nitrogen concentrations are NIRIM1, which is isotropic above around 20 K (g=2.0112, S=1/2,  $T_d$ ) but exhibits a lower symmetry at 4 K, and NIRIM2 with a trigonal symmetry,  $C_{3v}$  ( $g_{\parallel}=2.3285$ ,  $g_{\perp}\sim 0$ ,  $S=1/2^{(64)}$ ). The center names originate from a title of the institute where the samples

have been grown: National Institute for Research in Inorganic Materials (NIRIM), Japan. These signals were associated with Ni<sup>+</sup> in an interstitial site (NIRIM1,  $3d^9$ , T<sub>d</sub>) and with a complex  $Ni_i^+$ -X (NIRIM2, 3d<sup>9</sup>,  $C_{3v}$ ), where X is a vacancy or a local charge compensator; the latter is possibly some other impurity.<sup>(64)</sup> Taking into account the results of the uniaxial stress, Zeeman measurements,<sup>(36)</sup> MCD<sup>(37)</sup> and ODMR experiments,<sup>(65)</sup> most of the researchers associate the 1.40 eV optical system with the NIRIM2 EPR center.<sup>(52)</sup> The cluster calculations in refs. 53 and 55 showed a trigonal distortion and symmetry lowering for Ni,<sup>+</sup>, which allowed one to associate it with the 1.40 eV optical system and to explain in this way its polarization properties.<sup>(53)</sup> However, the other authors obtained  $T_d$  symmetry for Ni<sup>+</sup><sub>i</sub>.<sup>(54)</sup> On the other hand, in the case of trigonal Ni<sup>+</sup><sub>i</sub> symmetry, one should expect a relatively low energy barrier (0.5 to 1 eV) for defect reorientation and polarization removal, which is in contradiction with a high thermal stability for both the 1.40 eV system and the NIRIM2 signal (up to 2400 K with an activation energy of about 5 eV).<sup>(54)</sup> To provide high stability, one should suppose some structural component X that accompanies nickel. It is not a vacancy because recent *ab initio* calculations showed the Ni,<sup>+</sup>-V structure to be unstable with the Ni atom relaxing toward the vacant site.<sup>(55)</sup> Taking into account the fact that boron is present in low-nitrogen diamonds, one can suppose it to be this additional X component. Calculations carried out for  $Ni_{i}^{+}-B_{e}^{-}$ ,  $Ni_{e}^{-}-N_{e}^{+}$ and Ni,<sup>+</sup>-B,<sup>-</sup> donor-acceptor complexes of Ni showed that all these defects were stable, of trigonal symmetry and had a number of gap levels.<sup>(66)</sup> The identification of NIRIM1 as  $Ni_{i}^{+}$  is only tentative; the  $Ni_{s}^{+}$  model can also explain its properties in terms of the spin and multiplet ground state.(55,66)

In low-nitrogen boron-containing HPHT diamonds, there is another paramagnetic center, NOL1, with a  $C_{3v}$  symmetry, S=1,  $g_{\parallel}=2.0235(5)$ ,  $g_{\perp}=2.0020(10)$  and a partially resolved <sup>11</sup>B hyperfine structure. NOL1 was associated with the  $(Ni_i-B_s)^+$  complex.<sup>(67)</sup> Illumination produces correlated changes in the intensities of NIRIM2 and NOL1 signals; thus, they are supposed to be different charge states of the same defect with the 1.40 eV and 1.22 eV optical systems, respectively.<sup>(68)</sup> Other authors suggest Ni<sub>s</sub>B<sub>s</sub>,<sup>(54)</sup> Ni<sub>i</sub>CB<sub>s</sub><sup>(55)</sup> and Ni<sub>v-v</sub><sup>(68)</sup> structures for NIRIM2.

The stress around Ni<sub>s</sub><sup>-</sup> relaxes upon low-temperature annealing with  $T\sim1700-1800$  K due to the displacement of one carbon neighbor into an interstitial position. A nickel ion moves towards a created vacancy and sits in the center of a divacancy, thus forming a NE4 center (Fig. 4) with a 3d<sup>5</sup> electronic state, S=1/2, C<sub>3v</sub> in refs. 69 and 70 or D<sub>3d</sub> in ref. 17 (Table 2). This site is also known as a double semivacancy<sup>(17)</sup> or a semivacancy pair in silicon and germanium.<sup>(71)</sup> This defect is an association of Ni<sub>s</sub> and vacancy V, in which the site of Ni has been readjusted. In this state, the metal ion is covalently bonded with six, approximately octahedrically positioned ligands at 0.18 nm (1–6 in Fig. 4). It is a distorted octahedral arrangement with a nickel ion at its center. Cluster calculations show that the VNiV (or Ni<sub>v-v</sub>) defect is stable with the 8 eV bonding energy and the strains around the Ni ion are much lower than in the case of Ni<sub>s</sub> and Ni<sub>i</sub>.<sup>(72)</sup> There are two specific planes in this structure. One contains the Ni<sub>v-v</sub> fragment and two of the carbon ligands (1 and 2 in Fig. 4); the (1–10) plane for the Ni<sub>v-v</sub> fragment is aligned along [111]. The other, (332), contains the other four carbon ligands (3–6) and the Ni at their center; this plane is normal to the first plane, and almost normal to the [331]



Fig. 4. A model of nickel (cobalt)-containing centers with the double semivacancy structure: a perspective view of a unit cell showing the double semivacancy site<sup>(8)</sup> with ligands numbered as in ref. 17.

direction, which contains atoms 1 and 2.<sup>(70)</sup> A special study showed that both systems NE4 and AB1 (which was observed later in synthetic diamonds from NIRIM, Japan) are related to one and the same defect with  $g_{\parallel}$ =2.0027,  $g_{\perp}$ =2.0923 (Table 2).<sup>(73)</sup> The ODMR experiments<sup>(65)</sup> showed that the NE4/ABI paramagnetic defect is associated with the 1.72 eV optical system (with 1.7207/1.716 eV ZPL doublet) in PL.<sup>(46)</sup>

The ODMR experiments showed that the defect responsible for the 2.96 eV doublet in optical absorption, which is usually observed in as-grown synthetic diamonds but requires some HPHT annealing to form, was also paramagnetic.<sup>(74)</sup> There is a single line with an intensity rapidly decreasing for crystal orientations diverging from the (110) plane: The resonance position changes from  $B_{\parallel}$  [110] at 0.84 T (g=3.05) to 1.02 T (g=2.51) at  $B_{\parallel}$  [110]+25° away from the [100] orientation, where B is the external magnetic field.<sup>(74)</sup> There is no fine structure that could help in center identification. Taking into account the fact that the 2.96 eV center is present in PL spectra of natural and synthetic diamonds with nickel-related centers, it is likely also of Ni origin, although Fe and Al as common elements in these crystals cannot be excluded.<sup>(74)</sup>

In most *ab initio* calculations,<sup>(54,55,75)</sup> the formation energies of  $Ni_s^0$  and  $Ni_i^0$  differ by more than 7 eV, with that of  $Ni_s^0$  being lower, which is in contrast with ref. 76 where the value for  $Ni_i^0$  is ~1.2 eV smaller. Taking into account a significantly higher formation energy of  $Ni_i^0$  and a low activation barrier to diffusion, we can propose that isolated  $Ni_i$  is unstable: for typical HPHT growth, the equilibrium  $[Ni_s]:[Ni_i]$  ratio should be ten or more orders of magnitude, and mobile  $Ni_i$  should be trapped at impurity sinks and/or diffuse out of the material during the growth. Ni in a double semivacancy site is characterized by the minimum elastic strain energy and the maximum stability relative to both substitutional and interstitial nickel.<sup>(77)</sup>

# 3.3 *High-temperature annealing*

The green color of low-nitrogen diamonds grown using a nickel-containing solvent changes to dark brown upon their annealing at temperatures higher than 1850 K. The only significant change is the appearance of a line at 2.39 eV and the growth of the 2.618 eV system (Fig. 5). At T>1950 K, the 1.40 eV system begins to decay, and it anneals out at  $T\sim2150$  K, leaving just weak lines at 2.39, 2.618 and 3.1 eV. These are superimposed on a continium absorption that extends to UV and gives the diamond a rather dull gray/ brown color.<sup>(78)</sup>

In nitrogen-rich synthetic diamonds that were initially yellow, the 1.883 and 2.51 eV absorption lines as well as a continuous absorption at hv>2.3 eV due to donor nitrogen become progressively weaker after annealing at high temperatures T>1950 K. At these temperatures, nitrogen becomes mobile and more than 20 new absorption lines appear (Fig. 6). The most intense lines are listed in Table 3 and their behavior with respect to annealing temperature is demonstrated in accordance with ref. 78. Several groups



Fig. 5 (left). The absorption spectra recorded at 77 K of a nitrogen-poor green diamond grown using a Ni solvent with a nitrogen getter (1) before annealing, (2) after 4 h of annealing at 1850 K, and (3) after 4 h of annealing at 2050 K.<sup>(78)</sup> The spectra (a) and (b) were shifted upwards for clarity.

Fig. 6 (right). Absorption spectra recorded at 80 K of a yellow nitrogen-rich synthetic diamond before annealing (1), and after annealing at 1950 K (2) and 2200 K (3), and natural sample (4).<sup>(46)</sup> Spectrum (2) is shifted upwards for clarity. In the inset, a fine structure between 2.2 and 2.6 eV after the subtraction of the background absorption is shown. The arrows in the inset show ZPLs at 2.296, 2.404, 2.427 (with replicas), 2.589, 2.596 and 2.618 eV, which are also observed in the PLE spectra (Table 1).

Table 3

Ni-related features in the absorption spectra of nitrogen-rich synthetic diamond and their behavior after annealing at 1950, 2050 and 2150 K. $^{(78)}$ 

Feature (line positi	tion)	Ann	ealing tempera	ture	EPR center
Energy,	Wavelength, nm	1950 K	2050 K	2150 K	
eV					
1.562	793.6	1	↑		NE8
1.693	732.2		0	0	
1.744	710.7		0	0	
1.794	690.9		0	0	
1.847	671.1		0	0	
1.938	639.6	1			
2.240	553.3	1	$\downarrow$	$\downarrow$	
2.267	<u>546.7</u>	1	↑	1	
2.296	539.8	1	$\downarrow$	$\downarrow$	
2.351	527.2	1	$\downarrow$	$\downarrow$	
2.383	520.2		0	0	
2.392	518.6		0	0	
2.404	515.6	_	0	0	
2.427	510.7 }		0	0	
2.465	502.8	↑		$\downarrow$	
2.476	500.6		0	0	
2.523	491.3	_	0	0	
2.574	481.5	_	0	0	
2.589	478.8	↑	↑		NE3
2.596	477.5	1	↑		NE2
2.618	473.4		↑		NE1
2.648	<b>468.1</b> )	_	↑		

The features given in bold italic type are present at 2150 K. The changes after annealing are indicated as follows: (–) no change relative to previous annealing; ( $\uparrow$ ) an increase in absorption relative to the previous annealing; ( $\downarrow$ ) a decrease in absorption (relative to the previous annealing); (0) completely annealed out. The zero phonon lines are underlined.

of lines change in a similar way: they are shown with the braces and arrows in Table 3 and each can be related to one vibronic system/defect. One can separate the 1.562 and 1.693 eV systems at low photon energies whereas the other lines are concentrated in the 2.2 to 2.7 eV region, with two broad bands at ~2.85 and 3.5 eV (Fig. 6, curve 2).<sup>(46,78)</sup> The set and intensity of the systems depend on the annealing temperature. Most of the features are related to some transient centers and only several systems remain in the absorption spectra after annealing at *T*~2250 K; the most intense have ZPLs at 1.562, 2.267, 2.589, 2.596 and 2.618 eV (Fig. 6, curve 3). The last three systems are usually observed simultaneously in synthetic diamonds, but the 2.618 eV system appears and saturates first in comparison with two other systems as the annealing temperature increases (Fig. 7(a)). All changes that took place after the annealing of synthetic diamonds were described for the first time in ref. 79 but it was not recognized that they were related



Fig. 7. Dependence of low-temperature absorption (a) and PL (b) spectra of SD recorded at 80 K on the temperature of the thermal treatment for intensities of different ZPLs.<sup>(46)</sup> The lines connecting the points of different types are only visual guides showing the trends in the behavior of absorption/PL systems. The correlation between optical and EPR systems is shown where it exists.

to Ni defects at that time. The 2.240, 2.267 and 2.296 eV lines, where the first two are ZPLs and the third is a phonon replica of the 2.240 eV line, appear only after preliminary illumination.<sup>(80)</sup>

Diagrams showing the changes in intensity of different optical systems in absorption (a) and PL (b) after isochronic annealing at 1950 and 2150  $K^{(46)}$  are presented in Fig. 7. These changes in the defect system are supposed to be a result of nitrogen motion and mutual defect transformation.

PL spectra of synthetic diamonds are considerably different when excited with UV (hv~3.5 eV), green (~2.5 eV) and red (~2.0 eV) light: the corresponding PL spectra are given in Figs. 8–10. The changes depending on the excitation wavelength are explained by different energy level diagrams/absorption spectra for different defects. In Figs. 8–10, the PL spectra of as-grown and HPHT annealed synthetic diamonds (at 1950 and 2250 K) are compared. The PL spectra of a natural diamond recorded at different excitation wavelengths are shown in Fig. 11 for comparison. Under UV excitation, the most specific feature of an annealed SD is a bright green PL with a broad band at  $\sim 2.3$  eV (Fig. 8) and a set of ZPLs resulting from three centers. The most intense ZPLs are 2.369, 2.495 and 2.535 eV, all related to different defects. These systems appear at the first stage of annealing but the 2.496 eV system saturates first whereas the others continue to grow as the temperature increases (Fig. 7(b)). These systems are usually accompanied by a weaker 2.96 eV system with a ZPL doublet at 2.962/2.971 eV (Fig. 8), which has already been mentioned in §3.1. Many new systems can be observed upon excitation with visible light: the most intense and reproducible PL systems are shown by combs in Figs. 9 and 10; their details are given in Table 1.



Fig. 8. PL spectra recorded under UV excitation at 80 K of a SD: as grown (1) and annealed at 1950 (2) and 2200 K (3).<sup>(46)</sup> The position of ZPLs is shown while the braces correspond to phonon replicas. A detail of spectrum (2) is given with a ×10 magnification (2a). The energy level diagrams for ground and lower excited states of NE1, NE2 and NE3 centers are given in the upper right corner. Figures near the arrows in the diagram show a ZPL position for corresponding electronic transition. The ground state levels of all centers are placed at E=0 for convenience.



Fig. 9. PL spectra under 488 nm  $Ar^+$  laser excitation at 5 K of a SD: as-grown (1) and annealed at 1950 (2) and 2200 K (3).<sup>(46)</sup> R indicates the Raman line. Spectra (2) and (3) are shifted upwards for clarity.



Fig. 10. PL spectra under 632.8 nm He-Ne laser excitation at 80 K of a SD: as grown (1) and annealed at 1950 (2) and 2200 K (3).<sup>(46)</sup> R indicates the Raman line. Spectra (2) and (3) are shifted upwards for clarity.



Fig. 11. PL spectra of the type Ia/B natural diamond from Yakutia, with yellow-green PL. Spectra were recorded at 80 K with different excitations: at 365 (1) and 430 nm (2) from a Xe lamp; at 488 (3), 514 (4) and 632.8 nm (5) from  $Ar^+$  (3, 4) and He-Ne (5) lasers.<sup>(46)</sup> R indicates the Raman line; spectra 2–5 are shifted upwards for clarity.

Following ref. 46, we divided the Ni-related systems in the absorption and PL spectra of synthetic diamonds into three groups depending on their behavior during annealing. The ZPLs of the corresponding systems are given below:

 Group I includes the systems that are present in as-grown SD and disappear after annealing.

Absorption: 1.883 eV, 2.51 eV and 3.1 eV systems.

PL: systems with 1.4008/1.4035 eV and 1.508/1.534 eV doublets, 1.883, 2.136, 2.408 and 2.468 eV systems and broad bands at 1.9 and 3.1 eV.

 Group II includes the systems that appear after annealing at 1950 K but decrease in intensity or disappear completely after annealing at approximately 2200 K. Absorption: 1.693, 2.351, 2.404 and 2.427 eV systems and photoinduced 2.240 eV system.<sup>(80)</sup>

PL: 1.276, 1.414, 1.573, 1.601, 1.647, 1.660, 1.704 and 1.715/1.720 eV doublet, 1.753, 1.787, 1.826, 1.939, 2.071, 2.157, 2.259, 2.307 and 2.481 eV systems.

 Group III includes the systems that appear after annealing at approximately 1950 K and become stronger/more intensive after further annealing at 2200 K. Absorption: 1.562, 1.647, 2.202, 2.589, 2.596, 2.618 eV and photoinduced 2.267 eV

Absorption: 1.302, 1.047, 2.202, 2.389, 2.390, 2.018 eV and photomduced 2.207 eV systems.

PL: 1.562, 1.647, 1.737, 1.770, 1.921, 2.243, 2.316, 2.369, 2.495, 2.535, 2.541 and 2.596 eV systems and a complicated system with a set of ZPLs at 1.882, 1.854 eV and so on.

Only the most intense lines are given above. The full list with several tens of features can be found in ref. 46. The detailed data on vibronic systems are given in Table 1. The photoinduced 2.240 and 2.267 eV systems were related to groups II and III taking into account their behavior during annealing.<sup>(78,80)</sup>

For the most intense PL systems, the PLE technique was used to obtain the absorption spectra. The PLE spectra with the 14 most intense PL systems are shown in Figs. 12–14, whereas the most important parameters such as ZPL position, symmetry and phonon energies in absorption, PL and PLE spectra are summarized in Table 1. The symmetry of the corresponding point defects was determined in the uniaxial stress measurements: it was found to be triclinic for the 1.660 eV,<sup>(81)</sup> 1.704, 2.535 and 2.369 eV PL systems;<sup>(82)</sup> monoclinic II (C<sub>2</sub>) for the 1.562 eV absorption/PL system,<sup>(83)</sup> orthorhombic for the 1.693 eV absorption system<sup>(84)</sup> and rhombic I for the 2.428 eV absorption system.<sup>(85)</sup> One can notice here a disagreement between symmetries of the 1.660 eV PL system and the 2.428 eV absorption/PLE system, which have been both related to one defect.<sup>(46,85,86)</sup> The polarization-resolved measurements in ref. 88 confirmed that both these systems are related to one defect supposedly of triclinic or monoclinic-I symmetry.

A splitting of the excited level is a typical situation for nickel-related centers in diamond: as a result of thermalization between the excited sublevels, a set of ZPLs and PL decay time vary considerably with temperature. The energy diagrams for a lower excited state of three centers with ZPLs at 2.369, 2.535 and 2.495 eV in low-temperature PL spectra are given in the inset in Fig. 8. These centers are responsible for the bright green luminescence of the annealed synthetic diamonds. Their lower excited state was found to split into two sublevels, with the distance  $\Delta E$  between the components being



Fig. 12 (left). PLE spectra of the 1.72 (a), 1.534 (b), 1.276 (c), 1.413 (d) and 1.991 eV (e) PL systems.<sup>(46,86)</sup> Fig. 13 (right). PLE spectra of the 2.071 (a), 1.704 (b), 1.660 (c) and 1.80–1.88 eV (d) PL systems.<sup>(46,86)</sup>

220, 61 and 123 meV, respectively (inset in Fig. 8). Only in the 2.535 eV center with minimum  $\Delta E$ =61 meV, the upper excited level is populated at liquid nitrogen temperature and two ZPLs, at 2.535 and 2.596 eV, are present in the PL spectra, although the latter is considerably weaker. In the other two centers with larger  $\Delta E$ , a higher temperature is necessary to populate the upper level.

Most of the absorption lines in the 2.2-2.6 eV range in synthetic diamonds annealed at 1950 K (Fig. 6, curve 2 and the inset) have no analogues in PL. The nonradiative relaxation of excitation in these cases may be a result of a complicated energy diagram and large phonon energy in diamond. A multiphonon quenching takes place at electronic



Fig. 14. PLE spectra of the S3 (2.495 eV ZPL, curve a), 2.535 (b), 2.369 (c),<sup>(87)</sup> 1.647 eV (d),<sup>(85)</sup> and 1.562 eV (e)<sup>(85,88)</sup> PL systems. The spectra of the SD samples were recorded at 80 K; all centers are related to group III.

transitions between the neighboring levels when the gap between them is about 1 eV or below. As can be observed from the PLE spectra in Fig. 14, there are several excited states in the case of group III centers with a distance between these states in the energy diagram of  $\sim 1 \text{ eV}$ .<sup>(46,78,86–90)</sup> A short wave excitation to the upper excited states is also followed by a multiphonon nonradiating relaxation and only transitions from the lower excited state are radiative. The absorption bands related to group III centers limit the transmission in the visible range from both short- and long-wavelength sides, and result in their greenish color, which is observed in {111} growth sectors of synthetic diamonds after annealing.

The annealing process is accompanied by the following changes in the one-phonon IR absorption spectra of nitrogen-rich synthetic diamonds upon HPHT annealing:<sup>(78)</sup>

- The intensity of the C component decreases and that of the A component increases;
- The intensity of the X component related to N<sup>+</sup> decreases;
- Total C+A+N<sup>+</sup> concentration decreases.

Taking into account the fact that new PL/absorption systems appear only in nitrogen-rich diamonds, one can suppose that a process of impurity aggregation with the formation of nickel-nitrogen complexes takes place during annealing<sup>(78)</sup> and the number of nitrogen atoms in a defect structure is supposed to increase as the annealing temperature grows.

Isothermal annealing is an alternative way to study defect transformation.<sup>(48)</sup> It is possible to obtain necessary information when analyzing the intensities of ZPLs at different points of a diamond plate in the direction from the outer face towards the seed using the confocal technique.<sup>(48)</sup> Each point on this line can be regarded as a sample with a different annealing time at a growth temperature of 1750 K and the annealing time increases with the distance. The results of such analysis are shown in Fig. 15(a), with nitrogen content in C and A forms given in panel (b) for comparison. The latter was calculated using conventional coefficients relating concentration and optical absorption from the one-phonon absorption spectra recorded locally, with the same step as PL using a FTIR spectrometer combined with an IR microscope. It can be seen that the degree of nitrogen aggregation increases as the distance (annealing time) increases (from left to right in Fig. 15). The first center to anneal out is the 2.56 eV Ni-related center, which was related to Ni<sup>-</sup> (§3.2), whereas the next one is the 2.96 eV center. The centers responsible for green PL (2.495 and 2.535 eV) appear along with the 1.562 eV center, although the 2.495 eV defect is definitely the first one to appear. It is necessary to note the high stability of 1.40 eV centers: they do not usually anneal out at 1750 K. The lower and higher impurity contents at  $d\sim0.5$  mm and d>1.5 mm, respectively, are due to variations in the growth rate, which is highest near the seed and decreases as the crystal grows. This approach allows one to get detailed information without any danger of destroying a sample during repeated HPHT annealing, but unfortunately, it is possible only when studying the simplest low-temperature defects.

From a variety of Ni-related optical systems, those related to group III are most typical of natural diamonds (Fig. 11). The systems with ZPLs at 2.369, 2.495 and 2.535 eV were described for the first time in natural diamonds with green PL in 1966;<sup>(91)</sup> later they were named S3 (with a ZPL at 2.495 eV) and S2 (with ZPLs at 2.369 eV (A), 2.535 eV (B), 2.596 eV (C), 2.624 eV (D) and 2.635 eV (E)), and their structure in PL and PLE spectra was studied in detail.<sup>(92,93)</sup> The intensities of the C and D components of the S2 system increase with the temperature and exhibit a maximum at ~135 and ~100 K, respectively.<sup>(92)</sup> A weak 1.562 eV line was observed for the first time in natural diamonds from India.<sup>(94)</sup> Systems with ZPLs at 2.053 eV (603.8 nm), 1.770 eV (700.3 nm), 1.573 eV (788 nm) and 1.562 eV were found to accompany the S2 and S3 systems in PL spectra of natural diamonds where nitrogen was in an aggregated form, and a signal from nitrogen B complexes was present. The S2 intensity was shown to be proportional to that of 1.562 eV.<sup>(95)</sup> The S2 ZPLs become broader as the concentration of B centers in diamond increases and PL quenching is observed at B absorption >27 cm<sup>-1</sup>.<sup>(96)</sup> In



Fig. 15. Variations in PL intensity for Ni-related centers with ZPLs at 1.40 eV (curve 1), 2.56 (2), 2.96 (3), 2.495 (4), 2.535 (5) and 1.562 eV (6) along the line from the outer face to the seed (panel a) in comparison with the data on nitrogen concentrations in C (curve 7) and A form (8) defects as well as total nitrogen concentration (9) in (panel b).<sup>(48)</sup> The annealing time grows from left to right (from the outer face to the seed). The C<sup>+</sup> concentration was under the detection limit here and we have no information concerning nickel distribution, but it seems that it is low on the left and increases to the right as a result of changes in the growth rate.

synthetic diamonds, these defects were first produced after annealing in 1982:<sup>(97)</sup> the S3 signal was found in PL spectra after annealing at T=2150 K, whereas S2 and 1.562 eV centers appeared at a higher temperature (2200 K). The intensity of all these systems increased as the annealing temperature increased up to 2300 K. For a long time, it was not recognized that these spectroscopic features were related to Ni, and only after large, high-quality synthetic diamonds became available, the S2 and S3 systems were associated in ref. 89 with three paramagnetic nickel-nitrogen complexes: NE2+NE3 and NE1, respectively (§3.4).

Note that the intensity of PL from Ni-related defects is much lower (usually 1–2 orders or more) in natural diamonds than in synthetic ones and only in very rare cases is the signal from group III centers, namely, from 1.563, 2.591, 2.599 and 2.622 eV observed

in absorption spectra of natural diamonds (Fig. 6, curve 4). It may be a result of a much lower nickel concentration under natural growth conditions. Estimations gave  $\sim 0.35$  wt.% Ni in the surrounding rocks in the case of ultrabasic, peridotite-type paragenesis in contrast to several ten percent when growing synthetic diamonds. Another possible reason is a much faster growth process in the laboratory. A typical experiment lasts ~100 h in contrast to a geological temporal scale in nature. The impurity spatial distribution is not usually uniform in the sample. The maximum nickel concentration in diamonds (the same for nitrogen) can be found in the parts growing under nonstationary conditions with a high level of supersaturation and a high growth rate as it takes place in the near-seed area of synthetic diamonds as well as in the areas that exhibit a normal growth mechanism in an internal cuboid-shaped area of mixed-habit diamonds<sup>(98)</sup> or in a coat of coated diamonds.<sup>(99)</sup> In both cases, the growth mechanism changed during the diamond formation process. In the case of mixed-habit diamonds, an initial nonstationary growth stage was followed by a long-term period of layer-by-layer stationary growth whereas the opposite occurs in the second case. As a result, the impurities (Ni, N) captured in the internal cuboid zone underwent a long HPHT annealing and most complicated nitrogen (B defects) and nickel-nitrogen complexes such as S2, S3, 1.562 and 1.77 eV centers (group III), all with a highly resolved fine structure, are observed using confocal PL microspectroscopy.<sup>(98)</sup> For coated diamonds related to group III in Orlov's classification.<sup>(25)</sup> a coat of fibrous structure formed during the last relatively short period: nitrogen is partly aggregated to the A form and there is still some input from the C component according to EPR and optical absorption results at hv>2 eV.<sup>(99)</sup> An intense green PL is recorded in the coat but the S2 and S3 optical systems are strongly broadened and they are identified only from the analysis of the envelopes of the PL and PLE spectra.<sup>(99)</sup> Similar structural features in the state of point defects (nitrogen mainly in the A form and PL from the S2, S3 and 1.562 eV complexes) are observed in natural diamonds of cubic shape as well as in those of fibrous structure.<sup>(100)</sup>

#### 3.4 EPR in annealed diamonds and EPR-to-optics correlations

In annealed synthetic diamonds grown from a nickel solvent, two families of paramagnetic defects named NE1-NE9 and AB1-AB7 were found and defect concentrations versus annealing temperature are shown in Fig. 16 for nitrogen-poor (a) and nitrogen-rich (b) diamonds.

In nitrogen-poor diamonds, P1, W8, NIRIM1 and NIRIM2 centers are considerably stable and anneal out only at T>2150 K (Fig. 16(a)): such behavior is also typical of the 1.40 eV center in optical spectra, which is responsible for green color and is associated with the NIRIM2 center in EPR spectra. This center is very stable and is observed in PL even after annealing at 2700 K.<sup>(87)</sup> A transitory center AB7 appears at early annealing stages, before nitrogen shows a significant aggregation (this takes place at 1950–2250 K), and is likely a result of the capture of a mobile vacancy and/or interstitial by a nickel-related defect.<sup>(101)</sup>



Fig. 16. Concentrations of paramagnetic centers P1 (1), W8 (2), NIRIM1 (3), AB7 (4), AB5 (5), AB1 (6), AB3 (7), AB6 (8), NE1 (9), NE2 (10), and NE3 (11), measured in nitrogen-poor (a) and nitrogen-rich (b) synthetic diamonds during an isochronal (4 h) annealing sequence. The concentrations measured in the as-grown crystal correspond to the crystal growth temperature (1700 K).<sup>(101)</sup>

In nitrogen-rich synthetic diamonds, EPR study shows a decrease several times occurring both in Ni<sub>s</sub>- (W8) and donor nitrogen (P1) concentrations after annealing at T > 1800 K.<sup>(102,103)</sup> At first, a substitutional Ni<sub>s</sub> captures a vacancy and occupies a double vacancy site  $Ni_{yyy}$  (NE4 center). As temperature increases, the NE4 center captures nitrogen atoms, creating a big family of nickel-containing centers (Table 2, Fig. 16(b)). The only center that has one nitrogen atom near nickel in a double semivacancy site is NE7; this center appears after X-ray or UV illumination but there is very little information about it (Table 2). The next stage is NE1(46) and NE5,(70) which have two nitrogen atoms in different positions in the first coordination sphere around a double semivacancy; these centers appear at  $T \sim 1900$  K along with nitrogen aggregation. The NE5 center is nonparamagnetic in a usual state and appears in EPR spectra after proper illumination. The structure of most of the nickel-containing centers with nitrogen atoms in different positions around nickel in a double semivacancy site was deduced from the data for ligand <sup>13</sup>C and <sup>14</sup>N HFS. For NE1 and NE5, nitrogen positions are sites (1, 2) and (3, 4) in Fig. 4, respectively.<sup>(6,17)</sup> Further increase of the annealing temperature produces more complicated nickel-nitrogen centers with three (NE2, NE3<sup>(46)</sup> and NE9<sup>(17)</sup>) and four nitrogen atoms (NE8).<sup>(90)</sup> In the structure of these centers, nitrogen atoms are located in sites (1, 2, 3), (1, 3, 4), (3, 4, 5) and (3-6), respectively.<sup>(6,17)</sup> There is no interconversion between isomers such as NE2 and NE3. Thus, there is no migration of N from one site in the coordination sphere to another and there should be different pathways for the formation of the centers observed. The following graph demonstrates a sequence of defect transformation during the impurity aggregation process:



The structure of each center is given above. It shows the site that Ni occupies (the substitutional site for W8 and the double semivacancy site for other centers). The superscript shows positions of nitrogen atoms around nickel in a double semivacancy site. The enumeration of the sites in the first coordination sphere around nickel is given in accord with Fig. 4. The defect symmetry (point group) and the center name are given in the parentheses. If a nitrogen atom is added at center transformation, one can see +N near the arrow.

One can see that NE1 and NE5 appear simultaneously during annealing and they are precursors for NE2, and NE3 and NE9 respectively. The latter transforms further to the NE8 center.

There is also a photoinduced NE6 center with an unclear Ni position; this center contains no nitrogen.<sup>(69,70)</sup> Both NE6 and NE7 operate as shallow traps and are responsible for peaks at ~130–200 K in the thermoluminescence curves. The correlated changes but in the opposite directions were found for intensities of P1 and NE1 in annealed synthetic diamonds during irradiation/illumination.<sup>(69)</sup> This indicates that donor nitrogen serves as a bulk charge compensator in diamonds and nickel centers such as Ni<sub>s</sub><sup>-</sup>, NE1, NE6 and NE7 can exist in a different charge state. They change their charge state readily upon irradiation/illumination. The *ab initio* calculation using a local density functional technique (LDF) showed that Ni<sub>v-v</sub> -N<sub>n</sub> complexes are acceptors for  $n \leq 3$  and they should be stable in the neutral or negatively charged state whereas those with  $n \geq 4$  should be donors and stable in the positively charged state.<sup>(72)</sup>

It is surprising that the nickel-containing paramagnetic defects AB2-AB6 and AB7 (Table 2) are typical only of synthetic diamonds (nitrogen-rich and nitrogen-free, respectively) from NIRIM, Japan<sup>(101,104)</sup> and have never been found in samples from other research groups, including those from Novosibirsk, Russia, whereas NE1-NE9 centers are present in all samples.<sup>(73)</sup> These apparent differences in the formation of Nirelated centers in diamond may actually be caused by a shift in the Fermi level due to the incorporation of other impurities or due to changes in the impurity concentrations, and/or can be caused by peculiarities in the growth process.<sup>(73)</sup> Nothing is known about the optical analogues of AB2-AB7 centers.<sup>(99)</sup> In nitrogen-rich diamonds, AB5 centers and a few AB2 and AB3 centers are present in as-grown diamonds and their concentration decreases upon annealing: they are transitory centers, maybe the by-products of the creation of carbon interstitials by as-grown nickel defects (*e.g.*, W8), which are supposed to enhance nitrogen aggregation.

A large discrepancy between as-grown W8 concentration and the sum of the concentrations of NE1, NE2 and NE3 defects after annealing at 2200 K shows that not all W8 centers transform into known paramagnetic NE defects and there are a lot of undetected nonparamagnetic centers (maybe NE in another charge state or defects with a different structure). Alternatively, a considerable decrease in the Ni<sub>s</sub><sup>-</sup> center concentration may be due to a shift in the Fermi level; this converts some Ni<sub>s</sub><sup>-</sup> into Ni<sub>s</sub><sup>0</sup>, which has not been observed by EPR analysis.<sup>(101)</sup>

Absorption, PL, PLE and EPR spectra were recorded for hundreds of as-grown and annealed synthetic diamonds, as well as for several hundreds of natural diamonds from different deposits (Ural and Yakutia<sup>(105)</sup> and Argyle<sup>(106,107)</sup>), which all exhibit a yellow-green PL in 2.495 eV (S3), 2.535 eV, 2.369 eV (S2) and 1.562 eV systems. The identification of these four optical systems was based on the correlation between optical absorption and the EPR signals from NE1, NE2, NE3 and NE8 centers, respectively, as well as on similar changes following HPHT treatment (Figs. 7 and 16(b)) and X-ray radiation or optical illumination.<sup>(60,61,69,70)</sup> An alternative structure of monoclinic II (C<sub>2</sub>) symmetry with three nitrogen atoms around an interstitial nickel ion was suggested for the 1.562 eV center on the basis of the results of a uniaxial stress study, and the authors proposed the existence of complexes with interstitial nickel and one, two, three and four nitrogen atoms in the (010) plane.<sup>(83)</sup> Among synthetic diamonds, nickel-nitrogen complexes NE1-NE3, NE5, NE8 and NE9 are typical of HPHT-treated samples, although such defects can be formed in some areas during the crystal growth along with nitrogen A-defects.<sup>(108)</sup>

Note that the optical systems with paramagnetic analogues and reliably identified structures were found in all groups (I–III) of optically active Ni-related centers (§3.3):  $Ni_{s^-}$  (W8, group I),  $Ni_{v-v}$  (group II) and NE1-NE3 centers (group III). These centers can be regarded as milestones.<sup>(46)</sup> Thus, one can relate defects responsible for group I to the simplest nickel-containing, nitrogenless defects, whereas group II defects are considered to be relaxed nickel centers or nickel-nitrogen complexes with a single nitrogen atom. Group III centers are obviously the most complicated nickel-nitrogen complexes with two or more nitrogen atoms in their structure.

The following relations linking optical absorption and the concentration of paramagnetic defects were obtained for HPHT-treated synthetic diamonds with a relatively even spatial distribution of defects taking into account the results of the absorption spectrum decomposition into individual components related to NE1, NE2 and NE3 centers:<sup>(108)</sup>

NE1:	$C_{\rm NE1} = 0.028 \times \alpha (2.618 \text{ eV})$	
NE2:	$C_{\rm NE2}$ =0.22× $\alpha$ (3.380 eV)	
	$C_{\rm NE2}$ =0.58× $\alpha$ (2.596 eV)	
NE3:	$C_{\rm NE3} = 0.21 \times \alpha (2.589 \text{ eV}),$	(3)

where  $C_i$  is the concentration of a certain NE defect in ppm and  $\alpha$  is the ZPL absorption strength in cm<sup>-1</sup>, measured at 77 K with a spectral slit width of about 0.2 nm. The typical concentration of Ni<sup>+</sup> in the form of NE1-NE3 defects was about 3 ppm in synthetic diamonds whereas the nitrogen content in these defects was ~8 ppm and the total nitrogen content varied from ~100 to 300 ppm.

Two additional Ni-related centers were found in natural diamonds along with NE defects:

- A Ro1 center of tetragonal symmetry, S=1/2, and  $g_{\parallel}=2.0151$  and  $g_{\perp}=2.2113$  without a resolved HFS due to nitrogen. This center is observed along with NE1 and NE2 centers (supposedly Ni<sub>i</sub><sup>+</sup> with nitrogen around)<sup>(105)</sup> in natural diamonds of yellow, yellow gray or yellow brown color from Ural and Yakutia.
- A broad isotropic line at  $g\sim 2.02$  without any angular variation in blue-gray natural diamonds with high nitrogen (up to 3300 ppm, mainly in B form) and hydrogen concentrations from Argyle in Western Australia.<sup>(106,107)</sup> On the basis of the nitrogen state (B), the presence of NE2, and a strong signal from B' (platelets), the impurity is highly aggregated. The electron-nuclear double resonance (ENDOR) measurements enabled the development of a model of six N<sub>s</sub> atoms in the fourth coordination sphere (4nn) around Ni<sub>s</sub>.<sup>(106)</sup>

Photoinduced transitions (PTs) were studied by EPR analysis<sup>(59,109,110)</sup> and ionization energies were determined for some paramagnetic centers such as W8, NIRIM1, and AB2–AB5. They vary from 1.67 to 3.0 eV, correspond to a distance from the bottom of the ground state level to the conduction band and are shown in the last column of Table 2. The analysis of PT temperature dependence allowed one to estimate the relaxation energies  $E_{relax}$  of the above-mentioned nickel centers and establish it to be ~0.02 eV, which is much lower than that of nitrogen defects (~0.5 eV).<sup>(101)</sup> Small  $E_{relax}$  values are indicative of a weak electron-lattice coupling of Ni in diamond. Huang-Rys factors *S* of interacting vibrational modes, obtained for vibronic spectra of Ni optical spectra also reveal modest electron-phonon coupling. For instance, 1.40, 1.693, 1.883 and 2.51 eV optical features have the following *S* values and dominant phonon energy: 1.6 (60 meV), 1.3 (28 meV), 0.7 (61 meV) and ~0.25 (16.5 meV).<sup>(59)</sup> This is possibly a result of the high localization of the defect wave functions on the impurity. Moreover, the spin-orbit coupling, shown to be relatively strong in Ni defects (as derived from the deviations of *g*-values from  $g_e$ ), may play a predominant role in the stabilization of these defects, as compared with distortions due to the interaction between electrons and lattice vibrations.<sup>(59)</sup> For nickel-nitrogen complexes, *S* is much larger: 4.4 to 5.7 for NE1–NE3 (Table 1).

On the basis of both experimental optical and EPR results ( $\S3.2-3.4$ ) and *ab initio* calculations,<sup>(54)</sup> a variety of Ni-related spectroscopic features in the optical spectra (Figs. 7–14) of nitrogen-rich synthetic diamonds grown from a nickel solvent can be understood by taking into account the following features:

- A nickel ion can occupy different sites in the diamond lattice: interstitial (Ni<sub>i</sub>), substitutional (Ni<sub>s</sub>) and double semivacancy (Ni<sub>v-v</sub>) positions.
- Each of the present impurities can occur in different charge states: nitrogen can be neutral or positively charged, whereas nickel is also inclined to charge state variation: from 0 or even (-1) to (+2). The charge state of a center can vary depending on growth and annealing conditions as well as the application of irradiation and illumination.
- Since nitrogen and nickel are strongly pronounced donor and acceptor atoms, respectively, they are inclined to form donor-acceptor pairs and more complicated complexes with spectroscopic features depending on both the relative position of the components (isomers) and the distance between the components (transient centers are possible).
- Defects with heavy atoms such as Ni have narrow phonon replicas: As a result, the number of narrow lines in the optical spectra increases and there is usually a problem in distinguishing real ZPLs among them.

# 3.5 Spatial impurity distribution, orientation and aggregation

Nitrogen concentration and spatial distribution depend on different parameters such as temperature, growth rate and melt composition. In diamonds grown by the temperature gradient method from Ni (and Co) alloys, the maximum nitrogen concentration is usually higher in {111} sectors than in {100} growth sectors but this situation is reversed when synthetic diamonds are grown at lower temperatures.<sup>(11)</sup> In nitrogen-rich diamonds, the nitrogen concentration decreased as the temperature increased but when a nitrogen getter was added, the nitrogen concentration increased with increasing temperature supposedly because the effect of the nitrogen getter decreases with the increasing temperature.<sup>(112)</sup> Nickel-related absorption and PL are the most intense in {111} sectors whereas in {100} sectors, these features were not observed.<sup>(22)</sup> Nickel concentration was reported to be higher at higher growth rates according to visual observation(112) and spectroscopic studies;<sup>(113)</sup> the maximum nickel content is up to 70 ppm.<sup>(113)</sup> There is a correlation between concentrations of nitrogen and transition metal ions. When Ni or Co concentration increases, N concentration decreases, supposedly as a result of the formation of TM-N complexes.<sup>(113)</sup> Annealing experiments showed that the nitrogen aggregation process (C $\rightarrow$ A transformation) proceeds much faster in {111} sectors than in {100} sectors in synthetic diamonds: this was considered to be a result of high Ni concentration, which affected nitrogen diffusion.<sup>(11)</sup> In the presence of TM ions, the kinetics of nitrogen aggregation was found to differ considerably from the second order; the latter is typical of natural diamonds and TM-free synthetic diamonds.(102,103)

In the case of synthetic diamonds as-grown at a high temperature, the nitrogen aggregation process continues during the entire growth process. A study of synthetic diamonds grown at a temperature oscillation of  $\Delta T=3^{\circ}$  with a frequency of  $f=7.5\times10^{-4}$  Hz at an average growth temperature of about 1750 K showed that the linear growth rate decreased by more than an order of magnitude in the {111} sector. It varied from 180 µm/s near the seed to ~12 µm/s in the periphery when growing diamonds with a fixed input electric power. In the same region, the rate constant of A-defect formation was calculated to decrease from  $3.0\times10^{-7}$  to  $7.5\times10^{-10}$  ppm<sup>-1</sup>s<sup>-1</sup>, supposedly as a result of nonuniform nickel incorporation in the diamond lattice, which is highest near the seed. Such crystals demonstrate a considerable color gradient from colorless (or slightly brownish) in the internal near-seed area to intense yellow in the outer layer, where donor nitrogen dominates.<sup>(114)</sup>

The acceleration of nitrogen aggregation cannot be explained by a vacancy-assisted process as in the case of the electron-irradiated diamond<sup>(115)</sup> because there is no evidence of the presence of vacancies. However, some new signals in the mid-IR range were found in annealed diamonds including that at 1450 cm<sup>-1</sup> due to interstitial nitrogen.<sup>(102,103)</sup> Carbon interstitials may be released by the metal as large nickel (or Co) interstitial move to a lower energy configuration such as the substitutional position (i) and then to the double semivacancy structure (ii). These carbon interstitials rapidly move off to the neighboring substitutional nitrogen, where they exchange sites, releasing highly mobile interstitial nitrogen and reconfigures to nitrogen pairs with the corresponding release of a carbon interstitial, that can be recycled in the reaction (iv). According to ref. 116, the reactions governing this process are the following:

(i)  $Ni_i \rightarrow Ni_s + C_i$ (ii)  $Ni_s \rightarrow Ni_{v,v} + C_i$ (iii)  $C_i + N_s \rightarrow N_i$ (iv)  $N_i + N_s \rightarrow N_i N_s \rightarrow A + C_i$ (v)  $Ni_{v,v} + N \rightarrow Ni_{v,v} - N_s$  (4)

The complex aggregation kinetics proceeds from this point since the equation describing the loss rate of single nitrogen atoms would have three terms. One term would be proportional to the release rate of carbon interstitials, another term would be proportional to the concentration of nitrogen available for the exchange between interstitial carbon and substitutional nitrogen and the third term would represent normal second-order aggregation kinetics. The numerical solution of the equations with activation energies of  $3.8\pm0.8$  eV for (i) and (ii), and 1.6 eV for the migration of carbon and nitrogen interstitials (at 1550 K) showed good agreement with the experimental results.<sup>(113,116)</sup> The additional acceleration of nitrogen aggregation can be due to an increased N<sup>+</sup> diffusion

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rate in the Coulomb field of the negative charge state of nickel-containing centers ( $Ni_s^-$ , NE4, NE5, NE1).<sup>(60)</sup> Thus, the rate of nitrogen aggregation around nickel ions to form double semivacancies is higher than the rate of nitrogen aggregation into A and B centers.

A local study of {111} sectors of as-grown synthetic diamonds showed a deviation from even distribution among crystallographically equivalent <111> axes for the paramagnetic centers NOL1, AB1/NE4, AB5, AB7 and KUL18 exhibiting trigonal symmetry (but not for NIRIM2)<sup>(117)</sup> and for anisotropic 1.22, 1.40,<sup>(35,117)</sup> 2.618 (S3), 3.444 and 5.263 eV<sup>(117)</sup> optical systems in nitrogen-rich diamonds. Preferential alignment from some of the anisotropic nickel-related centers means that they were formed directly during the growth process.<sup>(117)</sup> This fact is particularly important for complicated defects with several nitrogen atoms around Ni in the double semivacancy site such as NE1 (S3 center with the 2.618 eV ZPL). Annealing at  $T \sim 1850$  K usually removes preferential polarization, which is a result of defect reorientation in optical spectra. As for the 1.40 eV center, a depolarization occurs only at  $T \sim 2050$  K, which means that it has enhanced reorientation stability.<sup>(117)</sup> Calculations show that the high reorientation stability of the 1.40 eV system is in accord with the Ni<sub>s</sub>-B<sub>s</sub> structure, whereas for the Ni<sub>i</sub> and Ni<sub>i</sub>-B<sub>s</sub> structures, the stability should be much lower (diffusion barrier ~1 eV).<sup>(54)</sup> An increase in the intensity of the corresponding absorption with simultaneous depolarization upon annealing is a result of both the formation of new defects and the reorientation of the existing ones.(117)

#### 3.6 Kinetics of luminescence decay

For the pure d-shell states in TM ions, the optical transitions should be spin-forbidden due to the parity selection rules: as a result, the absorption, if any exists, should be weak and the luminescence decay times should be in the millisecond range. The information concerning experimentally measured luminescence decay times for Ni-related centers is summarized in Table 4. One can see that the decay times vary considerably from tens of nanoseconds (for the 1.40 and 1.562 eV centers) to milliseconds for some other nickel-related centers. The short lifetimes and the strong absorption signals indicate that the transitions are electric-dipole ones that are allowed in these cases. It may be a result of the formation of covalent bonds between 3d ions and ligands (hybridization with ligand wave functions). Four of the items in Table 4 correspond to spin-forbidden transitions, with some spin sublevels being radiative and others nonradiative.<sup>(10)</sup> They thermalize typically between 20 and 40 K as indicated by the bi-exponential decay in this temperature range. The ratio of the high temperature to the low temperature exponential decay gives the ratio of the total to the emitting spin levels.<sup>(10)</sup> Several of these centers produce emission from an upper energy level when the temperature is increased, transition from which is spin-allowed.<sup>(118)</sup> In Table 4, the values ZPL1 and ZPL2 give positions for low- and high- energy sublevels;  $\tau_1$  is the low-temperature lifetime and  $\tau_2$  is the limiting lifetime value upon thermalization; R is the ratio of transition probabilities of emissions 2 and 1. The temperature range of nonexponential decay  $\Delta T$ , and the type of the spin-forbidden transition (T-S: triplet-singlet; Q-D: quartet-doublet) are indicated.<sup>(10)</sup>

ZPL1	ZPL2	R	$ au_1$	$\tau_2$	$\Delta T$	Transition	Reference
(eV)	(eV)		(µs)	(µs)	(K)	type	
1.40			0.033				(30)
1.562 (NE8)			0.027				
			0.097				(120)
1.660			3000				(119)
1.705			5700				(10)
			3000				
1.802			10000				(119)
2.052	2.163	104	170	350	15-30	Q-D	(10)
2.054			70				(119)
2.073			<10				(119)
2.266			150				(119)
2.369 (NE3)	2.591		500	1500	20-30	T-S	(121)
			240				(119), (120)
2.495 (S3, NE1)	2.621	$10^{4}$	180	360	20-30	Q-D	(120), (118), (119)
2.535 (NE2)	2.599		3.5				(119)
2.5569	2.5585	40	140	1500	8-20		(122)
2.964	2.974	65	40	130	20-40	T-S	(123)

Table 4	4							
Decay	times	of nickel-	related	lumines	cence i	n d	iamor	ıd

# 4. Co-Related Centers

Cobalt is considered to be the best solvent catalyst for growing synthetic diamonds, and so it is one of the most widely used catalysts.<sup>(124)</sup> Analysis of impurities in diamond using the X-ray absorption near edge structure (XANES) showed that cobalt is more difficult to incorporate than nickel. Cobalt concentrates mainly in the {111} sectors during growth, and is proposed to occupy tetrahedral sites.<sup>(125,126)</sup> The optical systems, which could be related to cobalt, were observed in CL and PL spectra of synthetic diamonds that have been grown from the cobalt alloy without any nitrogen getters and contained up to 300 ppm nitrogen (Table 4).<sup>(127)</sup> Two vibronic systems with ZPLs at 1.474 and 1.989 eV were found in as-grown samples. They both disappeared after annealing at temperature  $T \ge 1750$  K; however, five new systems with ZPLs at 2.135, 2.207, 2.277, 2.367 and 2.590 eV were observed (Fig. 17). The 2.135 and 2.277 eV systems appear first as the annealing temperature and duration increase and saturate to 1850 K, whereas the 2.207 and 2.367 eV systems continue to grow at this temperature.<sup>(127)</sup> Indeed, PL mapping shows that the 2.135 and 2.277 eV systems are typical of the areas with partial nitrogen aggregation (30 to 70% of the nitrogen impurities are in the A form), whereas the 2.207 and 2.367 eV systems are observed in places with almost complete nitrogen aggregation degree; the



Fig. 17. Low-temperature absorption (1), PL (2, 2a and 4) and PLE spectra (3, 5 and 6) of as-grown (1 and 3) and annealed at 2050 K (2, 4 and 5) synthetic diamonds grown from a cobalt-containing alloy. The PLE spectrum (3) is identical for both 1.474 and 1.989 eV PL systems, whereas (5) and (6) are related to the 2.367 and 2.277 eV PL systems, respectively. The position of the ZPLs is indicated. The spectra were reconstructed from refs. 127, 129 and 130.

latter varies from 70 to 100%.<sup>(128)</sup> After annealing at 1750 K, intense H3 and N3 systems already appeared in CL and PL spectra, thus showing nitrogen mobility and effective nitrogen aggregation. Both the 1.474 and 1.989 eV systems in as-grown diamonds are polarized, which shows the preferential orientation of the corresponding defects. The polarization degree decreases after HPHT annealing at ~1850 K as a result of defect reorientation.<sup>(128)</sup> The 2.135, 2.207, 2.277, 2.367 and 2.590 eV systems disappear upon annealing at T~2050 K and a new system with a 1.852 eV ZPL in absorption appears in the extensively annealed diamonds, in which all nitrogen is contained in the aggregated form.

The PLE spectra of both 1.474 and 1.989 eV centers are similar and show the only vibronic system with ZPL at 2.055 eV (Fig. 17). This system was also found in absorption spectra; thus, the 1.474 and 1.989 eV systems are related to one anisotropic defect.<sup>(129)</sup> The intensities of other ZPLs varied from sample to sample depending on the annealing conditions: thus, they are related to different centers. The ZPLs of most vibronic systems exhibit a multiplet structure: thermalization between PL components indicates splitting in the excited state. PLE spectra were measured for the most

intense 2.277 and 2.367 eV PL systems.<sup>(130)</sup> For the 2.277 eV center, the ZPLs at 3.004 and 3.673 eV, corresponding to two excited states lying above the emitting one, were revealed (Fig. 17). A vibronic system with a ZPL at 3.085 eV was found for the 2.277 eV center.

The  $C_{3v}$  symmetry with optical transitions between  $A_1$  (ground) and E (excited) states was established for the 2.367 eV center from the uniaxial stress measurements and it was associated with a cobalt-nitrogen pair with the components in the adjacent substitutional sites.<sup>(125)</sup> The symmetry of the 2.207 and 2.77 eV centers was established only tentatively (Table 5).<sup>(131)</sup>

Phonon energies  $h\omega$  are a little lower in PLE spectra than those in PL spectra, which means a lower curvature of the potential in the excited states relative to the ground state. Minimum phonon energies may be related to heavier atoms, supposedly Co in a defect structure.<sup>(3)</sup> As follows from the estimations in ref. 3, intense 2.277 and 2.367 eV systems with a vibration at 38 meV can be related to cobalt-nitrogen complexes (1Co+1N) whereas 2.135 eV (PL) and 1.852 eV (A) systems with  $h\omega$ =44 meV exhibit a vibration due to (1Co+1C). According to these predictions, the 1.989 eV center with a 29 meV phonon should contain 2 cobalt ions.<sup>(3)</sup> All data concerning optical Co-related systems are summarized in Table 5.

A set of new Co-related lines, with the most intense ones being at 1.249, 1.397 and 1.435 eV, was reported in ref. 113 upon the He-Ne laser excitation (632.8 nm) of the areas corresponding to a short-term temperature drop during growth. This is a result of 1) more effective excitation of some centers because of better matching with their absorption band and 2) the formation of some specific centers, supposedly with several Co ions.

Ab initio calculations were carried out for the simplest cobalt centers with a single Co atom in substitutional, interstitial and double semivacancy sites; in different charge states, their spin, symmetry and other properties were also estimated.<sup>(132)</sup> Taking into account the fact that 1.47 and 1.990 eV optical systems in as-grown diamonds are anisotropic and the samples contain donor nitrogen, they can be related to  $Co_s^0$  (C1 symmetry, S=1/2),  $Co_s^-(C1, S=1)$  or maybe to the cobalt ion in the double semivacancy site  $Co_{v-v}$ , which is also anisotropic.<sup>(132)</sup>

For the first time, a paramagnetic Co-related defect with  $g_{\parallel}=4.4117$ ,  $g_{\perp}=4.43$ ,  $A_{\parallel}=245$  MHz and  $A_{\perp}=260$  MHz, the HFS associated with a nuclear spin I=7/2 of the <sup>59</sup>Co related to interstitial Co<sup>2+</sup> (3d<sup>7</sup>, t<sub>2</sub><sup>5</sup>e<sup>2</sup> state) in an octahedral environment, in powder synthetic diamond was reported in ref. 133 but not confirmed by anyone else. Later, three (at first one<sup>(17)</sup> and later two others<sup>(134)</sup>) paramagnetic centers were found in synthetic diamonds with a nitrogen content of about several hundred ppm that were annealed afterwards for 18 h at T=2073 K<sup>(17)</sup> or 2173 K.<sup>(133)</sup> Parameters of the paramagnetic Co-related centers are given in Table 6.<sup>(134)</sup> After such annealing, only ~10% of the nitrogen remained in the P1 form whereas most of the nitrogen aggregated to the A form. After the second annealing for 18 h at  $T\sim2573$  K, which aggregated almost all nitrogen into A and B forms, all optical systems and EPR signals related to Co centers disappeared.<sup>(17,127,130)</sup>

The distinctive features of three EPR spectra in diamonds grown in the Co solventcatalyst system are HFSs consisting of eight lines from the 100% abundant <sup>59</sup>Co isotope with I=7/2, the electron spin S=1/2 and closely similar directions of the principal values

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Table 5

Optical systems in the {111} sectors of nitrogen-containing synthetic diamonds grown from a cobalt alloy.

ZPL	Phonon	ZPL	Phonon	PL	Symmetry	Model	Comments
position	energy $h\omega$	position in	energy $h\omega$	decay			
in CL, PL	in PL/CL	A, PLE	in A, PLE	time $\tau_1$			
(eV)	(meV)	(eV)	(meV)	$(\mu s)^{(129)}$			
1.249*							As-grown SD,
1.397							He-Ne laser excitation
1.4354*							at 1.959 eV(113)
1.474	85±3,	2.055	30±2,	<2	Anisotropic		As-grown SD,
	146±5,	A, PLE	109±5		(116)		annealed at
	235±5	(129)					<i>T</i> ~1850 K <sup>(117,129)</sup>
	(129)						
1.852							As-grown SD,
							1.959 eV excitation <sup>(113)</sup>
1.9835	24, 56,			≤0.02	Anisotropic		As-grown, annealed at
1.9886,	119				(117)		<i>T</i> ~1850 K;
1.9906	<i>S</i> ~1.4						PL: excited state split
2.135	45±5			235±5	Monoclinic	$(C_3Co_{v-v}NC_2)^-,$	Annealed at
2.140					Ι	$(O4)^{(6)}$	<i>T</i> >1750 K
2.207				159±2	Rhombic I?	$(C_{3}Co_{v-v}N_{2}C)^{0}$ or	Annealed at
2.211					(131)	$(C_2 NCo_{v-v} NC_2)^0$ :	T>2050 K,
						(NLO2, NWO1)?	PL: excited state split
2.2771	38±3,	PLE:	33±3,	109±1	Trigonal?	(C <sub>3</sub> VCoVNC <sub>2</sub> ) <sup>-</sup>	Annealed at
2.2831	100±5	3.004	100±5		(131)	(O4 in EPR)	T>1750 K,
2.2907		3.673					PL: excited state split
		(130)					1
2.3666	38±3,	PLE:	36±3,	63±1	C <sub>3v</sub>	A Co-N pair with	Annealed at
2.3784	100±5	3.085 +	105±5		A↔E	components in	<i>T</i> >1750 K,
2.3850		3.9 eV			(131)	adiacent	PL: excited state split
		band(130)				substitution sites(131	)
2.590				~0.08		$(C_2Co_y N_2C)^0$ or	Annealed at
						$(C_2NC_{0}, NC_2)^0$ :	<i>T</i> >1750 K
						(NLO2, NWO1)?	
		A:	44			. , ,	Annealed at
		1.852					T>2050 K,
							maximum impurity
							aggregation degree

The symmetry of the 2.207 and 2.277 eV systems is given tentatively. The symmetry of these optical systems (rhombic and trigonal, respectively) is higher than that in EPR (monoclinic). Some authors suppose that the paramagnetic O4 defect corresponds to the 2.135 eV center of monoclinic symmetry in PL spectra.<sup>(6)</sup> Systems\* are typical of areas with the highest growth rate.<sup>(113)</sup>

Table 6			

Spin-Hamiltonian parameters for the o	observed cobalt-related centers. <sup>(17)</sup>
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Center	$g_1$	$g_2$	$g_3$	Angle	$A_1$	$A_2$	A <sub>3</sub>	Model
		[010]		< <i>g</i> <sub>1</sub> , [100]>	(MHz)	(MHz)	(MHz)	
O4	2.3463	1.8438	1.7045	29°	248	180	163	$(C_3Co_{v-v}NC_2)^-$
NLO2	2.3277	1.7982	1.7149	28°	230.8	183.9	161.2	$(C_2 NCo_{v-v} NC_2)^0$ or
NWO1	2.3463		1.9458	29°	248		187.4	$(C_{3}Co_{v-v}N_{2}C)^{0}$

of *A*- and *g*- tensors. These data suggest that the symmetry of all three Co centers is  $C_{1h}$  or  $C_{2h}$ . There was no HFS from <sup>14</sup>N and <sup>13</sup>C in contrast to the case of nickel-related centers.<sup>(17,134)</sup> As a result, no information about the *g*-matrix and defect structure was obtained.

Since three very similar EPR centers are typical of annealed synthetic diamonds with mainly aggregated nitrogen, they were all supposed to be related to a family of centers with a Co ion in a double semivacancy site, but with the number and relative location of nitrogen atoms being different as in the case of NE1-9 nickel defects.<sup>(17,134)</sup> The observed sites have g values very similar to those observed in strong-bonded octahedral complexes of  $t_2^5$ , S=1/2, with a mean/average g value less than  $g_{ex}^{(15)}$ . The three observed defects can be formed when a nitrogen atom is incorporated into a ligand shell and also accepts an electron from another nitrogen donor. Taking into account the fact that a slightly greater [NLO2]/[O4] ratio was observed after annealing at 2573 K than at 2173 K, the NLO2 center was supposed to contain an extra N ligand in comparison with O4.<sup>(17)</sup> The proposed structures of these centers are  $(C_3Co_{y,y}NC_2)^-$  for O4 with the  $C_{1h}$  symmetry and NLO2 and NWO1 might be (C<sub>2</sub>NCo<sub>v-v</sub>NC<sub>2</sub>)<sup>0</sup> or (C<sub>3</sub>Co<sub>v-v</sub>N<sub>2</sub>C)<sup>0</sup>, with the C<sub>2h</sub> and C<sub>1h</sub> symmetries, respectively. Thus, the O4 paramagnetic defect can be related to the intense 2.77 eV system, which is the first to appear during annealing, and the remaining systems (2.207 eV and 2.590 eV) may be associated with NLO2 and NWO1 EPR centers.

All three centers are present in synthetic diamonds after annealing at 2173 K and no changes were found upon X-ray irradiation and illumination; hence, they are very stable. The addition of another N atom can give a 3d<sup>6</sup> electronic state with S=0, which is nonparamagnetic. The absence of structures with a larger number of nitrogen atoms may be a result of neutral-state cobalt-containing centers with two and three nitrogen atoms and the absence of a mechanism of nitrogen diffusion in the Coulomb field.<sup>(17)</sup> The absence of the <sup>14</sup>N-related HFS can be explained by two features that make the unpaired spin density at a ligand N nucleus smaller for Co than for Ni: (i) the smaller nuclear charge will reduce the binding energy of 3d electrons and so increase the energy difference between 3d and lone pair 2sp<sup>3</sup> levels on N; (ii) it is possible that the unpaired 3d electrons are  $t_2^5$ , which have no overlap with the lone pair for an undistorted octahedral arrangement of ligands (the same for <sup>13</sup>C ligands).<sup>(17)</sup>

To date, both optical and EPR spectra related to cobalt have been observed only in synthetic diamonds grown from cobalt-containing alloys; there are no observations in natural diamonds in contrast to nickel defects. This is due to both the lower average natural abundance of cobalt, which is 2 to 5 times lower than that of nickel according to different authors,<sup>(135)</sup> and the more difficult cobalt incorporation into the diamond lattice.

#### 5. Features Related to Other 3d Transition Metal Ions in Diamond

#### 5.1 Titanium (Ti)

Titanium is well known as an efficient nitrogen getter when added to the starting charge during the growth of HPHT synthetic diamond; it allows us to obtain colorless low-nitrogen diamonds. Titanium is considered to produce a stable component, titanium nitride; thus, nitrogen is removed from the growth process. In natural diamonds, anatase TiO<sub>2</sub> is usually found in inclusions using microprobe analysis. After the implantation of Ti<sup>+</sup> ions into the diamond lattice and subsequent annealing at 1750 K, several new vibronic systems with ZPLs at 1.25, 1.277 and 2.5075 eV are found in CL spectra (Fig. 18(a)).<sup>(3,4)</sup> The 1.25 eV center interacts predominantly with a quasilocal vibration of 32 meV energy (two Ti atoms) and acoustic  $\Sigma$  phonons at the K point (energies 89 and 119 meV). A possible model of the Ti center is a pair of interstitial Ti atoms bound along the <110> direction.<sup>(124)</sup>

A vibronic system with a ZPL doublet at 2.975/2.2965 eV observed in PL spectra of brown natural diamonds and synthetic diamonds that were grown in the presence of Ti and Al was also tentatively related to Ti.<sup>(47)</sup> Narrow lines at 88.5 and 108.1 meV (with a shoulder at 105.1 meV) and a broad band at 180 meV have recently been reported in the absorption spectra of synthetic diamonds as grown from a Ti-containing melt and irradiated afterwards with 3 MeV fast electrons<sup>(136)</sup> at room temperature. However, further examination showed that this system was due to the surface contamination of the diamonds.

### 5.2 Chromium (Cr) and zinc (Zn)

The optical systems corresponding to these two species were observed in lowtemperature CL spectra of type IIa natural diamonds after the ion implantation of  $Cr^+$  and Zn<sup>+</sup> into the diamond lattice with further annealing at 1650 K (Figs. 18(b) and 18(c)).<sup>(3)</sup> A vibronic system with a ZPL at 1.673 eV (741 nm) and a phonon energy of 31 meV was related to Cr, whereas a system with a ZPL at 2.393 eV (518 nm), and phonon energies of 30 and 152 meV was due to Zn. Estimations based on the phonon energies allow one to suppose that two TM ions exist in the center structure in both cases.<sup>(3)</sup>

### 5.3 Iron (Fe)

Iron is an element that is commonly found in nature; its averaged natural abundance is ~1000 times higher than that of Ni and Co.<sup>(135)</sup> Thus, it was expected to form defect centers both in synthetic diamonds grown from Fe-containing alloys and natural diamonds. Using synchrotron X-ray fluorescence (XRF) microanalysis, including XRF topography, and X-ray absorption near-edge structure (XANES) analysis, Fe was found to exist in the form of microaggregates or inclusions (supposedly as FeO) and distribute with no observable sector correlation<sup>(137)</sup> in contrast to nickel and cobalt, that concentrate mainly in the {111} sectors.<sup>(111)</sup> The Mössbauer spectroscopy shows that Fe exists in



Fig. 18. Low-temperature CL spectra of type IIa natural diamonds implanted with different TM ions:  $Ti^+$  (spectrum (a)),  $Cr^+$  (b) and  $Zn^+$  (c) after subsequent annealing at 1640 K.<sup>(3)</sup> The spectra were recorded at 80 K.

the form of  $\alpha$ -Fe, Fe<sub>3</sub>C and Fe<sub>x</sub>N phases/inclusions in synthetic diamonds as grown with the addition of Fe<sub>90</sub>Ni<sub>10</sub> and NaN<sub>3</sub>.<sup>(138)</sup> A study of diamond magnetic properties shows that most natural diamonds demonstrate a positive sign for the magnetic susceptibility  $\chi$  and a hysteresis loop in the magnetization  $\sigma(H)=\chi(H)\times H$  dependence on magnetic field: they both indicate the presence of some ferromagnetic (supposedly Fe-containing) inclusions.<sup>(139)</sup> In synthetic diamonds grown from the Fe-C system, a large content of ferromagnetic inclusions is supposed to mediate and enhance indirect exchange between the P1 centers in EPR spectra at room temperature; as a result, a HFS from <sup>14</sup>N is unresolved.<sup>(17)</sup> This mechanism is switched off as the temperature increases and HFS becomes observable at *T*>400 K. A new vibronic system with a ZPL doublet near 1.787 eV was found in CL/PL spectra<sup>(140)</sup> and it is related to some Fe-containing point defect in such synthetic diamonds. However, further precise examination showed that the center parameters match well the R<sub>1</sub> and R<sub>2</sub> ZPLs of the Cr<sup>3+</sup> center in ruby. The vibronic system can be related to PL in small Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup> inclusions in diamond.<sup>(141)</sup> Point defect formation after the implantation of <sup>57</sup>Fe ions has been established using Mossbauer spectroscopy<sup>(142)</sup>; Fe was shown to incorporate at two distinct sites: one of cubic symmetry (either a substitutional or interstitial site) and the other having a very low symmetry. According to CNDO molecular orbital calculations, these centers are probably a substitutional Fe atom and a Fe atom adjacent to a lattice vacancy.

### 5.4 *Copper (Cu) and manganese (Mn)*

Cu. A paramagnetic center possibly related to Cu is W36.<sup>(143,144)</sup> The W36 center with S=1, g=2.002, D=155 MHz,  $A_s=6.9$  and  $A_p=0.9$  MHz, typical of type IIb natural diamond was originally associated with a boron-vacancy complex (maybe BV<sub>4</sub>) because of a four-line HFS attributed to <sup>11</sup>B with I=3/2.<sup>(143)</sup> An alternative model is copper in a double semivacancy site (C<sub>3</sub>Cu<sub>v-v</sub>C<sub>3</sub>)<sup>+</sup>.<sup>(144)</sup> Both stable Cu isotopes <sup>63</sup>Cu and <sup>65</sup>Cu of 69.17% and 30.83% natural abundance have I=3/2 and match the four-component HFS structure.

Mn. The KUL7 center with S=1, g=2.002,  $A_i=4.2$  and a six-line HFS due to <sup>55</sup>Mn (I=5/2) was found only in spontaneous HPHT synthetic powders obtained using a Ni-Mn catalyst.<sup>(145)</sup> In view of the presence of nitrogen donors ( $N_s^{0}$ ), one might associate the KUL7 center with a  $Mn_i^{-}$  center.<sup>(145)</sup> There are no optical systems related to these TM ions.

# 6. Quasilocal Vibrations Related to Heavy TM Ions in Optical Vibronic Spectra<sup>(3)</sup>

The parameters of quasilocal vibrations of different 3d TM ions calculated using eq. (1) in §2 are compared in Table 7 with the experimental ones, with the number of impurity atoms being given in parentheses. Only a few Ni and Co-related centers are given as an example but all known centers related to other TM ions are listed. The analysis of the vibronic spectra showed that the quasilocal vibrations with (i–iii) features from §2 are present in many TM-related centers. In a large family of Ni-related centers, the quasilocal vibrations are present in most defects but minimum phonon energies, replica widths and S values are typical of the simplest centers, related to group I, whereas for complicated nickel-nitrogen complexes, they become larger (Tables 1 and 7). For example, S varies from 0.4–0.6 (group I) to 4.4–5.7 for S3 and S2 systems (group III) (Table 1). Valuable information concerning the defect structure should be obtained from phonon energy.<sup>(3)</sup> As you can see, a considerable part of centers in Table 7 should contain two TM ions according to the above-described approach (eq. 1). It is of great importance to check this conclusion using independent techniques. Unfortunately, for few of the most studied Ni-related centers, this conclusion is in contradiction with widespread identifications. Thus, the 2.51, 2.56 and 3.1 eV optical systems with low vibration energies in the 21 to 26 meV range as well as a doublet at about 1.72 eV (31 meV) should be related to centers containing two nickel atoms, which does not agree with their present interpretation as Ni<sub>s</sub>- (W8) and Ni<sub>vv</sub> (§3.2). This means that it is necessary to make structural conclusions on the basis of this approach<sup>(4)</sup> with caution. On the other hand, recent ab initio calculations confirm the existence of low-energy modes in

Species and	$h\omega_{ m QL}$	$\Delta h \omega_{\rm OL}$	Impurity	Phonon energies	$h\omega_{\rm OL}$
atomic mass	(meV)	(meV)	content	(meV)	(cluster
(a.m.u.)	(number of impurity				calcula-
	atoms in parentheses)				tions)(54)
Ti (48)	Exp. 32	5	2Ti	85, 119 (Σ acoustic	
1.249 eV	Calc. 51 (1Ti);	Calc. 26 (1Ti);		at K point)	
	32.7 (2Ti)	11.2 (2Ti)			
Cr (52)	Exp. 31	<12	2Cr	Not detected	
1.673 eV	Calc. 47 (1Cr);	Calc. 24 (1Cr);			
	31.3 (2Cr)	10 (2Cr)			
Ni (58.7)	Exp. 16.5	7	2Ni ?		33.4
2.51 eV	Calc. 44 (1Ni);	Calc. 20 (1Ni)			$(N_s)$
	29.2 (2Ni)	8.9 (2Ni)			
	35.7 (1Ni+2C);	13.3 (1Ni+2C)			
	24.2 (2Ni+4C)	6.1 (2Ni+4C)			
Ni (58.7)	Exp. 26	9	2Ni ?	157	33.4
<u>3.1 eV</u>					$(N_s)$
Ni (58.7)	Exp. 21	8	2Ni ?	125 (147?)	33.4
2.56 eV					$(N_s)$
Ni (58.7)	Exp. 31	3	2Ni ?		
1.715/					
1.720 eV					
Ni (58.7)	Exp. 41	18	1Ni	72	
2.496eV(S3)					
Co (59)	Exp. 44	13	1Co		
1.852 eV	Calc. 43 (1Co)	Calc. 20 (1Co)			
	29 (2Co)	8.8 (2Co)			
	38.4 (2Co+1N)	15.4 (1Co+1N)			
Co (59)	Exp. 25, 56	13; 20	1Co+1N		
1.989 eV					
Co (59)	Exp. 38	13	Co+N	100	
2.277 eV					
Co (59)	Exp. 38	13	Co+N		
2. 367 eV					
Zn (65)	Exp. 30	8	2Zn	152	
2.393 eV	Calc. 41.2 (1Zn);	Calc. 17.7 (1Zn);			
	27.6 (2Zn)	8 (2Zn)			

### Table 7

Vibrational parameters of impurity-related optical centers in diamond (based on ref. 3).

vibrational spectra of centers with a single Ni atom.<sup>(54)</sup> Thus, a strongly localized  $T_2$  symmetry mode at about 33.4 meV with localized modes at about 62, 111, 124, 127 and 151 meV were obtained for Ni<sub>s</sub><sup>-</sup>, whereas the vibrations at 22–25 meV and around 177 meV were calculated for Ni<sub>i</sub>.<sup>(54)</sup>

# 7. General Trends in the TM Series in Diamond

By carrying out systematic *ab initio* studies of substitutional, interstitial and double semivacancy TM defects, the following trends in their stability and properties were established:<sup>(75,77,146)</sup>

- Generally, the double semivacancy exhibits the lowest strain, supporting an intuitive feeling that moving a large substitutional atom to a double semivacancy site should relieve strain in the lattice.
- The stability of TM centers (TM<sub>s</sub>, TM<sub>i</sub>, TM<sub>v-v</sub>) increases in the TM series as the atomic radius of a TM ion and the strain in the diamond lattice decrease. Since the atomic radius is minimum for Ni among 3d TM atoms, the stability of nickel defects should be the greatest (Fig. 19). The next is Co. TM ions that are larger than Ni and Co can be incorporated only into a thin near-surface layer of a diamond sample using ion implantation with further annealing.
- The impurities that are most likely to be found in the diamond are those of increasing d-character. Nickel is predicted to be the most stable metal impurity in diamond; the second most stable impurity in diamond is Co.
- The Ludwig/Woodbury (LW) and vacancy models should be taken only as extremes when analyzing the TM electronic structure; interstitial defects conform to the LW model, whereas substitutional and double semivacancy defects move from approximating the LW model above in the TM series to approaching the vacancy model for the heaviest metals.
- Substitutional defects were found to be the most stable and double semivacancy defects are similar in energy to the substitutional ones late in the TM series. Interstitial defects are only metastable, but given appropriate charge compensators, neutral and positively charged TM<sub>i</sub> may be sufficiently stable.<sup>(54,75)</sup>
- Optical transition energies decrease in the  $TM_i$  series as TM atomic mass increases and for  $TM_i^0$ , the transition energies are higher than those for  $TM_i^+$ . For  $TM_s$ , the transition energy is found to peak in the closed-shell species  $(Mn_s^-, Co_s^+, Fe_s^0)$  and then drop.<sup>(75)</sup>

# 8. Applications

# 8.1 Single-photon devices

Optically active defects in solids offer many potential uses in quantum information processing (QIP) applications such as quantum computing and quantum cryptography.<sup>(147)</sup> The main goal of QIP is the flexible generation of quantum states from individual two-level systems (qubits). The state of individual qubits should be changed coherently and the interaction strength among them should be controllable. Such systems should show high oscillator strength for an electric dipole transition between their ground and some optically excited state. The first structures used for such applications were organic dye molecules, but they have low photostability at room temperature.<sup>(147)</sup> The disadvantages of the other candidate, quantum dots, are a limited emission wavelength range and low-temperature operation.<sup>(147)</sup> Diamond is the only material presently known to contain



Fig. 19. Stability of TMs located in different sites in diamond (a): substitutional (1), interstitial (2) and double semivacancy ones  $(3)^{(75)}$  and the TM atomic radii (b).<sup>(135)</sup>

room-temperature photostable defects capable of producing single-photon pulses. Other advantages of diamond are a weak electron-phonon coupling (small S values particularly for simple TM-related centers<sup>(3)</sup>) and a high Debye temperature. The nitrogen-vacancy (N-V) color center in diamond was already demonstrated to be an effective source of single photons<sup>(148)</sup> and has been used to implement quantum key distribution in free space.<sup>(149)</sup> It is also being explored as a spin qubit in quantum computing.<sup>(150)</sup> Recently, a nickel-related defect with the 1.562 eV ZPL and four<sup>(90)</sup> or three nitrogen atoms<sup>(83)</sup> around Ni<sub>vv</sub> in diamond has been identified to be an efficient source of single photons in the near-IR region.<sup>(151)</sup> Its advantages are a narrower width at room temperature (1.2 nm in contrast to 100 nm for N-V), and better matching with standard fiber-optic communications. It is necessary to have a technique for producing nanostructural systems with controlled element structure, size and location. A controlled fabrication of 1.563 eV nickel defects in diamond by CVD was already demonstrated;<sup>(152)</sup> another promising technique is ion implantation. A search for new suitable centers is in progress. One can suppose that the 1.40 and 1.98 eV centers, both with a short lifetime (<35 ns) in as-grown HPHT diamonds, obtained with Ni and Co catalysts, respectively, may also be promising.

#### 8.2 Diamond thermoluminescent dosimeters of ionizing radiation

Diamond (Z=6) is a tissue-equivalent material ( $Z_{eff}$ =7.42 for human tissue; thus, there is no need to correct energy dependence in dosimetry), which is physically robust, chemically inert and nontoxic, and can be used *in vivo*.<sup>(153)</sup> For clinical applications, it is important that it can be sterilized by heating and is reusable. Its cohesion energy of 7.37 eV per atom makes this material insensitive to radiation damage (up to estimated doses of 1 MGy). Finally, the high thermal conductivity of diamond (1200–1800 Wm<sup>-1</sup>K<sup>-1</sup>), combined with small sample sizes, allows high heating rates, which are ideal for routine thermoluminescent dosimetry.

Synthetic diamonds from the Ni+2%Ti alloy annealed at 2100 K are characterized by an intense TL peak at 490 K emitting in a broad band centered at 2.35 eV (528 nm).<sup>(153)</sup> Donor substitutional nitrogen has a detrimental effect on the TL properties; thus, it is necessary to use a Ti getter during growth and perform postgrowth annealing to decrease nitrogen content and to stimulate the formation of nickel-nitrogen complexes supposedly of the NE1-NE3 group, which are stable against temperature and are the main recombination centers. Such diamonds can be selected as a useful TL material in the field of ionizing radiation dosimetry. Moreover, being nearly tissue equivalent, it can also be useful in the range of low-energy photons (<100 keV), especially when compared with widely used dosimeters made from alumina or silicon, as well as in the case of high resolution where a small-size dosimeter is required.

In synthetic diamonds as grown from the Co solvent, TL curves demonstrate a main peak at 564 K with an emission in the 2.13 eV (580 nm) band,<sup>(154)</sup> which may be associated with the above-described PL systems (§4, Fig. 18); the 2.35 and 1.989 eV systems in as-grown diamonds and the 2.367 eV+2.277 eV systems in the annealed ones. Crystals grown from the Co catalyst are less satisfactory because of weaker sensitivity to radiation, nonlinearity in the TL response, the higher temperature of the TL peak (564 K) and lower photon energy (680 nm). All these factors lower the signal-to-noise ratio output.<sup>(154)</sup>

# 8.3 Magnetic field calibration

An optical method for the calibration of pulsed magnetic fields using PL from synthetic diamond was proposed.<sup>(155)</sup> Generally, the pulsed magnetic field profile was reconstructed by measuring the pickup voltage in a small coil with an effective area that is to be known accurately. A fine PL structure of the 1.40 eV nickel center, due to Zeeman splitting, is analyzed and the field value is calculated using the *g*-factor previously characterized by EPR.

#### 9. Conclusions

Extensive experimental and theoretical studies of 3d transition metals in natural and synthetic HPHT diamonds have been carried out to propose plausible models for the numerous optically active impurity defects involved. A wide set of structuresensitive physical techniques including EPR was used to determine the structure of the existing defects and the main trends in impurity transformation upon annealing. The defects ranged from the simplest, such as TM in substitutional, interstitial and double semivacancy sites, to complicated TM-nitrogen complexes. Better understanding has been reached for nickel, which is incorporated into the diamond lattice more readily and demonstrates a well-pronounced HFS in many cases in EPR. In contrast to nickel and cobalt, which produce a number of optically active centers, most TMs have one defect related to each of the 3d ions. Optics-to-EPR correlations and structure identification have been proved reliably only for very few Ni centers. Many TM defects are nonparamagnetic and it is difficult to determine their structure. Despite considerable effort, the correlation of optical centers and EPR with microscopic structures is controversial in many cases and much remains to be explained about 3d TM-related defects in diamond as well as about the differences in the behavior of nickel and other TM ions. Diamonds with nickel centers have some applications in single-photon devices and thermoluminescent dosimeters of ionizing radiation as well as for the calibration of pulsed magnetic fields.

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