Chapter 8
Intrinsic Defects and Their Associates in Diamond

The intrinsic defects (lattice vacancies, self-interstitials, and their associates with impurities) give rise to over 60 defects in diamond (see Tables 8.1.1–8.1.7.2 and 8.2.1–8.2.4). Many of the configurations in these tables are proposals which need confirmation (marked by a preceding *).

From the isolated lattice vacancy and divacancy, four optical centers are observed (see Table 8.1.1).

Associates of the single or double lattice vacancy with one to four nitrogen atoms are observed in 21 centers (see Table 8.1.3.1–8.1.3.6).

One to three nickel atoms form 16 associates with single, double, or triple lattice vacancies (see Tables 8.1.4–8.1.5, 9.5.1.1–9.5.1.2).

A total of 22 centers from other impurities with one or multiple lattice vacancies are listed in Table 8.1.7.1–8.1.7.2 (see also Sects. 9.1–9.7).

The isolated lattice vacancy and self-interstitial are produced by irradiation. These defects have limited thermal stability (see Sect. 8.3.1). Therefore, they are absent in natural diamond. However, associates of the vacancy with nitrogen, nickel, silicon, or hydrogen atoms are stable up to ca. $2,000\,°\mathrm{C}$, and are well-known defects in natural diamond, especially those with historical names: NV center for $V_1N_1^\circ$, N3 center for $V_1N_3^\circ$, and B center for $V_1N_4^\circ$.

8.1 Lattice Vacancies and Associates

8.1.1 The Isolated Single Vacancy

The isolated single vacancy is a typical radiation center and can be created by high energy irradiation (e.g., electrons, ions, neutrons, and γ-rays). The properties of this important defect have been investigated by theory, electron paramagnetic resonance (EPR), and optically.

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Theory. The results of theoretical calculations [Lan68, Bre95, Jou96, Mai97] are summarized in recent reviews [Dav01a, New01c]. The vacancy can exist in three charge states: $V_1{}^-$, $V_1{}^\circ$, and $V_1{}^+$. There is a special situation, where the relative stability of the different charge states depends on the position of the Fermi level E_F. The most stable charge state are $V_1{}^-$ for $E_F > (E_c - 2.2\,\text{eV})$ (typical for type Ib), $V_1{}^\circ$ for $(E_v + 1.0\,\text{eV}) < E_F < (E_c - 2.2\,\text{eV})$ (typical for types Ia and IIa), and $V_1{}^+$ for $E_F < (E_v + 1.0\,\text{eV})$ (typical for type IIb).

The $\mathbf{V_1}^-$ center has stable T_d symmetry with a $^4A_2$ ground state, and allowed transitions to a calculated $^4T_1$ state at +3.3 eV.

The $\mathbf{V_1}^\circ$ center distorts from T_d to D_{2d} symmetry with a gain in Jahn–Teller energy of 0.36 eV. However, the Jahn–Teller effect is dynamic in producing effective T_d symmetry, and a splitting in the ^1E ground state of a few meV (observed is 8 meV).

The $\mathbf{V_1}^+$ center is stable in the Jahn–Teller distorted D_{2d} symmetry with a $^2T_2$ ground state. The excited states are “well above “the ground state.

The carbon atoms of the first shell relax radially outward by ca. 13% of the initial bond length (independent of the charge state).

EPR measurements: The EPR and ENDOR results confirm the theoretical description [New01c]. Fortunately, also the $\mathbf{V_1}^\circ$ center with its diamagnetic ^1E ground state has a paramagnetic $^5A_2$ excited state, which can be populated via ND1 absorption (see Table 8.1.1).

Optical measurements: The close correlation of EPR intensity and optical absorbance allows to assign the ND1 center to $V_1{}^-$ and the GR1 center to $V_1{}^\circ$, even with calibration factors [Twi99]. The GR2–GR8 lines, which are now interpreted as donor–acceptor pair transitions of $V_1{}^+$, were previously assigned to ZPL transitions of $V_1{}^\circ$.

All three charge states of the vacancy have sideband systems from donor–acceptor pair transitions ($V_1{}^-$: DAP93, $V_1{}^\circ$: DAP33/34, and $V_1{}^+$: DAP32, see Table 8.1.1). The $V_1{}^+$-DAP32 sidebands are very efficient in the excitation of the $V_1{}^\circ$(a, b) luminescence, and have been named GR2 to GR8. The broad $V_1{}^\circ$(b)-DAP33 absorption band, centered at 1.98 eV (630 nm), is (together with a blue-violet absorption band) responsible for the green color of some irradiated diamonds [All98a]. The green color of rare natural diamonds (e.g., the 41 karat volume colored green diamond gemstone of Dresden) is ascribed to irradiation from natural radioactivity [Bos89, Col97]. In a different case, a natural green skin (about 0.02-mm thick) has been reported [Wel94].

Table 8.1.1 The single and double lattice vacancy in diamond

Defect	Observed	ZPL (eV)	SB-DAP	D (eV)	Name/comment
$V_1{}^-$	MA, EPR(S1, S2) $S = 3/2$	3.150	93a–d	+1.10	**R10 = ND1**/LVM: (4×) +80 meV; peak of broad band at 3.45 eV; *no luminescence (e^- emission in exc. st.)*; photochromic with GR1 at $1.1 < E < 2.8$ eV; stable T_d symmetry with $^4A_2$ gr. st.
$V_1{}^\circ$	MA, EPR, $S = 4$, (only in $^5A_2$ exc. st.; obs. via ND1 absorption)	1.673	33a–k	+1.20	**GR1**b; line(a) at 1.665 eV/QLVM: +41, LVM: +68, +93 meV; gr. st. spl. = 8 meV from dynamic JT; effective T_d symmetry with ^1E ground state; peak of broad band at 1.95 eV; photochromic with ND1 at $E > 3.1$ eV
$V_1{}^\circ$	ML	1.673	34a–g	−1.20	**GR1**b; line(a) at 1.665 eV/QLVM: −37, −91; LVM: −70 meV; gr. st. *spl.* = 8 meV from dynamic JT
$^*V_1{}^+$	MA, ME; EPR (NIRIM3) $S = 1/2$	2.781	32a–m	+1.31	**GR2b-GR8e** (at 2.881–3.060 eV), very weak ZPL (GR2a), PLE of GR1, observed only in irradiated type IIb or boron doped CVD diamonds; *no luminescence (e^-capture in exc. st.)*; resolved spectrum also in photoconductivity [Ver74]; D_{2d} symmetry from JT distortion, $^2T_2$ ground state ($S = 1/2$)
$(V_2{}^-)$	EPR (W29)	–	–	–	**W29**(EPR), $S = 3/2$; *no optical lines*; C_{2h} symmetry from JT distortion
$V_2{}^\circ$	MA, EPR(R4 = W6) $S = 1$	2.419	15a–l	+1.63	**TH5**/weak ZPL; DAP lines at 2.543 (former ZPL) to 2.909 eV/no QLVM or LVM SBs, C_{2h} symmetry from JT distortion

EPR see [New01c]

SB-DAP = sideband DAP with ZPL = L = limiting energy, and D = dielectric factor; gr. st. spl. = ground state splitting, exc. st. = excited state; JT = Jahn–Teller effect

8.1.2 The Isolated Divacancy

The isolated divacancy occurs in the neutral state (V_2° = optical TH5 center). The negative charge state (V_2^-) is observed only in EPR (W29) [New01b]. Divacancies are formed by aggregation of two single vacancies at anneal temperatures $T > 600\,°C$. The concentration of V_2° in irradiated and annealed diamond is always low because the migrating single vacancies are preferentially trapped by nitrogen centers, and seldom by other single vacancies. A group of weak absorption lines is observed in the 2.4–2.9-eV range and has been named TH5 [Cla56c]. The group of 13 lines arises from the sideband V_2°-DAP15 (see Table 8.1.1) with a very weak ZPL at 2.419 eV (previously the first sideband at 2.543 eV was erroneously assigned to the ZPL).

8.1.3 Associates of Single or Double Vacancies with Nitrogen

When the vacancies begin to migrate (at a typical anneal temperature of 800 °C, $E_A = 2.4\,eV$), most of them are trapped by impurities before reaching the surface. Some very stable (beyond $T = 1{,}600$–$2{,}300\,°C$) associates with nitrogen are observed in natural, and also in as-grown synthetic HPHT or in as-grown synthetic CVD diamond. They are named: The NV center ($= V_1N_1^\circ$), the 638 nm center ($= V_1N_1^-$), the H3 center ($= V_1N_2^\circ$), the S1 center ($= V_1N_2^-$), the N3 center ($= V_1N_3^\circ$), the 2,526-eV center ($= V_1N_3^-$), the B-center ($= V_1N_4^\circ$), and the N9 center ($= V_1N_4^-$).

Metastable centers are $H1(a) = V_1C_4N_1^\circ$ (precursor of $NV = V_1N_1^\circ$, Table 8.1.3.1), $H1(b, d, g) = V_1C_4N_2^\circ$ (precursor of $H3 = V_1N_2^\circ$, Table 8.1.3.1), and $H1(c, e, f) = V_1N_4V_1^\circ$ (precursor of $H4 = N_3V_2N_1^\circ$, Table 8.1.3.4). Similar to the SB-DAPs with hydrogen centers (see Sect. 9.3), the precursor DAPs 30 and 31 are sidebands of a dominant infrared vibration. The DAP analysis yields $L = 154\,meV$ (from the A-center $= N_2$, see Table 9.1.1.3) for H1(b,d,g)-DAP30, and $L = 147\,meV$ (from the B-center $= V_1N_4$, see Table 8.1.3.5) for H1(c,e,f)-DAP31. The sharpness of the precursor DAP sidebands indicates a similar sharpness for the involved infrared vibrations (pseudo ZPL), which in direct observation are evidently broadened by resonance with lattice vibrations.

The trapping of a vacancy by nitrogen centers has been theoretically analyzed [Mai94a], see Sect. 9.1.6.2.

Table 8.1.3.1 Associates of the single vacancy with one or two nitrogens

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^{*}V_1N_1^{-}$(a)	NA, HA, LA, MA	1.943	48a–j	+1.24	**638 nm** or NV^{-} center/QLVM: +63; LVM: +75, +143; (combinations +213, +417, +520, +587) meV
$^{*}V_1N_1^{-}$(a)	NL, HL, LL, ML	1.943	49a–o	−1.24	**638 nm** or NV^{-} center/QLVM: −63; LVM: −123 meV
$^{*}V_1N_1^{-}$(b)	MA	4.328	...	...	NV^{-}(b) center; trigonal symmetry
$V_1N_1^{\circ}$	NA, HA, LA, MA	2.154	46a–f	+1.39	**NV = 575-nm** center/QLVM: +90; LVM: +164 meV
$V_1N_1^{\circ}$	NL, HL, LL, ML	2.154	47a–i	−1.39	**NV = 575-nm** center/QLVM: −48(1N+3C); LVM: −155 meV
$^{*}V_1C_4N_1^{\circ}$	MA	0.180	...	...	**H1(a)/**in irradiated and annealed diamond/precursor of $V_1N_1^{\circ}$ = NV
$^{*}V_1C_4N_1^{\circ}$	MA	1.702	45a–i	+1.53	In irradiated and annealed diamond/weak ZPL, precursor of $V_1N_1^{\circ}$ = NV; three luminescence lines at mirror positions; DAP lines at **1.909**, named **1.908 eV center** (hole burning [Sil95]); **2.087**(named **595 nm center**), QLVM: +70 (61 + 80?), LVM: +165 meV
$^{*}V_1N_2^{-}$	MA	1.256	77a–k	+1.35	**H2/**LVM: +65, +167 (sharp) meV
$^{*}V_1N_2^{-}$	ML	1.256	78a–g	−1.35	**H2**/LVM −62 meV
$^{*}V_1N_2^{\circ}$(a)	NA, HA, LA, MA	2.464	50a–h	+1.34	**H3(a)**/DAP lines **H6–H12** at 2.975–3.343 eV ($s = 8 - -1$)/QLVM: +46 meV
$^{*}V_1N_2^{\circ}$(a)	NL, HL, LL, ML	2.464	51a–f	−1.34	**H3(a)**/QLVM: −41; −81; LVM: −157 meV

(continued)

Table 8.1.3.1 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	D (eV)	Name/comment
$^*V_1N_2{}^\circ$(b)	NA, HA, LA, MA	3.361	52°-g	+1.34	**H3(b)** = **H13**/DAP lines **H15-H18** at 3.457–3.560 eV (s = 228–34)
$^*V_1N_2{}^+$	NL, HL, LL, ML	2.429	…..	…..	**S1(a)**; line (a) 2.429 eV (20× weaker than (b))/34 meV exc. st. splitting
$^*V_1N_2{}^+$	NL, HL, LL, ML	2.463	43a–g	−1.33	**S1(b)**; line (a) 2.429 eV (20×weaker)/QLVM: −48; LVM: −67 meV; energy transfer between S1(b) and H3(a) centers
$^*V_1C_4N_2^\circ$	MA	0.154	30a–d	+1.45	In irradiated and annealed type IaA/ZPL indirect, precursor of H3(a, b) = $^*V_1N_2$; DAP lines **H1(d)** at 0.331 eV (s = 50), **H1(g)**, at 0.551 eV (s = 10), **H1(b)**, at 0.612 eV (s = 8)/QLVM: +64; LVM: +154 meV/ZPL resonant with A(e′), see Table 9.1.1.3

SB-DAP = *sideband* DAP with ZPL = L = limiting energy, D = dielectric factor, and s = shell number

Table 8.1.3.2 Associates of the single vacancy with three nitrogens

Defect	Observed	ZPL (eV)	SB-DAP	D (eV)	Name/comment
$^*V_1N_3{}^-$	NL, ML	2.526	76a–n	−1.19	QLVM: −48; LVM: −144 meV/dyn. JT
$V_1N_3{}^\circ$(a)	NL, HL, ML,	2.297	55a–e	−1.33	**N3(a)** (formerly **N3b**)/delayed luminescence; observed only in samples with *large* platelets (with *small* platelets see the 2.202 eV line below)/QLVM: −67 meV/dyn. JT

(continued)

Table 8.1.3.2 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$V_1N_3{}^\circ$(b)	NL, HL, ML	2.680	56a–d	−1.33	**N3(b)** (formerly **N3a**)/delayed luminescence/QLVM: −59 meV/dyn. JT
$V_1N_3{}^\circ$(c)	NA, HA, LA, MA, NE, HE, LE, ME	2.985	23a–o	+1.33	**N3(c)** (formerly **N3**); ZPL split by 0.59 meV; DAP lines N4 at 3.610 ($s = 3$) and N5 at 3.730 eV ($s = 1$)/PLE of N3(a, b, c)/QLVM: +36, +64 meV; IR: +177 meV/dyn. JT
$V_1N_3{}^\circ$(c)	NL, HL, LL, ML	2.985	24a–q	−1.33	**N3(c)** (formerly **N3**)/QLVM: −36, −69; LVM: −160 meV/dyn. JT
$^*V_1N_3{}^+$	NL	3.414	22a–l	−1.36	QLVM:-36, −74 meV
$^*(V_1H_1)N_3{}^\circ$	NA	0.178	–	–	nat. N–H bend
	NA	0.390	–	–	nat. N–H stretch
$^*V_1N_3(C_2)_i{}^\circ$	NA	2.202	–	–	(Named **563-nm** center) in natural brown diamonds with high hydrogen content/QLVM: +32, +72 meV
$^*V_1N_3(C_2)_i{}^\circ$	NL, HL, ML	2.202	–	–	Delayed luminescence/similarity with N3(a); observed only in samples with *small* platelets

SB-DAP = sideband DAP with ZPL = *L* = limiting energy, *D* = dielectric factor, and *s* = shell number; dyn. JT = dynamic Jahn–Teller effect

Table 8.1.3.3 Associates of the single vacancy with four nitrogens

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*V_1N_4^-$	NA, NE	5.252	63a–g	+1.43	**N9**(a); lines (b) 5.262 eV, (c) 5.277 eV/QLVM:+75, LVM: +120, +140 meV
$^*V_1N_4^-$	NL	5.252	64a–i	−1.43	**N9**(a); lines (b) 5.262 eV, (c) 5.277 eV/LVM: −65, −76 meV

(continued)

Table 8.1.3.3 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$V_1N_4^\circ$	NA, MA	4.191	82a–g	+1.64	**B**(b); lines (a) 4.184, (c) 4.197 eV/QLVM: +36, +72 meV; IR: +94,+125, +134, **+146**, +165 meV (see Table 9.1.3.5)/dyn. JT
$^*V_1N_4^+$	HL	2.510	–	–	Four sidebands at +40 meV
$^*(V_1H_1)N_4^\circ$	MA	0.192	–	–	NH bend
$^*(V_1H_1)N_4^\circ$	MA	(0.424)	–	–	Expected NH stretch
$^*V_1N_4(C_2)_i^\circ$(a)	NA, HA	2.145	–	–	*__F(a)__/QLVM: +23 meV/IR lines F(a′)–F(i′), see Table 8.1.7
$^*V_1N_4(C_2)_i^\circ$(a)	NL, HL	2.145	–	–	*__F(a)__/ZPL of F(α1) = “Red band” with 1.80-eV peak, 14 SBs 31 meV
$^*V_1N_4(C_2)_i^\circ$(b)	NE, HE	2.721	–	–	*__F(b)__/PLE of F(β1) = “Yellow band” with 2.25-eV peak
$^*V_1N_4(C_2)_i^\circ$(b)	NL, HL	2.721	–	–	*__F(b)__/ZPL of F(β1) = “Yellow band” with 2.25-eV peak, seven SBs 34 meV
$^*V_1N_4(C_2)_i^\circ$(c)	NA, HA	4.567	81a–f	+1.67	*__F(c)__/QLVM: +55; LVM: +136, +154 meV

SB-DAP = sideband DAP with *L* = ZPL = limiting energy, *D* = dielectric factor, and *s* = shell number; dyn. JT = dynamic Jahn–Teller effect

Table 8.1.3.4 Associates of the double vacancy with one to four nitrogens

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*V_2N_1{}^\circ$	LL, ML	2.329	–	–	Very strain sensitive, variable 2.322–2.335 eV
$^*V_2N_2$	MA	2.086	–	–	**595 nm** center; in irradiated and annealed (275–800°C) type Ib diamond; resonant with DAP45, s = 12 line of $^*V_1C_4N_1^\circ$ at 2.086 eV; QLVM: +75 (2N), LVM: +165 meV
$^*V_2N_3{}^\circ$	MA	2.916	–	–	Very weak line

(continued)

Table 8.1.3.4 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*V_1N_4V_1{}^\circ$	MA	0.147	31a–e	+1.45	In irradiated and annealed type IaB/ZPL indirect, precursor of H4(a,b) = $^*N_3V_2N_1$; DAP lines **H1(e)** at 0.362 eV (s = 50), **H1(f)**, at 0.545 (s = 10), **H1(c)**, at 0.641 eV (s = 8)/QLVM: +64; LVM: +154 meV/ZPL resonant with B(d′), see Table 8.1.3.5
$^*N_3V_2N_1{}^\circ$	MA	2.498	37a–h	1.60	**H4**(b); line (a) at 2.417 eV (ten times weaker than H4(b)/QLVM: +38 meV
$^*N_3V_2N_1{}^\circ$	ML	2.498	38a–g	−1.60	**H4**(b);/QLVM: −42, −81 meV

SB-DAP = sideband DAP with L = ZPL = limiting energy, D = dielectric factor, and s = shell number

Table 8.1.3.5 IR absorption bands and vibronic UV absorption lines and bands from four nitrogens surrounding a vacancy: ($V_1N_4{}^\circ$ = **B center**)

Line/band	*E* (meV) *(cm^{-1})*	Width (meV) *(%)*	Rel. Intens (%)	Comment
B(a′)	93.5 *754*	14 *15*	6	Variable 93.5–96.7 meV
B(b′)	125.2 *1,010*	8 *6*	7	–
B(c′)	134.5 *1,085*	3 *2*	2	–
B(d′)	145.7 *1,175*	10 *7*	53	Close to the ZPL of $^*V_1N_4V_1$-SB-DAP31 (see Table 8.1.5)
B(e′)	150.6 *1,215*	6 *4*	6	Overlapping band
B(f′)	158.9 *1,282*	14 *9*	14	Overlapping band
B(g′)	165.1 *1,332*	1 *0.6*	9	–
Line/band	*E* (eV)	Width (eV)		Comment
*B(a1)	4.184	0.003	–	ZPL(a1) of B(α2)
*B(a2)	4.191	0.003	–	ZPL(a2) of B(α2)
*B(a3)	4.197	0.003	–	ZPL(a3) of B(α2)

(continued)

Table 8.1.3.5 (continued)

Line/band	*E* (meV) *(cm^{-1})*	Width (meV) *(%)*	Rel. Intens (%)	Comment
B(α2)	4.70	0.56	–	Absorption band, same band in photoconductivity [Den67]
DAP82a-d	4.307–4.431	–	–	SB-DAP; L = B(a1–3) ZPL (4.191 eV), $D = 1.64$

No luminescence from UV center

DAP: L = limiting energy, D = dielectric factor of donor–acceptor pair

Table 8.1.3.6 Absorption lines and bands from four nitrogens surrounding a vacancy associated with a self-interstitial: $V_1N_4(C_2)_i{}^{\circ}$ = **F center**

Line/band	*E* (meV) *(cm^{-1})*	Width (meV) (%)	Rel. Intens (%)	Comment
F(a′)	121.0 *976*	6 x*5*	4	–
F(b′)	126.7 *1,024*	6 *5*	2	Also observed as +127 meV LVM sideband at *F(c) (4.567 eV)
F(c′)	144.1 *1,162*	8 *6*	32	Close to B(d′) center line at 145.7 meV (see Table 8.2e)
F(d′)	154.0 *1,242*	7 *5*	23	Also observed as +154 meV LVM sideband at *F(c) (4.567 eV)
F(e′)	157.5 *1,270*	7 *5*	21	–
F(f′)	161.0 *1,299*	6 *4*	13	–
F(g′)	164.0 *1,323*	1.5 *1*	2	–
F(h′)	191.4 *1,544*	3 *2*	1	Typical for $(C_2)_i$, see Table 8.2.1
F(i′)	195.9 *1,580*	5 *3*	2	Typical for $(C_2)_i$, see Table 8.2.1

(continued)

Table 8.1.3.6 (continued)

Line/band	*E* (eV)	Width (eV)	Rel. Intens.(%)	Comment
*F(α1)	1.80	0.30	–	Lumin. "Red band"; 14 SBs 31 meV [Col82b]
*F(a)	2.145	–	–	ZPL(absorption and luminescence) of F(α1, α2); very weak [Col82b], SBs: +23, −31 meV
*F(α2)	2.55	0.27	–	Absorption band; SBs 23 meV; correlates with F center IR absorption [Col82b]
*F(β1)	2.25	0.55	–	lumin. "Yellow band"; 7 SBs 34 meV [Col82b]
*F(b)	2.721	0.001	–	ZPL (absorption and PLE) of F(β1, β2) [Col82b], SBs: −34, +38 meV
*F(β2)	3.05	0.45	–	Absorption band; nine SBs 38 meV [Col82b]
(*F(γ1))	(4.30)	–	–	(Expected luminescence band)
*F(c)	4.567	0.01	–	ZPL (absorption) of F(γ2) and of $^*V_1N_4(C_2)_i{}^\circ$(c) DAP81a-g (*D* = 1.67, see Table 8.2.3),/LVM: +55 (harmonic 106), 126, 154 meV [Naz87]
*F(γ2)	5.00	0.60	–	Absorption band [Naz87]

DAP: ZPL = *L* = limiting energy, *D* = dielectric factor

8.1.4 Associates of the Single Vacancy with Ni_1, Ni_2, *and* Ni_3

Nickel is a frequent impurity in natural and HPHT diamonds (in the latter case from the melt). Of the six nickel centers in Table 8.1.4, two centers occur in natural diamond, especially the Ni 1.4 eV (=* $V_1Ni_1{}^+$) center. The number of associated Ni atoms is obtained from the Ni isotope shifts (Ni_1) or from the QLVM frequency (Ni_2 and Ni_3).

Table 8.1.4 Associates of the single vacancy with Ni_1, Ni_2, and Ni_3 (see also Tables 9.5.1.1 and 9.5.6)

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*V_1Ni_1{}^\circ$(a)	HA, MA	1.704	83a–e	+1.34	***Ni 1.70(a),** line (b) at 2.401eV/LVM: +61, +80 meV
$^*V_1Ni_1{}^\circ$(a)	HL, ML	1.704	84a–c	−1.34	***Ni 1.70(a),** QLVM: −44 meV/Ni_1 from QLVM (calc. 1Ni: 44.0 meV)
$^*V_1Ni_1{}^\circ$(b)	HA,MA, ME	2.401	29a–f	+1.34	***Ni 1.70(b),** QLVM: +34, LVM: +74 meV
$^*V_1Ni_1{}^+$	NA, HA, MA/EPR: NIRIM2 $Ni_1{}^+$; $S = \frac{1}{2}$	1.404	25a–k	+1.33	***1Ni 1.40**; weaker line at 1.401 eV from 2.8 meV gr. st. spl.; trigonal center, ⟨111⟩ polarized line, photochromic/Ni_1 from isotope shifts/QLVM: +45; LVM: +80 meV
$^*V_1Ni_1{}^+$	NL, HL, ML	1.404	26a–i	−1.33	***1Ni 1.40**/QLVM: −45, LVM: −80 meV
$^*V_1Ni_2{}^-$ (a)	ML	2.071	87a–k	−1.34	***Ni 2.07(a),** line (b) at 2.298 eV/LVM: (3×) −55 meV
$^*V_1Ni_2{}^-$ (b)	ME	2.298	27a–j	+1.34	***Ni 2.07(b),** QLVM: +30, LVM:+51 meV/Ni_2 from QLVM/PLE of *Ni 2.07(a)
$^*V_1Ni_2{}^-$ (b)	ML	2.298	28a–h	−1.34	***Ni 2.07(b),** QLVM: −32; LVM: −55 meV
$^*V_1Ni_2{}^\circ$ (a)	HL, ML	1.660	–	–	***Ni 1.66(a)**/LVM: (2×) −66 meV/slow luminescence (1.1 ms)

(continued)

Table 8.1.4 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	D (eV)	Name/comment
$^*V_1Ni_2^\circ$ (b)	HA, MA, HE, ME	2.427	–	–	***Ni 1.66(b)**/QLVM: +28, LVM: (6×) +49 meV/Ni_2 from QLVM
$^*V_1Ni_2^\circ$ (b)	HL, ML	2.427	–	–	***Ni 1.66(b)**/LVM: (2×) −61 meV
$^*V_1Ni_2^+$ (a)	HA, MA	1.693	–	–	***Ni 1.69(a),** lines(b,c) at 1.940, 1.991 eV/LVM: (3×) +51 meV/C_{2v} symmetry
$^*V_1Ni_2^+$ (a)	HL, ML	1.693	–	–	***Ni 1.69(a)**
$^*V_1Ni_2^+$ (b)	HA, MA	1.940	–	–	***Ni 1.69(b)**/LVM: (7×) +50 meV
$^*V_1Ni_2^+$ (b)	HL, ML	1.940	–	–	***Ni 1.69(b)**/LVM: −59, −64 meV
$^*V_1Ni_2^+$ (c)	HA, MA/E	1.991	–	–	***Ni 1.69(c)**/LVM: (6×) +50 meV
$^*V_1Ni_2^+$ (c)	HL, ML	1.991	111a–f	−1.34	***Ni 1.69(c)**/LVM: (3×) −57 meV
$^*V_1Ni_2N_2^\circ$	NL, ML	2.101	62a-f	−1.42	***Ni 2.10;** intense DAP lines at 1.660 and 1.890 eV (see also Table 9.5.1.2)
$^*V_1Ni_3^+$	NA, MA	2.370	91a–g	+1.34	***Ni 2.37,** named**A line;** QLVM: +37, +49 meV
$^*V_1Ni_3^+$	NL, ML	2.370	92a–f	−1.34	***Ni 2.37,** named**A line;** QLVM: −23, −38; LVM: −70 meV/Ni_3 from QLVM (calc. 3Ni: 23.3 meV)

SB-DAP = sideband DAP with ZPL = L = limiting energy, and D = dielectric factor, gr. st. spl. = ground state splitting

8.1.5 *Centers of* Ni_1 *in the Double Vacancy and Association with Nitrogen Ligands (S2-*S9)*

Eight centers (S2–*S9) are known with a single nickel atom at the center of a divacancy, see Table 8.1.5. The DAP transitions of these centers coincide in absorption and luminescence, i.e., they are of the standard type (see Sect. 10.1). Additional lines are observed for S2 and *S4, which indicate the existence of a second electronic transition for these centers.

Table 8.1.5 Centers of interstitial Ni_1 in the double vacancy and association with nitrogen ligands (S2, S3, *S4–*S9), see also Sect. 9.5.12

Defect[a]	Observed	Lines (eV)	Stand.-DAP[b]	L (eV)	D (eV)	Name/comment
$(V_2Ni_1)N_{2+0+1}{}^{+}$	NA, HA, MA, ME, NL, HL, ML EPR(**NE2**)	2.515–3.341	57a–m	2.422	+1.63	**S2**/DAP lines: ***B*** = 2.537, ***C*** = 2.597, ***D*** = 2.623, ***E*** = 2.634 eV/QLVM: +29, LVM: +34, −39, +41, −46; (3×) +63, (2×)+71, −90, ±102 meV/inactive in CL
$(V_2Ni_1)N_{2+0+0}{}^{+}$	NA, HA, MA, ME, NL, HL, ML EPR(**NE1**)	2.496– 2.800	58a–h	2.383	+1.63	**S3**/QLVM: +30, LVM: −41; −79, ±117 meV/inactive in CL
$^{*}(V_2Ni_1)N_{1+2+0}{}^{\circ}$	NA, NE, HA, HE, MA,ME EPR(**NE3**)	3.333– 3.820	59a–i	3.191	+1.53	*__S4__/PLE of *Ni 2.37(V_1Ni^{3+}, ZPL = line A, see Table 8.3a)/QLVM: −31, LVM: −38; −97, ±117, −144 meV
$^{*}(V_2Ni_1)N_{x+y+z}{}^{\circ}$	NA, HA, MA, ME, NL, HL, LL, ML	1.563–2.320	60a–g	1.460	+1.53	*__S5__/QLVM: −33, LVM: +43, −44, −61; −70, −113, −135, −153 meV
$^{*}(V_2Ni_1)N_{x+y+z}{}^{+}$	LE, ME, EPR(NE8)?	2.750–3.530	61a–m	2.637	+1.63	*__S6__/QLVM: +42; LVM: +99 meV/PLE of *S5
$^{*}(V_2Ni_1)N_{x+y+z}{}^{+}$	LE, LL, EPR(S = 1 center.)	1.802–2.620	11a–i	1.724	+1.60	*__S7__/PLE of *S5/Ni_1 from Ni isotopes (9-meV splitting); PLE in own spectrum
$^{*}(V_2Ni_1)^{-}$	HAEPR(NE4)?	1.212–1.383	16a–l	1.036	+1.45	*__S8/__broad band at 1.40 eV (named Ni 1.4 eV band)/in some samples resonance DAP 16 with 12 lines, peaking at 1.22 eV; photochromic/LVM: +64, +113, +152 meV
$^{*}(V_2Ni_1)N_{x+y+z}{}^{+}$	NL, MA, ML	1.678–1.812	4a–i	1.509	+1.66	*__S9/__spectral hole burning in absorption [Sil94a]

Standard DAP transitions (abs. = lum., *no* ZPL), for further DAP information see Table 9.5.10

[a] N_{a+b+c} indicates the number of nitrogen atoms in the first (a), second (b), or third shell (c), (as obtained from hyperfine interaction [Nad93]; see Sect. 9.5)

[b] Donor–acceptor pairs: (see Chap. 10) standard DAP57-61, 11, 16, 4 with L = limiting energy and D = dielectric factor

Four centers (S2–*S5) occur in *natural* diamond. The structure of S2–*S4 has been determined by analysis of the hyperfine interaction (HFI) between the nickel nucleus and the unpaired electron spin, which is partially located on the nitrogen ligands. The correspondence of EPR and optical centers is NE1 = S3 = $(V_2Ni_1)N_{2+0+0}{}^+$, NE2 = S2 = $(V_2Ni_1)N_{2+0+1}{}^+$, and NE3 = *S4 = $(V_2Ni_1)N_{1+2+0}{}^+$ [Nad93]. In the notation $(V_2Ni_1)N_{x+y+z}{}^+$, the nitrogen subscripts N_{x+y+z} mean: N_x in the first shell (average HFI 15.5 G), N_y in the second shell (average HFI 5.6 G), and N_z in the third shell (average HFI 2.6 G). These HFI values follow closely a $1/r^3$ rule ($x : y : z = 1.0 : 0.34 : 0.22$), where r is the distance in the unperturbed lattice (see also Sect. 9.5.10).

The nucleus for nitrogen trapping is the nitrogen-free *S8 center $(V_2Ni_1)^-$. The charge state of the center influences the dielectric factor D (see Table 8.1.5; positive: neutral: negative): $N_2 : N_1 : N_0 = 1.63 : 1.53 : 1.45$ eV (see also Sect. 8.1.5).

8.1.6 Centers of Si_2, Ni_2, or Co_2 in the Triple Vacancy

$^*(V_3Si_2)^\circ$: For the 1.681-eV silicon center, the line shifts and intensities for the natural isotopes clearly reveal two equivalent Si atoms [Ste95]. From theory and detailed experimental analysis (observed $\langle 110 \rangle$ oriented dipole), it is known that each of the two equivalent Si atoms is situated midway between two vacancies of a triple vacancy, forming a $\langle 110 \rangle$ oriented defect [Bro95]. The 1.681-eV silicon center is a prominent defect in HTHP and CVP synthetic diamonds, and is stable above 2,200 °C. The other two charge states ($^*(V_3Si_2)^-$ at 2.523 eV and $^*(V_3Si_2)^\circ$ at 2.052 eV) are also thermally stable, as indicated by their presence in natural diamond (see Table 8.1.6). It appears that this unusual but very stable structure is the preferred incorporation of Si in natural diamond, see Sect. 9.4.

$^*(V_3Ni_2)^\circ$: This center is observed in as-grown HTHP synthetic diamonds, grown from a nickel melt, and with a nitrogen content > 50 ppm. The only LVM frequency (+61 meV) is unchanged in ^{13}C diamond, indicating a Ni–Ni vibration (see Table 8.1.6).

$^*(V_3Co_2)^\circ$: This center is observed in HPHT synthetic diamond, grown from a cobalt melt, see Tables 8.1.6 and 9.6.

Table 8.1.6 Associates of the triple vacancy with two equivalent interstitial silicon, cobalt, or nickel atoms

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*(V_3Si_2)^-$	NE, NL, Si impl. ME, ML	2.523	75a–j	−1.25	*2Si 2.52/QLVM: −31($w = 25$), 44 ($w = 40$) meV, Si_2 from QLVM (calc. 2Si = 44.9 meV)/PLE of *2Si 1.68/decay time 1.0–1.8 μs
$^*(V_3Si_2)^\circ$	NL	2.052	65a–e	−1.39	*2Si 2.05/QLVM: −45($w = 23$); LVM: −70 meV, Si_2 from QLVM (calc. 2Si = 44.9 meV)/PLE of *2Si 1.68
$^*(V_3Si_2)^+$	HA, LA Si impl. MA	1.682	53a–m	1.60	*2Si 1.68/QLVM: +43($w = 30$); LVM: +67 meV, Si_2 from QLVM (calc. 2Si = 44.9 meV)/ photochromic
$^*(V_3Si_2)^+$	HL, LL Si impl. ML	1.682	54a–g	−1.60	*2Si 1.68/QLVM: −42($w = 25$); LVM: −65 meV/gr. st. spl. = 0.2 meV; exc. st. spl. = 1.1 meV/Si_2 from shifts of two equivalent Si isotopes (see Table 9.4.2)/⟨110⟩ oriented dipole, decay time from 2.4 ns to 105 μs, photochromic
$^*(V_3Co_2)^+$	HL	1.989	112a–f	−1.37	*2Co 1.99/QLVM: −25, LVM: −56 meV
$^*(V_3Ni_2)^\circ$(a)	HA, LA	1.883	107a–g	+1.36	*2Ni 1.88a/LVM: (2×)+61 meV/lines (b, c) from exc. st. spl., see below
$^*(V_3Ni_2)^\circ$(a)	HL	1.883	108a,b	−1.36	*2Ni 1.88a/QLVM: −26, LVM: −65 meV
$^*(V_3Ni_2)^\circ$(b)	HA,HL	1.905	–	–	*2Ni 1.88b/LVM: (2×)+61 meV
$^*(V_3Ni_2)^\circ$(c)	HA,HL	1.913	–	–	*2Ni 1.88c/LVM: (2×) +61 meV
$^*(V_3Ni_2)^+$(a)	NA,HA MA	2.562	105a–c	+1.55	*2Ni 2.56a/weak ZPL/line (b) at 2.588 eV from 26 meV exc. st. spl.

(continued)

Table 8.1.6 (continued)

Defect	Observed	ZPL (eV)	SB-DAP	D (eV)	Name/comment
$^*(V_3Ni_2)^+$(a)	NL,HLML	2.562	106a–f	−1.55	*2Ni 2.56a/line (b) at 2.588 eV from 26 meV exc. st. spl./QLVM: −25, −36 meV/Ni_2 from shifts of two equiv. Ni isotopes (Table 7.5)/gr. st. spl. 0.36 and 0.66 meV/slow luminescence (140 μs at 2.3 K)
$^*(V_3Ni_2)^+$(c)	NA,HA HE,MA	3.064	–	–	*2Ni 2.56c/line (d) at 3.076 eV from 12 meV exc. st. spl./QLVM: +26 meV/PLE of line (a)

SB-DAP = sideband DAP with ZPL = L = limiting energy and D = dielectric factor; gr. st. spl. = ground state splitting; exc. st. spl. = excited state splitting

8.1.7 Associates of the Vacancies with H, (H + N), He, Li, B, N, Al, Si, Ti, Cr, Co, Ni, Zn, As, Zr, Ag, Xe, Ta, W, and Tl

Only the associates of the vacancy with hydrogen, boron, aluminum, and silicon occur in natural diamond, the others being produced by implantation or doping (see Tables 8.1.7.1 and 8.1.7.2).

The single lattice vacancy can be filled with one hydrogen atom (with concentrations up to 1 at. %). Optical absorption is observed from two fundamental vibrations: C–H bend at 174 meV and C–H stretch at 385 meV, see Table 8.1.7.1. There are six harmonic and combination sidebands [Dav84b], see Table 9.3.1. A five-line sideband system from DAP transitions is observed for the C–H stretch line at 0.385 eV.

In homoepitaxial CVD diamond, a center with T_d symmetry (as evidenced by isotopic deuterium substitution [Fuc95a, b]) is observed. In a tentative assignment, a fourfold vacancy is filled by four hydrogen atoms. There are two ZPL lines at 165 meV (C–C stretch?) and 412 meV (C–H stretch?). For both lines, a sideband DAP system (DAP39, 40) is observed, see Table 8.1.7.2 and Sect. 9.3.

The $^*V_1B_1$(a, b) centers occur only in boron-rich type IIb diamonds, while the $^*V_1Al_1{}^\circ$ is found in HPHT synthetic diamonds (with Al in the melt) and in rare natural diamonds.

The other centers in Tables 8.1.7.1 and 8.1.7.2 are observed after implantation of the respective ions. The QLVM frequencies have the expected values (see Tables 11.2 and A.3). For these centers, the dielectric factor (D = 1.25–1.60 eV) is similar to those for $V_1{}^\circ$ and $V_2{}^\circ$ (1.24–1.63 eV) or V_1N_n (1.33–1.69 eV).

Table 8.1.7.1 Associates of the single vacancy with H_1, H_1+N_1, H_1+N_3, $H_1 + N_4$, He, Li, B, Al, Cr, Zn, and As

Defect	Atomic Radius (nm) [1)]	Observed	ZPL (eV)	SB DAP	*D* (eV)	Name/comment
$^*(V_1H_1)^\circ$	(140)	NA	0.174	–	–	nat. CH bend (see Table 9.3.1)
$^*(V_1H_1)^\circ$	(140)	NA	0.385	41a–e	1.54	nat. CH stretch (see Table 9.3.1)
$^*(V_1H_1)N_1{}^\circ$	(140)	NA	0.182	–	–	nat. NH bend, harmonic at 0.362 eV, (see Table 9.3.1)
$^*(V_1H_1)N_1{}^\circ$	(140)	NA	0.401	–	–	nat. NH stretch, combination line at 0.583 eV (=0.401 + 0.182 eV)
$^*(V_1H_1)N_3{}^\circ$	(140)	MA	0.198	–	–	NH bend (see Table 9.3.1)
$^*(V_1H_1)N_3{}^\circ$	(140)	MA	0.390	–	–	NH stretch (see Table 9.3.1)
$^*(V_1H_1)N_4{}^\circ$	(140)	MA	0.192	–	–	NH bend (see Table 9.3.1)
$^*(V_1H_1)N_4{}^\circ$	(140)	MA	(0.424)	–	–	Expected NH stretch (see Table 9.3.1)
$^*V_1He_1(a)^\circ$	(90)	ML (He impl.)	2.212	95a–f	−1.57	Line (b) 2.316 eV/QLVM: −38; LVM: −91 meV
$^*V_1Li_1{}^\circ$	77	ML (Li impl.)	1.881	68a–g	−1.58	QLVM: −36 meV
$^*V_1B_1(a)^\circ$	(86)	NL	2.395	73a–f	−1.30	Also broad band at 2.20 eV
$^*V_1B_1(b)^\circ$	(86)	NL	3.120	74°-f	−1.30	Also broad band at 2.85 eV
$^*\boldsymbol{V_1N_n}$	***70***	–	–	–	–	***See Tables 8.1.3.1–8.1.3.6***
$^*V_1Al_1{}^\circ$	141	NL,HL (Al dop.)	2.974	66a–e	−1.52	QLVM: −42 meV

$^*V_mSi_n$	***119***	–	–	–	–	***See Tables 8.1.6 and Sect. 9.4***
$^*V_mNi_n$	***127***	–	–	–	–	***See Tables 8.1.4–8.1.6 and Sect. 9.5***
$^*\mathrm{V}_1\mathrm{Cr}_1{}^{\circ}$	126	ML (Cr impl.)	1.673	–	–	QLVM: −31 meV
$^*V_mCo_n$	***128***	–	–	–	–	***See Tables 8.1.6 and Sect. 9.6***
$^*\mathrm{V}_1\mathrm{Zn}_1{}^{\circ}$	134	ML (Zn impl.)	2.394	114a–f	−1.42	QLVM: (2×) −30 meV
$^*\mathrm{V}_1\mathrm{As}_1{}^{\circ}$	120	MA (As doped)	0.113	115a–f	+1.32	QLVM: +25 meV

[a] [Fin56], Fig. 1, with (interpolated) values, SB-DAP = sideband DAP with ZPL = L = limiting energy and D = dielectric factor; QLVM see Table 11.2

Table 8.1.7.2 Associates of the multiple vacancy with H_4, N, Si, Ni, Ti, Co, Zr, Ag, Xe, Ta, W, and Tl

Defect	Atomic radius (nm) [a]	Observed	ZPL (eV)	SB/*sta.* DAP	D (eV)	Name/comment
$^*(V_4H_4)^-$	(140)	LA	0.165	39a–j	+1.31	homo-epi-CVD: *C–C stretch
$^*(V_4H_4)^\circ$	(140)	LA	0.412	40a–g	+1.43	homo-epi-CVD: *C–H stretch
$^*\boldsymbol{V_mN_n}$	***70***	–	–	–	–	***See Tables 8.1.3.4 and Sect. 9.1***
$^*\boldsymbol{V_mSi_n}$	***119***	–	–	–	–	***See Tables 8.1.6 and Sect. 9.4***
$^*(V_2Ti_1)^\circ$	150	ML (Ti impl.)	1.249	–	–	QLVM: −28, 85; LVM: 32, 119 meV
$^*\boldsymbol{V_mCo_n}$	***128***	–	–	–	–	***See Tables 8.1.6 and Sect. 9.6***
$^*\boldsymbol{V_mNi_n}$	***127***	–	–	–	–	***See Tables 8.1.5, 8.1.6 and Sect. 9.5***
$^*(V_2Zr_1)^\circ$	163	HL (Zr melt)	$L = 1.364$	*stand., 5a–j*	+1.39	Zr–Ni–Si melt
$^*(V_2Ag_1)(a)^\circ$	144	ML (Ag impl.)	3.111	85a–f	−1.31	Line (b) 3.117 eV/QLVM: (2×) −21(1Ag+8C); LVM: −67 meV/gr. st. spl. = 6 meV
$^*(V_2Xe_1)$, distorted°	233	ML (Xe impl.)	1.528	42a–j	−1.33	QLVM: −29 meV(1 Xe)
$^*(V_2Ta_1)$	141	LL (hot filament)	$L = 1.667$	*stand, 7a–g*	+1.23	DAP7b with LVM: −48 meV
$^*(V_2W_1)$	138	LL (hot filament)	$L = 1.608$	*stand, 6a–f*	+1.24	DAP6b with LVM: (5×) −24 meV(1 W)
$^*(V_2Tl_1)^\circ$, distorted	199	ML (Tl impl.)	2.019	94a–f	−1.57	QLVM: −21(1 Tl); LVM: −45 meV

[a] [Fin56], Fig. 1, with (interpolated) values, SB-DAP = sideband DAP/*sta. DAP* = *standard* DAP with $ZPL = L =$ *limiting energy*; D = dielectric factor; QLVM see Table 11.2

8.2 The ⟨100⟩ Split Self-Interstitial and Associates

In a fundamental theoretical analysis, it has been shown that the only stable structure for the self-interstitial in diamond (in the 1−, neutral, 1+, and 2+ charge state) is the ⟨100⟩ split interstitial [Bre95]. Earlier theoretical work [Wei73, Mai78] had already favored the ⟨100⟩ split self-interstitial configuration. The ⟨100⟩ split self-interstitial configuration has also been confirmed experimentally by detailed analysis of the ^{13}C isotope shifts [Ste99a, Dav00, Twi01] (see Sect. 8.3.6). A Jahn–Teller distortion from D_{2d} to D_2 is predicted for the 1−, neutral, and 1+ charge state [Bre95]. The calculated activation energy for migration of the neutral self-interstitial is 1.7 eV [Bre95]. The notation used here is $(C_2)_i$.

The isolated self-interstitial is optically observed in the negative charge state (3H center at 2.462 eV), in the neutral charge state (1.685-eV center = R2 in EPR), and in the positive charge state (TR12 center at 2.638 eV); see Sect. 8.2.1 and Table 8.2.1. For the neutral charge state (1.685-eV center), an energy level scheme was calculated and yielded good agreement with the experimental data, especially with the 6-meV splitting of the ground state [Dav01b, Gos01a, Mai01].

By association with one nitrogen ($(^*C_2)_iN_1{}^\circ = $ 5RL center at 4.582 eV), the ⟨100⟩ split self-interstitial can be "stabilized" (up to $T = 1{,}000\,°C$ and thus observable in as-grown CVD diamond).

Association with two nitrogens is observed after heavy electron irradiation of nitrogen-rich diamond [Col79c]. The ZPLs of the three charge states are at 2.367 eV ($(^*C_2)_iN_2{}^-$), at 1.979 eV ($(^*C_2)_iN_2{}^\circ$), and at 2.535 eV $\left((^*C_2)_iN_2{}^+\right)$.

A very stable center (observed in as-grown HPHT and CVD diamond) consists of the split interstitial with one interstitial carbon replaced by nitrogen, here denoted by $(C_1N_1)_i$. This center is optically observed in the negative charge state (3.988-eV center = R11), in the neutral charge state (0.212-eV center), and in the positive charge state (*2.807-eV center); see Sect. 8.2.4 and Table 8.2.4.

8.2.1 The Isolated ⟨100⟩ *Split Self-Interstitial*

The isolated ⟨100⟩ split self-interstitial is observed in three charge states.

$\mathbf{(C_2)_i{}^+}$ = **TR12**: In irradiated diamond, optical spectra of the TR12 center with two ZPLs at 2.638 eV (TR12) and 2.670 eV (TR13, in absorption only) are observed. There are numerous sidebands (TR14-TR18 in absorption). With the exception of the TR17 LVM line at +188 (absorption) and −199 meV (luminescence), these absorption sidebands belong to $(C_2)_i{}^+$-DAP35 transitions (absorption) and $(C_2)_i{}^+$-DAP36 transitions (luminescence). The TR12 center anneals out above 700 °C.

Table 8.2.1 The isolated and multiple ⟨100⟩ split C_2 self-interstitial in diamond

Defect	Observed	ZPL (eV)	SB-DAP	*D* (eV)	Name/comment
$^*(C_2)_i^-$	ML	2.462	86a–i	−1.31	**3H**/LVM: −139, −165, −169, −182, −187, −218(C) meV/dyn. JT
$^*(C_2)_i^-$	MA	2.462	–	–	**3H**/LVM: +67 meV (see Table 11.1)
$^*(C_2)_i^+$(a)	MA, ME	2.638	35a–n	+1.30	**TR12**/LVM: +67, +77, +139 = **TR14**, +188 = **TR17**, +225 meV/IR: +190 meV/dyn. JT
$^*(C_2)_i^+$(a)	ML	2.638	36a–n	−1.30	**TR12**/LVM: −65, −80, −143, −199, −209 meV/dyn. JT
$^*(C_2)_i^+$(b)	MA, ME	2.670	–	–	**TR13**/from 32 meV excited state splitting/LVM: +188 meV/no luminescence
$^*(C_2)_i^\circ$	MA, EPR (R2)	1.685	71a–c	+1.30	**R2**/QLVM: +40,+80; LVM: +169 meV/IR: +167 meV/gr. st. spl. = 6 meV; ZPL starting from upper gr. st./dyn. JT
$^*(C_2)_i^\circ$	MA	((1.859)	–	–	**pseudo** ZPL, LVM sideband (169 meV) starting from lower gr. st. of R2 center (1.685 eV)
$(C_4)_i^\circ$	EPR (R1)	–	–	–	**R1**(EPR) = $\mathbf{I}_2$ [Twi01]; no optical lines
$(C_6)_i^\circ$	EPR (O3)	–	–	–	**O3**(EPR) = $\mathbf{I}_3$ [Twi01]; no optical lines
$^*(C_{2n})_i^\circ$	NL, ML	1.528	96a–g	−1.30	**D(a) = platelets**/weak ZPL; broad band at 1.25 eV/IR bands D(a′)–D(f′) see Table 8.2.2

SB-DAP = sideband DAP with*L* = *ZPL* = limiting energy and *D* = dielectric factor; IR: = observed IR bands (LVM absorption); From ^{13}C and ^{15}N isotope shifts [Col88c]; (C) = established as C–C vibration by full ^{13}C (and no ^{15}N) isotope shift; (N) = established as N–C vibration by ^{15}N (and reduced ^{13}C) isotope shift; dyn. JT = dynamic Jahn–Teller effect; gr. st. spl. = ground state splitting; exc. st. spl. = excited state splitting

$(C_2)_i{}^\circ$: The neutral charge state gives rise to a ZPL at 1.685 eV and an intense sideband line at 1.859 eV. The ground state is split by 6.2 meV and, due to selection rules, the ZPL starts at the upper ground state, while the sideband line starts at the lower ground state. The 6.2-meV ground state splitting is interpreted as a "tunneling splitting" arising from the movement between two equivalent equilibrium sites [Dav01b]. Only the excited state couples to a phonon with an energy of 169 meV. The 1.685-eV ZPL couples to the sideband $(C_2)_i{}^\circ$-DAP71 transitions with three lines. Thermal annealing of the 1.685 eV center $= (C_2)_i{}^\circ$ occurs at relatively low temperatures (typically 420–540 °C). In the first stage, the $(C_2)_i{}^\circ$ is quantitatively converted into $(C_2)_i{}^+ =$ TR12 [All98a]. In a second stage ($T > 700$ °C), all isolated self-interstitials are annihilated by migration to vacancy centers (GR1 etc).

$(C_2)_i{}^- =$ 3H: From the singly negative charge state, a luminescence spectrum of the 3H center with the ZPL at 2.462 eV and several sidebands is observed. The LVM sidebands have energies of −169, −182, −187, and −218 meV. At least nine sidebands can be assigned to $(C_2)_i{}^-$-DAP86 transitions. The 3H center is not observed in p-type diamond. Strong optical (reversible) bleaching of the 3H center occurs for 488 nm or UV illuminations [Ste99a].

8.2.2 *The Multiple* ⟨100⟩ *Split Self-Interstitial*

Aggregates of self-interstitials are observed in EPR [Twi01], but not optically. These are $(2 \times (C_2)_i{}^\circ =$ EPR-R1 named I_2) and $(3 \times (C_2)_i{}^\circ =$ EPR-O3 named I_3).

$(C_{2n})_i$ = platelets = D center: Much larger self-interstitial aggregates (with dimension up to 100 μm) with orientation in (100) planes are observed in natural or

Table 8.2.2 Lines and bands from the D center (platelets, B′): $^*(C_{2n})_i = D(a'$–f′) and D(α), D(a)

Line/band[a]	E (meV)*(cm⁻¹)*	Width (meV)*(%)*	Rel. Intens (%)	Comment/for vibrations see also Table 11.1
D(a′)	40.9 *331*	–	–	Out of plane bend sp^2–sp^2; [Zai01]
D(b′)	150.0 *1,210*	6 *4*	34	Mixed sp^2–sp^3 stretch at the *surface* of the platelet; Figs. 3.20 [Woo83], 3.25 [Cla84b]
D(c′)	156.1 *1,258*	7 *4*	32	Mixed sp^2–sp^3 stretch at the *surface* of the platelet; Fig. 3.25 [Cla84b]
D(d′)	167.6 *1,352*	2 *1*	31	Mixed sp^2–sp^3 stretch at the *surface* of the platelet, very asymmetric line shape; Figs. 3.20 [Woo83], 3.25 [Cla84b]

(continued)

Table 8.2.2 (continued)

Line/band[a]	*E* (meV)(*cm*$^{-1}$)	Width (meV)(*%*)	Rel. Intens (*%*)	Comment/for vibrations see also Table 11.1
D(e′1)	168.0 *1,355*	0.7 *0.4*	1	**Large** platelets; mixed sp^2–sp^3 stretch at the *rim* of the platelet; Figs. 3.7 [Fer96], 3.20 [Woo83]
D(e′2)	172.0 *1,387*	3 *2*	2	**Small** platelets; mixed sp^2–sp^3 stretch at the *rim* of the platelet; Figs. 3.20 [Woo83], 3.26 [Fri91a]
D(f′)	177.3 *1,430*	–	–	Very weak; symmetric sp^2–sp^2 stretch; [Zai01]
Line/band	*E* (eV)	Width (eV)(*%*)	Rel. Intens (*%*)	Comment/for vibrations see also Table 11.1
D(α)	1.250	0.300 *24*		Strongly polarized E ‖ (100) platelet plane; Fig. 5.9 [Ruo91a]
D(a)	1.526	0.038 *2*		ZPL of D(*α*), Fig: 5.9 [Ruo91a], 5.15 [Sil95], 7.80 [Dav77c]; LVM: (2×) −45 meV (corresponding to IR line D(a′)), (2×) −163 meV (corresponding to IR lines D(b′), D(c′), D(d′)); ZPL of DAP97a-f

[a] D(a′–f′) observed in NA, HA, MA; D(α), D(a) observed in NL, HL, ML

annealed diamond (see Tables 8.2.1 and 8.2.2), and also in heavily neutron irradiated diamond. These aggregates have been named "platelets", and can be observed as X-ray or electron microscopy spikes. Optically, there is characteristic IR absorption (with the historical name "D center") and a ZPL at 1.525 with a broad sideband at 1.25 eV (see Table 8.2.1 and 8.2.2). In absorption, there are three infrared lines at 41, 158–173, and 177 meV. The position of the intense sharp line depends on the size of the platelets and varies from 173 meV (for small) to 158 meV (for large platelets). In luminescence, a broad band at 1.25 eV with a weak ZPL at 1.526 and seven DAP96 lines is observed (see Table 8.2.1 and 8.2.2).

8.2.3 Associates of the $(C_2)_i$ Split Interstitial with N_1, N_2, with B_1, B_2, B_3, or with Ni

Ten associates of $(C_2)_i$ with nitrogen, boron, or nickel are listed in Table 8.2.3.

Table 8.2.3 Associates of the $(C_2)_i$ ⟨100⟩ split interstitial with N, B, or Ni

Defect	Observed	ZPL (eV)	DAP[a]	D (eV)	Name/comment[b–d]
$^*(C_2)_iN_1^-$	LA, MA	3.188	–	–	**3.188 eV** center (weak absorption)/IR: +180 (51% C, 49% N), +190 (98% C), +232 (98% C) meV
$^*(C_2)_iN_1^-$	LL, ML	3.188	72 a-n	−1.26	**3.188 eV** ce./QLVM: −58,−80; LVM: −77 ? −108 (46% C), −138 (54% C, 46% N), −161 (78% C), −179 (54% C), −190 (95% C), −238 (100% C), (combinations: −290, −300, −322, −393, −413, −468, −491) meV
$^*(C_2)_iN_1^\circ$	LA, MA	4.582	79a–j	+1.26	**5RL**/QLVM: +42; LVM: +167, 195, 202 meV/IR: +167 (100% C), +186 (56% C, 44% N), +201 (61% C, 39% N), +245 (100% C) meV
$^*(C_2)_iN_1^\circ$	LL, ML	4.582	80a–e	−1.26	**5RL**/QLVM: −58; LVM: −146 (68% C, 32%N), −175 (88% C, 12% N), −193 (93% C, 7% N), (4×) −237 (100% C) meV
$^*(C_2)_iN_1^+$	ML	4.676	–	–	QLVM: −58; LVM: −195, (4×) −240 (C)/IR: +238 meV
$^*(C_2)_iN_2^-$	MA	2.367	88a–f	+1.25	More lines at 2.378, 2.385, 2.678 eV/QLVM: +38 meV; LVM combination: +314 meV/gr. st. spl. = 3.2 meV/N_2C_4 from QLVM (calc 37.3 meV)/ photochromic with $^*(C_2)_iN_2^\circ$ at 1.979 eV
$^*(C_2)_iN_2^-$	ML	2.367	89a–j	−1.25	QLVM: −38; LVM: −90, −160, −232 meV/N_2C_4 from QLVM (calc. 37.3 meV)
$^*(C_2)_iN_2^\circ$	MA	1.979	–	–	QLVM: +37, +67 meV/gr. st. spl. = 4.1 meV
$^*(C_2)_iN_2^+$	MA	2.535	90a–c	+1.25	QLVM: +70 meV (calc. 74.5 meV for N_2)
$^*(C_2)_iB_1^\circ$	ML (type IIb, irrad.)	4.777	97a–d	−1.25	**2BD**(F); split off lines at 4.773, 4.781 eV/LVM: (3×) −210 meV/dyn. JT?
$^*(C_2)_iB_2^\circ$	ML (type IIb, irrad.)	4.698	–	–	**2BD**(G)/LVM: (3×) −220 meV

(continued)

Table 8.2.3 (continued)

Defect	Observed	ZPL (eV)	DAP[a]	D (eV)	Name/comment[b–d]
$^*(C_2)_iB_3^\circ$	ML (type IIb, irrad.)	4.803	–	–	**2BD(C)**/LVM: (3×) −236 meV
$^*(C_2)_iNi_1^\circ$	ML	2.436	14a–f	−1.22	Resonance/SB DAP14(2.066–2.271 eV), resonance lines at 2.156 ($V_1N_1^\circ$) and 2.427 eV ($V_1Ni_2^+$(b)); QLVM: −75 meV

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[a] All DAPs are of the sideband type with L = ZPL = limiting energy and D = dielectric factor

[b] ***5RL**-IR: LVM absorption including ^{13}C and ^{15}N isotope line shifts [Col88c]; from precise data, the percentage of C or N vibrational involvement could be calculated for this table

[c] dyn. JT = dynamic Jahn–Teller effect

[d] gr. st. spl. = ground state splitting

***(C$_2$)$_i$N$_1^-$**: The 3.188 eV center is observed in luminescence with the ZPL at 3.188 eV, and with a rich sideband structure. This center occurs in as-grown HPHT and CVD diamond and in irradiated nitrogen containing diamond. Valuable information for the assignment of the LVM sidebands is obtained from the isotope shifts (see Sect. 8.3.6) The 238-meV LVM (central N–C vibration) is hidden under an intense combination sideband (see below). There are nine LVM combination bands at 238, 290, 300, 322, 393, 404, 413, 468, and 491 meV. It has been shown [Dis94a], that a complete assignment is possible, and this in turn confirms the frequencies of the one phonon LVM lines. If the latter are denoted by $a = 108$, $b = 138$, $c = 161$, $d = 179$, $e = 190$, and $f = 238$ meV, than the combinations are $a + b = 238$, $a + d = 290$, $a + e = b + c = 300$, $2c = 322$, $2a + d = 393$, $2a + e = c + f = 404$, $d + f = 413$, $2d = 468$, and $b + 2e = 491$ meV. Thanks to the high luminescence intensity of the 3.188-eV center, 14 weak lines (in addition to the phonon sidebands) have been identified [Zai01], which can be assigned to **(C$_2$)$_i$N$_1^-$**-DAP72a-n transitions.

***(C$_2$)$_i$N$_1^\circ$**: From this 5RL center, a luminescence spectrum is observed, both in irradiated diamond and in as-grown CVD diamond. The 5RL spectrum is also observed in absorption. The ZPL is at 4.582 eV. The luminescence sideband structure is very unusual and has been analyzed by isotopic substitution [Col93b]. The 237-meV phonon (typical for the vibration of the central C–C bond, and dipole enhanced by the associated nitrogen) arises from two almost equivalent carbon atoms. This vibration produces not only an intense first-order sideband (which is more intense than the ZPL), but also a second, third, and fourth harmonic sideband. Combination lines from the harmonics and the other phonons are also observed. Five weak lines can be assigned to $(C_2)_iN_1$-DAP79 transitions. The 5RL center anneals out at temperatures from 800 to 1,200 °C [Zai01].

***(C$_2$)$_i$N$_1^+$**: The QLVM frequency (−58 meV in luminescence) is the same as for the neutral charge state, and both are in excellent agreement with the theoretical value of 58.5 meV, calculated for N_1C_2.

$^*\mathbf{(C_2)_iN_2{}^-}$: This 2.367-eV center is observed in absorption (DAP88, QLVM at +38 meV from N_2C_4) and in luminescence (DAP89, QLVM at −38 meV from N_2C_4, LVM at −232 meV from $(C_2)_i$). Cathodoluminescence from the 2.367-eV line is observed in cobalt grown synthetic HPHT diamond after heating at 1, 500 °C [Col85b].

$^*\mathbf{(C_2)_iN_2{}^\circ}$: The 1.979-eV center is created after optical bleaching of the 2.367 eV center ($^*(C_2)_iN_2{}^-$) [Col79c]. The reverse process occurs by thermal recovery with an activation energy of 0.7 eV [Col79c].

$^*\mathbf{(C_2)_iN_2{}^+}$: The 2.535-eV center is relatively weak in samples showing also the 1.979 and 2.367-eV centers. Only three DAP90 sidebands and one QLVM at 73 meV (from N_2) are observed.

From thermal data, a ground state splitting of 3.25 meV for the 2.367 eV center ($=^*$ $(C_2)_iN_2{}^-$), and 6.7 meV for the 1.979 eV center ($=^*$ $(C_2)_iN_2{}^\circ$) have been determined [Col79c]. The above three centers disappear at $T > 350\,°C$ from the 1.6 to 2.9 eV spectral range [Col79c], possibly by transformation into $^*(C_2)_iN_2{}^{2+}$ with an expected ZPL in the 4.0–4.5 eV range.

$^*\mathbf{(C_2)_iB_1{}^\circ}$, $^*\mathbf{(C_2)_iB_2{}^\circ}$, $^*\mathbf{(C_2)_iB_3{}^\circ}$: In irradiated boron-rich type IIb diamonds, three 2BD centers are observed (2BD stands for IIb damaged). These centers are also observed in as-grown boron doped CVD diamond [Yok92]. Similar to the 5RL = $(C_2)_i$ $N_1{}^\circ$ center, very intense high frequency sidebands (210–237 meV from $(C_2)_i$) are observed for the 2BD centers. In an attempt, to interpret the three similar spectra, the following assignment can be proposed: The 4.698 eV (2BD(G)) center has one boron ligand, the 4.777 eV (2BD(F)) center has two boron ligands, and the 4.803 eV (2BD(C)) center has three boron ligands (see Table 8.2.3). The ZPL of the 2BD(F) center is a triplet with 10-meV spitting (lines at 4.767, 4.777, and 4.787 eV at 100 K). At 50 K, the 4.767-eV component disappears. For the 2BD(F) center, weak sidebands from DAP97a-d can be identified.

$^*\mathbf{(C_2)_iNi_1{}^\circ}$: In low-nitrogen natural or HPHT synthetic diamond after ion (e.g., Ni or C^+) implantation and > 700 °C anneal. The seven DAP lines at 2.066, 2.101, 2.123, 2.181, 2.202 2.234, and 2.271 (ZPL at 2.436 eV) are resonant with $V_1N_1{}^\circ$ at 2.154 eV and with $^*V_1Ni_2{}^\circ$(b) at 2.427 eV.

8.2.4 The ⟨100⟩ *Split Nitrogen–Carbon Interstitial* $(\mathbf{N_1C_1})_i$ *and Associates with* $B_1{}^-$, $B_1{}^\circ$, $B_1{}^+$

Substitution of nitrogen for carbon in the ⟨100⟩ self-interstitial leads to $(N_1C_1)_i$ (three charge states listed), and associates with boron (three charge states), in Table 8.2.4. The $(N_2)_i$ center (IR line at 0.230 eV = LVM) is not a truly “intrinsic” defect).

Table 8.2.4 The $(N_1C_1)_i$ split ⟨100⟩ interstitial and associates with boron, and the ⟨100⟩ split $(N_2)_i$ interstitial in diamond

Defect	Observed	ZPL (eV)	SB-DAP[a]	D (eV)	Name/comment[b]
$^*(N_1C_1)_i{}^-$	MA	3.988	69a–l	+1.26	**R11** ce./QLVM:+38, +79; LVM: +120, +195?, +188, +218, +230?, (combinations: +308, +338) meV/IR: +186 (100% C), +195 (50% N)
$^*(N_1C_1)_i{}^\circ$	NA	0.212	3a–i	+1.24	Pseudo ZPL from N–C stretch (51% C, 49% N) = first DAP-SB (s = 38, at 0.386 eV) in resonance with nat. C–H stretch (0.385 eV)
$^*(N_1C_1)_i{}^+$	LA, MA	2.807	–	–	ZPL is weak in absorption/IR: +190 (100% C), +212 meV (51% C, 49% N)
$^*(N_1C_1)_i{}^+$	LL, ML	2.807	98a–i	−1.25	QLVM: −58; LVM: −171 (98% C, 0% N), −175 (87% C, 13% N); N_1 from (50%) ^{15}N isotope doublet [Col89c]
$^*(N_1C_1)_iB_1{}^-$	LL (B doped)	2.992	101a–h	−1.20	Hot filament CVD, [Ste96a]
$^*(N_1C_1)_iB_1{}^\circ$	LL (B doped)	2.792	99a–h	−1.25	QLVM: −50 meV [Ste96a], [Dis94a, b]
$^*(N_1C_1)_iB_1{}^+$	LL, ML (B doped)	3.092	100a–g	−1.27	QLVM: −58; LVM: −105, −165, −205, −216 meV [Col89d, Dis94a]
$^*(N_2)_i{}^\circ$	MA	0.230	–	–	IR LVM: +230 meV/N_2 from isotopes (55%) ^{15}N: +225, +227, +230 meV [Col87c]/*not truly intrinsic!* see also Table 9.1.4

[a] SB-DAP = sideband DAP with L = ZPL = limiting energy and D = dielectric factor

[b] IR: LVM absorption including ^{13}C and ^{15}N isotope shifts [Col88c, Col89b]; from the precise data, the percentage of C or N vibrational involvement could be calculated for this table

$^*\mathbf{(N_1C_1)_i}^-$: In the negative charge state (R11 center), an absorption spectrum with the ZPL at 3.988 eV and a rich sideband structure is observed. There are two fundamental differences in comparison with the $(N_1C_1)_i^+$ and $(N_1C_1)_i^\circ$ centers, which occur in as-grown samples. (1) The $(N_1C_1)_i^-$ center is observed only in irradiated diamond, and it starts to anneal out above 400 °C, while the $(N_1C_1)_i^+$ and $(N_1C_1)_i^\circ$ centers occur in as-grown samples; (2) the $(N_1C_1)_i^-$ center is observed only in absorption, while the other charge states are intense in luminescence and very weak in absorption. Unfortunately, no results from isotopic substitution are reported for the $(N_1C_1)_i^-$ center. It is therefore difficult to separate vibrational sidebands from the DAP69 transitions. Assuming that the slightly sharper sidebands at 120, 308, and 338 meV are LVM lines (the latter two as LVM combinations), LVM frequencies of 120, 188, and 218 meV can be deduced, which coincide with two weak lines at 188 and 218 meV in the spectrum. Twelve sidebands can be assigned to $(N_1C_1)_i^-$-DAP69 transitions.

$^*\mathbf{(N_1C_1)_i}^+$: The 2.807 center is observed in irradiated diamond [Zai01] and in as-grown CVD diamond [Dis94a]. The 2.807-eV center has sharp sidebands from at least seven LVM frequencies. In a detailed ^{13}C and ^{15}N isotope shift analysis [Col89a], it has been found that five vibrations (168, 171, 172, 177, and 199 meV) are localized at carbon atoms, one vibration (191 meV) at a nitrogen atom, and one vibration (175 meV) mainly at a carbon and partly at the nitrogen atom. Remarkable are the DAP3 donor–acceptor transitions of the pseudo ZPL at 0.212 eV (N–C stretch vibration). This DAP is a mixture of sideband DAP and resonance DAP (observed are weak lines (0.386–0.421 eV) from nine shells ($s = 46$–32), and a sharp cut-off at the energy of the coexisting natural C–H stretch vibration at 0.385 eV). Effective in the creation of this center is the implantation of nitrogen or nickel, but normally the 2.807-eV center is 30 times weaker than, e.g., the $(N_1C_1)_i^\circ = 3.188$-eV center [Col89a]. The center anneals out at 1,200–1,400 °C.

$^*\mathbf{(N_1C_1)_iB_1}^-$: This center with four DAP101 lines (ZPL at 2.992 eV) is observed in boron doped CVD diamond. The spectra of the boron associates are very similar to those of the respective isolated centers (see above and Table 8.2.4); however, the DAP sidebands are considerably enhanced by the presence of the boron.

$^*\mathbf{(N_1C_1)_iB_1}^\circ$: In boron contaminated CVD diamond, this center with eight DAP99 lines (ZPL at 2.792 eV) is observed, together with $V_1N_1^\circ$ (2.156 eV), $^*(N_1C_1)_i^\circ$ (3.188 eV), and $^*(C_2)iN_1^\circ$ (4.582 eV).

$^*\mathbf{(N_1C_1)_iB_1}^+$: This center with a ZPL at 3.092 eV is occasionally observed in the luminescence spectrum of as-grown CVD diamond [Col89c, Dis94a]. The low intensity is not sufficient for a detailed sideband analysis.

$^*\mathbf{(N_2)_i}^\circ$: This center is not truly intrinsic, but closely related to the $^*(N_1C_1)_i$ centers. So far, only the infrared LVM line at 0.230 eV is observed (C–C stretch). The structure is revealed by the three-line splitting for 55% ^{15}N substitution [Col87c].

8.3 Discussion of Spectral Data from Intrinsic Defects

8.3.1 Thermal Stability of the Intrinsic Defects

The existing data on the thermal stability of intrinsic defects can be summarized as follows:

1. The isolated ⟨100⟩ split self-interstitial anneals out by migration at temperatures of 420–700 °C ($E_a = 1.7$ eV for $(C_2)i^{\circ}$).
2. The single vacancy anneals out at temperatures of 500–1, 000 °C. The theoretical activation energy for V_1° migration is 2.4 eV [Mai94a]. A first reduction in V1° concentration occurs, when the self-interstitials (with the lower activation energy of 1.7 eV) start to recombine with the vacancies. The divacancy is created from two isolated vacancies by 1, 000 °C anneal. While the isolated V1° is absent inside natural or as-grown HPHT synthetic diamonds, a significant concentration of V1° can be found near the growth surface of CVD diamond [All98b].
3. Increased thermal stability (evidently by reduced mobility) is observed for associates of the vacancies with impurities like nitrogen (see Tables 8.1.3.1–8.1.3.6), nickel (see Tables 8.1.4–8.1.6), hydrogen or boron (see Tables 8.1.7.1 and 8.1.7.2), and silicon (see Table 8.1.6). All these associates are found in natural diamond, which demonstrates their thermal stability.
4. For the ⟨100⟩ split self-interstitial, the gain in thermal stability by association (see Table 8.2.3) or substitution with one nitrogen ($(N_1C_1)_i$, see Table 8.2.4) is not sufficient to observe these centers in natural diamond. However, the thermal stability of the 3.188-eV center $=^* (C_2)N_1{}^-$ (up to 1, 500 °C) is sufficient for observation in as-grown HPHT and CVD diamond. In as-grown CVD diamond the centers 5RL $=^*(C_2)_iN_1{}^{\circ}$ and 2.807-eV $=^*(N_1C_1)_i{}^+$ are observed.
5. Confirmation of the stability data on the isolated defects $(C_2)_i{}^{\circ}$ and $V_1{}^{\circ}$ (taking into account the increased mobility in the damaged lattice), was obtained by a study, where the temperature dependence of the production rate of these defects during 2-MeV electron irradiation was measured. The results are: Zero production of $(C_2)_i{}^{\circ}$ at $T > 350$ °C and zero production of $V_1{}^{\circ}$ at $T > 800$ °C [Dav01b].

8.3.2 Donor–Acceptor Pair Transitions at Intrinsic Defects

For the majority of the intrinsic defect centers the ZPL couples to donor–acceptor pair transitions of the *sideband* type (Tables 8.1.1—8.2.4). Exceptions are the centers with a (V_2Ni_1) nucleus, which have DAP transitions of the *standard* type (S2–*S9, Table 8.1.5).

It is worth noting, that all 60 DAP centers of the *sideband* type in Table 10.1 can be ascribed to intrinsic defect centers. It is likely, that, that all 75 intrinsic defects in Tables 8.1.1–8.2.4 are accompanied by DAP transitions. However, the DAP transitions are often difficult to identify, and for 15 intrinsic centers in Tables 8.1.1—8.2.4 they are not yet found.

This special property (SB-DAPs) of intrinsic defects is probably due to the occurrence of *dangling bonds* (there are four dangling bonds at the lattice vacancy and two at the self-interstitial). In agreement with this interpretation would be the fact, that for the centers with a (V_2Ni_1) nucleus (S2–*S9) the DAP transitions are of the *standard* type, probably because the nickel "d" orbitals can saturate the carbon dangling bonds.

The DAPs of the sideband type have only one free parameter, namely the dielectric factor "D" for the Coulomb energy. The other parameter "L" for the limiting energy coincides with the ZPL.

In Tables 8.1.1–8.2.4, the dielectric factor D of the DAP analysis is included. For the centers with *vacancies*, the D values are in the range 1.10–1.69 eV (see Table 8.1.1–8.1.7.2). For centers with *self-interstitials*, the variation of the D values is very small (1.22–1.31 eV, see Tables 8.2.1–8.2.4 and Sect. 10.4).

If a defect exists in several charge states, there is a tendency for increasing D values when going from the negative to the neutral and to the positive charge states (see Sect. 10.5).

Characteristic for *sideband* DAPs is the "mirror image" behavior of the luminescence (low energy side of the ZPL) and absorption (high energy side of the ZPL). Consequently, the dielectric factor D is *negative* for luminescence, and *positive* for absorption. The N3(c) center at 2.985 eV is a well-known example for the mirror image (DAP23 and DAP24). Note that two different DAP numbers are required for absorption and luminescence of the same center.

Characteristic for DAPs of the *standard* type is the coincidence of absorption and luminescence lines, as observed for the S2–*S9 centers in Table 8.1.9. Also characteristic for standard DAPs is the photoluminescence excitation in the own spectrum (see $^*(V_2Ni_1)N_{x+y+z}$-DAP11 in Table 8.1.5). Another characteristic occurs with the LVM frequencies of those phonons, which couple to the standard DAP transitions. As can be seen in Tables 8.1.4–8.1.5, these frequencies are identical in absorption and luminescence.

In the past, it was tempting to interpret standard DAP lines (which coincide in absorption and luminescence) as zero phonon lines, (e.g., the B, C, D, and E line of the S2 center). The present book reveals a non-ZPL character for these and many other lines.

8.3.3 Quasilocal Vibrational Mode Sidebands at Intrinsic Defects

In a pioneering study [Zai00a] it was shown, that the quasilocal vibrational mode (QLVM) frequency is directly determined by the vibrating mass (see Sect. 11.2).

Therefore, the observed frequencies are very helpful for the determination of the atomic composition of intrinsic defects. Examples are given in Tables 11.2 and A.3. The maximum deviations between observed and calculated frequencies are only a few percent, which is of the order of experimental uncertainty or variation.

A problem exists for centers when a *dynamic Jahn–Teller effect* occurs. Numerous QLVM frequencies are observed for the isolated vacancy and vacancy-nitrogen associate centers. However, the values in the range 36–46 and 55–72 meV cannot be assigned to the expected calculated frequencies. Exceptions are the associates of the vacancy with atoms, which have a mass sufficiently different from carbon (see Table 8.1.7.2 and 11.2).

For associates of the vacancy with one impurity atom, the QLVM cluster can include the three impurity ligands (C_3), plus the three vacancy ligands (total $= C_6$). With Jahn–Teller distortion, three impurity ligands (C_3) and one vacancy ligand (C_1) (total $= C_4$) may be involved:

8.3.4 Local Vibrational Mode Sidebands at Intrinsic Defects

Vibronic sidebands from local vibrational modes (LVM) are sharper than the QLVM sidebands. Six types of C–C vibrations can be distinguished (see Table 11.1). Very similar frequencies are expected for N–C vibrations, because there is little difference with respect to atomic mass and bonding force constant.

The observed LVM frequencies are in the expected range. Remarkable is the considerable reduction (ca. 25%) of the LVM frequencies in platelets = (C2n)i compared to the isolated self-interstitial $= (C_2)_i$.

Theoretical calculations for $(C_2)_i$ [Bre95] yield 198 meV for the *ligand-central* C–C bond vibration (observed 120–199 meV) and 251 meV for the *central* C–C bond vibration (observed 202–245 meV).

The results from Table 11.1 can be extrapolated for the LVM frequencies of the heavier metal atoms. Assuming comparable force constants, and replacing C–C by M–C in the vacancy associates, the predicted bending frequencies are for ^{48}Ti in the range 28–57 (observed 32) meV, for ^{59}Co 26–52 (observed 44) meV, for ^{108}Ag 20–40 (observed 21) meV, and for ^{204}Tl 15–30 (observed 21) meV. The predicted stretching frequencies are for ^{59}Ni in the range 70–97 (observed 70–80) meV, for ^{108}Ag 54–75 (observed 67) meV, and for ^{204}Tl 40–56 (observed 45) meV.

8.3.5 Infrared Vibrational Absorption Lines

Characteristic infrared vibrational absorption lines are observed from the B-center ($V_1N_4{}^\circ$ see Tables 8.1.3.3 and 8.1.3.5) and from the platelets (see Tables 8.2.1 and 8.2.2). The vibrational lines are broadened to bands by resonance with the lattice phonons in the range 69–165 meV. At higher frequencies, the vibrational lines are sharp and allow to observe ^{13}C and ^{15}N isotope shifts [Col88c]. In Tables 8.2.1 and 8.2.3, these lines are marked by (IR:).

8.3.6 Vibrational Isotope Shifts from ^{13}C and ^{15}N Substitution

The observed isotope shifts after partial or full ^{13}C or ^{15}N substitution provide very important information on the structure of the intrinsic defects.

$^{+}\mathbf{(C_2)_i}^{-}$ at 2.462 (see Table 8.2.1): The isotope shifts in a sample with 50% ^{13}C reveals localization of the vibrations on different sites [Ste99a]. The 218-meV sideband splits into a perfect triplet with 1:2:1 intensities, i.e., two equivalent interstitial carbon atoms vibrate with an energy, which is typical for $C = C$ double bonds (see Table 11.1). This observation strongly supports the theoretical split interstitial model. The 182- and 187-meV sidebands split into quartets with 1:3:3:1 intensities, indicating a vibration of *one* central carbon with *two* carbon ligands. The 169-meV sideband shifts to a bell-shaped band with its maximum at 50% isotope shift. This vibration is clearly located at the four carbon ligands and their 12 carbon lattice neighbors, i.e., 16 carbon atoms are involved.

$^{*}\mathbf{(C_2)_iN_1}^{-}$ at 3.188 eV (see Table 8.2.3): A detailed analysis of the LVM lines at 179 and 190 meV in luminescence spectra after partial substitution with 50% ^{15}N [Col87b] or with 40% ^{13}C [Col93b] enables the present author to determine the distribution of the vibrational energy on one central atom C(1) with ligands N and C(3), and the other central atom C(2) with the ligands C(4, 5). For the *178.5 meV ("N")* vibration, the result is: N: 47%, C(1): 34%, C(2): 13%, and C(3): 6%. For the *190.5 ("C")* vibration the result is: C(2): 50%, C(1): 32%, C(4): 8%, C(5): 7%, N: 3%. The LVMs at 168, 170, and 232 meV are pure carbon vibrations, because they are not influenced by ^{15}N substitution [Col87b].

8.3.7 Isotope Shifts of the Zero Phonon Lines by ^{13}C and ^{15}N Substitution

Frequency shifts of the zero phonon lines (see Tables 7.2–7.3) are reported for ten vacancy centers (Tables 8.1.1–8.1.7.2) in the range +0.5 (for $^{*}V_2N_2^{\circ}$ at 2.086 eV) to +6.6 meV (for V_2° at 2.543 eV), and for five interstitial centers (Tables 8.2.1–8.2.4) in the range +1.2 for ($(C_2)_i^{\circ}$ at 1.685 eV) to +8.0 meV (for $^{*}(C_2)_iN_1^{\circ}$ at 4.582 eV) [Dav99a].

In a theoretical treatment, *four* contributions to the ZPL isotope shifts have been discussed [Dav99a]. Typical values for these contributions are:

1. +0.9 meV from lattice compression (in case of 13C)
2. +1.5 meV for lower vibrational frequencies in the excited state
3. +0.4 meV for anharmonicities (if applicable)

4. −0.8 meV for a transition between a dynamic Jahn–Teller active ground state and a non-Jahn–Teller active excited state

Unexpected isotope shifts clearly reveal non ZPL transitions. Examples are the −5.2-meV shift for the luminescence pseudo ZPL line at 1.859 eV of $(C_2)_i{}^{\circ}$, and the +6.7 to +7.2 meV shifts for the GR2–GR8 PLE and absorption lines at 2.880–3.005 eV ($V_1{}^{+}$ SB-DAP32).