

Handbook of Spectral Lines in Diamond

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Handbook of Spectral Lines in Diamond

Volume 1: Tables and Interpretations

With 203 Tables

 Springer

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Preface

The number of observed spectral lines in diamond is steadily increasing. For example, the remarkable review by J. Walker in 1979 described 30 centers with some 100 lines [Wal79]. The compilation by J. E. Field in 1992 had 118 entries [Fie92]. A. M. Zaitsev in his valuable data collections, had 465 entries in his book chapter of 1998 [Zai98] and 838 entries in his book of 2001 [Zai01]. This book has more than 2,000 entries from some 300 centers. The main entries are presented in 23 tables (see Chaps. 2–7), according to the type of sample, the method of observation, etc. (see Sect. 1.4). Specific tables follow in Chaps. 8–13.

Of special interest for the present author is (1) the interpretation of spectra and (2) the assignment of structures to the optical centers.

In the field of **interpretation**, it was found that in 113 cases line groups arise from resolved donor–acceptor pair (DAP) transitions (see Chap. 10). Only two of them have been published before [Dis94a, Dis94b, Ste99a, Ste99b], i.e., 111 DAPs of this book are unpublished [Dis03]. Unresolved DAP transitions were proposed in 1965 to explain the band-A luminescence [Dea65a]. With the present knowledge, a final proof for this hypothesis is provided (see Table 10.2.2).

The **structure assignment** of optical centers is established for some 15 cases (e.g., $A = N_2^{\circ}$, $B = V_1N_4^{\circ}$, $C = N_1^{\circ}$, $NV = V_1N_1$, $N = V_1N_3^{\circ}$, $GR1 = V_1^{\circ}$). However, for the large number of some 200 proposed structures (preceded by *), confirmation is desirable (e.g., $H3 = *V_1N_2^{\circ}$, $TH5 = *V_2^{\circ}$, $5RL = *(C_2)_iN_1^{\circ}$).

In contrast to previous reviews, where up to three possible structures are cited, only the most probable structure is presented here. This selection is based on the available information, like (1) isotope shifts, (2) frequencies of local vibrational modes (LVM), or (3) of quasilocal vibrational modes (QLVM), (4) involvement of intrinsic defects (vacancies or self-interstitials) as evidenced by the connection to a special type of DAP transitions (the sideband DAP, see Chap. 10), and (5) relationships of the value of the DAP dielectric factor with the number of electrons involved (see Sect. 10.4) or with the charge state of the defect (see Sect. 10.5).

Certainly, the large amount of data (especially the new structure proposals) require a critical examination. Each reader is urgently invited to inform the author about errors, improvements, and new results.

The author regrets that no figures are included in this book. It was decided to collect the figures and diagrams in a separate book. Fortunately, the experienced diamond researcher Prof. Alexander M. Zaitsev has agreed to write this book (together with the present author):

Handbook of Spectral Lines in Diamond, Volume 2, Figures and Diagrams by A. M. Zaitsev and B. Dischler, Springer-Verlag, to be published.

This second book provides a good opportunity to update the present data on spectral lines in diamond.

In the meantime, the reader will find figures for most of the lines and bands in two previous books [Zai98, Zai01]. The respective figure numbers are indicated in an extra column in the tables.

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First of all, I am grateful to Prof. Peter Koidl, who established and headed the diamond research group at the Fraunhofer Institut für Angewandte Festkörperphysik (IAF, Institute for Applied Solid State Physics) in Freiburg. The present author has been concerned with the spectroscopy of diamond like carbon (DLC) since 1982 and with the optical spectra of diamond since 1992.

I want to thank the members of this diamond group for the fruitful cooperation: Gernot Brandt, Achim Bubenzer, Roland Locher, Karin Maier, Wolfgang Müller-Sebert, Manfred Ramsteiner, Wolfram Rothemund, Ram Ekwil Sah, Harald Schneider, Joachim Wagner, and Christoph Wild.

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Invaluable support came from my wife Heidrun, who made a substantial contribution to this book by her persistent encouragement, a critical reading of the manuscript, valuable discussions, and new ideas.

This book is dedicated to the many diamond researchers worldwide, who contributed to the impressive amount of data, which is now available. Instrumental for the present book were the exhaustive data collections by Alexander M. Zaitsev, both in a review article [Zai98] and in a book [Zai01]. Of great help were the reviews of John Walker [Wal79] and of Alan T. Collins [Col97].

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Chapter 1

Introduction

1.1 Diamond in History and Research

The word “diamond” (or “adamas,” “adamant”) is of Greek origin with the meaning “indomitable” or “invincible.” Diamond is a material with many outstanding properties (a) extreme hardness (ten on the Mohs scale), (b) chemical inertness, (c) high refractive index and dispersion ($n = 2.463$ at 400 nm and $n = 2.405$ at 700 nm), (d) large optical transparency range, and (e) high thermal conductivity (better than copper).

A large number of optical centers can be observed in diamond, due to a combination of (d) the extended optical transparency and (a) the extreme hardness. Diamond is transparent from the bandgap absorption edge in the ultraviolet (at 5.49 eV) through the visible and infrared spectral range to the microwave region. Because of the hardness, defect migration (e.g., vacancies to the surface) requires high activation energies, and most defects remain immobile up to temperatures of 420–2,500 °C (see Sects. 8.3.1, 9.1.6, and 9.5.6).

The number of lines (ca. 2,000) is much larger than the corresponding number of centers (ca. 300), because most zero phonon lines (ZPL) have typically 1–10 phonon or vibrational sidebands (see Chap. 11). The centers with resolved donor–acceptor pair transitions form groups of 3–23 lines (see Chap. 10).

To give a first impression, 45 typical defects are listed in Tables 1.1.1 and 1.1.2. These Tables are given in matrix form, because the majority of centers consist of associates. For some ten centers in Tables 1.1.1 and 1.1.2 the structure is generally accepted, while for the remaining 35 centers (marked by a preceding *) the structure is proposed in the literature or in this book.

In five sections, the principal types of diamonds are described: Natural diamond (Sect. 1.2.1, including Table 1.2), high pressure synthetic (HPHT) diamond (Sect. 1.2.2), low pressure synthetic (CVD) diamond (Sect. 1.2.3), modified diamond (Sect. 1.2.4), and diamond-related materials (Sect. 1.2.5).

The introduction ends with a short description of the optical techniques (Sect. 1.3) and explanations on the organization of the tables (Sect. 1.4).

Table 1.1.1 Fundamental defects in diamond^{ab,c} (mostly with vacancies, see Chap. 8)

Defect-composition	+1N	+2N	+3N	+4N	+1B	+1H
-	$N_1^\circ = \text{C center}$ 0.105-0.167, 4.059	$N_2^\circ = \text{A center}$ 0.060-0.159, 3.928, 4.567	-	-	$B_1^\circ = \text{boron acc.}$ 0.304-0.372	-
V_1^-	$*V_1N_1^- = 638 \text{ nm}$ 1.943, 4.328	$*V_1N_2^- = \text{H2}$ 1.256, DAP77/78	$*V_1N_3^-$ 2.526, DAP76	$*V_1N_4^- = \text{N9}$ 5.252, DAP63/64	$*V_1B_1^-$ 3.684, DAP67	-
V_1°	$V_1N_1^\circ = \text{NV}$ 2.154, DAP46/47	$*V_1N_2^\circ = \text{H3}$ 2.464, 3.361 DAP	$V_1N_3^\circ = \text{N3}$ 2.985 DAP	$V_1N_4^\circ = \text{B cent.}$ 0.093-0.165 4.191, DAP82	$*V_1B_1^\circ$ 2.395, DAP74 3.120, DAP73	$*(V_1H_1)^\circ$ 0.1742, 0.3852, DAP41
V_1^+	$*V_1^+ = \text{GR 2-8}$ 2.781, DAP32	$*V_1N_2^+ = \text{S1(b)}$ 2.463, DAP43	-	-	-	-

V_2°	$*V_2^\circ = 7H5$ 2.543, DAP15	$*V_2Ni_1^\circ$ 2.329	-	$*V_2Ni_3^\circ$ 2.916	$*N_3V_2Ni_1 = H4(b)$ 2.498, DAP37/38	-
V_1Ni_1+	$*V_1Ni_1+ = 1.40$ eV 1.404, DAP25/26	-	-	-	-	-
(V_2Ni_1)	-	-	$+N_2+0+0 = S3$ 2.496– 2.800 sta. DAP58	$+N_2+0+1 = S2$ 2.515– 3.341 sta. DAP57	-	-
$*(V_3Ni_2)^\circ$	$*(V_3Ni_2)^\circ$ 2.562, DAP106	-	-	-	-	-
$*(V_3Si_2)^\circ$	$*(V_3Si_2)^\circ$ 2.052, DAP65	-	-	-	-	-

^aEnergies in eV

^b**Bold** = natural, *italics* = irradiated

^cDAP donor–acceptor pair transitions (see Chap. 10)

Table 1.1.2 Fundamental defects in diamond^{a,b,b,c} (with split interstitials, see Sect. 8.2)

Defect-composition	+1N	+2N	+1-3B
$(C_2)_i^-$	$*(C_2)_i^- = 7R12$ 2.638, DAP35/36	$*(C_2)_iN_1^- = 3.19$ eV, 3.188, DAP72	-
$(C_2)_i^0$	$*(C_2)_i^0 = R2$ 1.685, DAP71	$*(C_2)_iN_2^0$ 1.979	$*(C_2)_iB_1^0 =$ <i>2BD(F), 4.777, DAP97*</i> $(C_2)_iB_2^0 =$ <i>2BD(G), 4.698, *</i> $(C_2)_iB_3^0 =$ <i>2BD(C), 4.803</i>
$(C_2)_i^+$	$*(C_2)_i^+ = 3H$ 2.462, DAP86	$*(C_2)_iN_2^+$ 2.535, DAP90	-
$(C_2)_i^{2+}$	-	$*(C_2)_iN_2^{2+}$ 2.322	-
$(C_2)_n)_i^0$	Platelets = D center <i>0.041-0.177</i> 1.528, DAP96	-	-
$(N_1C_1)_i^-$	$*(N_1C_1)_i^- = R11$ 3.988, DAP98	-	$*(N_1C_1)_iB_1^-$ 2.992, DAP101
$(N_1C_1)_i^0$	-	-	$*(N_1C_1)_iB_1^0$ 2.792, DAP99
$(N_1C_1)_i^+$	$*(N_1C_1)_i^+ = 0.212,$ 2.807, DAP98	-	$*(N_1C_1)_iB_1^+$ 3.092, DAP100

^aEnergies in eV^b**Bold** = natural, *italics* = irradiated,

unmarked* = CVD diamond, as-grown or irradiated. (* = normal type)

^cDAP donor-acceptor pair transitions (see Chap. 10)

Table 1.2 Classification scheme for diamond types (see Sect. 1.2.1)

Defect/ property	Types				
	IaA	IaB	Ib	IIa	IIb
A-center = N_2°	Dominant	Weak	Weak	Absent	Absent or weak
B-center = $V_1N_4^\circ$	Weak	Dominant	Weak	Absent	Absent or weak
C-center = N_1°	Weak	Weak	Dominant	Absent	Absent or weak
Defining defect	A-center	B-center	C-center	Absent	Boron-acceptor
Boron content	Low	Low	Low	Very low	Dominant
Typical natural hydrogen content	500 ppm	200 ppm	70 ppm	$<10^{18} \text{ cm}^{-3}$	$<10^{16} \text{ cm}^{-3}$
Electrical resistance ($\Omega \text{ cm}$)	$>10^{15}$	$>10^{15}$	$>10^{15}$	$>10^{16}$	Semiconducting

1.2 Types of Diamond Samples

1.2.1 Natural Diamond

In its long history (from 400 BC), natural diamond gem stones (clear or colored) came first from India and later from South America, South Africa, and Russia [Mey98]. In a recent study [Shi02], it was shown that natural diamonds are very old. There are three groups with an age of 3.3, 2.9, and 1.9 billion (10^9) years. Originally, they grew at a depth of 150–300 km under the surface from carbon-containing compounds like CO_2 or CaCO_3 . From there the diamonds have been transported to regions near the surface by volcanic activity. They are either still enclosed in the volcanic rocks kimberlite or lamproite (primary sources in diamond mines), or have been liberated by erosion and transported by rivers toward the sea (secondary sources, e.g., in Namibia).

The value of natural diamond gemstones is closely related to the four “C”s: (1) carat, (2) cut, (3) color, and (4) clarity.

1. The weight is given in the traditional unit “carat.” One carat = 100 points = 200 mg, (the weight of a dried carobtree seed).
2. A good cut (e.g., “brilliant”) produces the “fire” from reflected light, making use of the high refractive index and dispersion: $n = 2.463$ at 400 nm (3.10 eV) and $n = 2.405$ at 700 nm (1.77 eV) [Zai01].
3. The diamonds can be absolutely colorless (“River”), white (“Wesselton”), or colored. Common colors are yellow, brown, or gray. More seldom colors are red, blue, green, pink, or violet (see Chap. 6 in [Zai01]).
4. Most natural diamonds contain inclusions. Their number and dimension determines the value, i.e., their absence in clear diamonds makes a gemstone very valuable.

In 1934 Robertson et al. introduced a classification scheme for natural diamonds [Rob34]: Type I diamonds (98% abundance) are transparent at > 300 nm (< 4.13 eV), and type II diamonds (2% abundance) are transparent at > 230 nm (< 5.39 eV). After the detection of boron, type II diamonds were subdivided into IIa (< 10 ppm boron) and IIb (dominant boron, semiconducting) [Cus52]. Finally, characteristic infrared absorption allowed discrimination between three different nitrogen centers, and type I was subdivided: A centers (type IaA), B centers (type IaB), and C centers (type Ib) [Dye65b] (see Table 1.2).

Many lines are observed in natural diamonds, see Tables 2.1.1.1–2.4.3.

1.2.2 High Pressure Synthetic Diamond (HPHT)

The successful synthesis of diamond in a high pressure and high temperature apparatus was reported in 1955 [Bun55]. Graphite is transformed into diamond in the presence of transition metals (Fe, Co, Ni, Mn, or Pt), which act as a solvent–catalyst. Typical conditions are a pressure of 6–7 GPa and a temperature of 1,500–1,700 °C [Set94]. The standard HPHT diamonds are of type Ib, and the isolated substitutional nitrogen (C center) causes a yellow color. By the use of a nitrogen getter (e.g., Al or Ti), the concentration of C centers can be reduced [Kan98]. Lines from HPHT samples are given in Tables 3.1.1.1–3.4.3.

1.2.3 Low Pressure Synthetic Diamond (CVD)

In 1981 and 1982 it was shown that low temperature synthetic (CVD) diamonds can be deposited with practical growth rates (up to 1 $\mu\text{m}/\text{h}$) [Mat81, Kam82]. With the standard CVD (chemical vapor deposition) method diamond films are grown on a heated substrate [Spe94, Dis98, Pre98]. In a typical MW-CVD apparatus the feed gas (3% CH_4 , 97% H_2) is decomposed in a 2.45-GHz *microwave* plasma (200 mbar pressure), and the (polycrystalline) diamond film is deposited on a silicon substrate (at 850 °C). Instead of the MW plasma a *hot filament* (2,000 °C) can be used for the decomposition of the feed gas (HF-CVD). Alternate methods use a *combustion flame* or a *plasma jet* (see e.g., [Dis98]).

Typical for CVD diamond films is the incorporation of silicon and sometimes boron (from the substrate), nickel (from the steel vessel), and also Ta or W (from the hot filament), see Tables 4.1.1.1–4.4.3.

It has been shown that the prominent hydrogen lines of CVD diamond films arise from hydrogen in an amorphous carbon surrounding (grain boundaries), and are essentially identical to the hydrogen lines in diamond-like carbon (DLC), see Tables 9.3.2–9.3.5 [Dis93]. Therefore, these CVD hydrogen lines are classified as diamond related and listed in Tables 6.1.1.1–6.3.2.

1.2.4 *Modified Diamond*

When diamond is irradiated with high energy electrons, fast neutrons, or X-rays, the typical intrinsic defects (vacancies and $\langle 1\ 0\ 0 \rangle$ split self-interstitials) are created. At anneal temperatures of $T > 420\text{ }^\circ\text{C}$ for interstitials and $T > 500\text{ }^\circ\text{C}$ for vacancies, migration of the intrinsic defects starts and the typical associates with impurities are formed (see Tables 5.1.1.1–5.4.4 and Chap. 8).

1.2.5 *Diamond-Related Materials*

There are several carbon compounds, which differ in their structure from diamond, but have similar properties (see Tables 6.1.1.1–6.3.2). Five of these are natural:

1. *Lonsdalite* (LON), a carbon mineral with a hexagonal structure
2. *Carbonado* (CAR)
3. *Ballas* (BAL), a naturally occurring polycrystalline diamond
4. *Natural brown/gray diamond* (NBD/NGD), often with high H content
5. *Natural diamond coat* (NDC)

The remaining two materials are synthetic films:

6. *Diamond-like carbon* (DLC)
7. *Polymer-like amorphous carbon* (PAC)

Typical films of DLC are obtained by high frequency (2.3 MHz) plasma deposition from a C_6H_6 feed gas (30- μ bar pressure). In the negative self-bias voltage of 1 kV, the ionized fragments arrive at the substrate with high kinetic energy, forming a compact and hard film. The structure is amorphous (also named a-C:H) with a high concentration of 13–38 at. % hydrogen, which is bonded to carbon. The infrared analysis yields a typical carbon hybridization of 68% sp^3 , 30% sp^2 , and 2% sp^1 (see Sect. 9.3).

The low cost and flexible deposition methods of DLC films opened a wide field of applications, making use of the high hardness, low friction, and exceptional smoothness [Gri99]. More recently, high power deposition methods allowed the preparation of “superhard” hydrogen-free DLC (named “tetrahedral” carbon, taC) [Gri99].

PAC films are obtained, if the kinetic energy is lowered. These films are of scientific interest (see Tables 9.3.2 and 9.3.3), but have no practical applications.

In the next section, the optical techniques (Sect. 1.3) and the organization (Sect. 1.4) of the tables in Chaps. 2–7 are explained.

In Chap. 8, the intrinsic defects (lattice vacancy or split self-interstitial) and their associates are treated.

Impurity defects (with sections on N, B, H, Si, Ni, Co, and others) are discussed in Chap. 9.

Very important new information on donor–acceptor pair (DAP) transitions is contained in Chap. 10.

The Chaps. 11–14 deal with vibrational frequencies (Chap. 11), modification of diamond by irradiation and heat (Chap. 12), isotopic line shifts (Chap. 13), and spectroscopic discrimination between natural and nonnatural diamond (Chap. 14).

The book ends with conclusions and outlook (Chap. 15) and an Appendix.

1.3 Optical Techniques

1.3.1 Absorption

The absorption coefficient α (in cm^{-1}) is defined by (1.3a)

$$I(E_1) = I_0(E_1)e^{-\alpha x}, \quad (1.3a)$$

here, $I(E_1)$ is the measured intensity of monochromatic light at energy E_1 , $I_0(E_1)$ is the initial intensity (corrected for reflection loss), and x is the path length (in cm). With a scan of E_1 , an absorption spectrum is obtained.

1.3.2 Photoluminescence Excitation

The definition is given by (1.3b), which is similar to (1.3a)

$$I(E_1) = I_0(E_2)e^{-\alpha x}. \quad (1.3b)$$

However, now E_1 is fixed (monitoring energy of a luminescence line), while E_2 is scanned ($E_1 < E_2$). This photoluminescence excitation (PLE) spectrum is (in general) similar to an absorption spectrum, but it can reveal relationships between different lines of the same defect center.

1.3.3 Luminescence

A luminescence spectrum is obtained, when the optical emission of a sample is monochromatically scanned. The standard luminescence is excited (a) by light (photoluminescence, PL), (b) by an electron beam (cathodoluminescence, CL), or (c) by X-rays (XL). Typical light sources for photoluminescence are mercury lamps, argon, or krypton lasers. Cathodoluminescence is a “near surface” technique. The

penetration depth is 9–18 μm for a typical 50-kV electron beam [Col92b]. In X-ray luminescence, the high energy can modify the centers.

In contrast to the *quantitative* absorption, the luminescence intensity is only *qualitatively* related to the concentration of the respective defect center.

In time resolved luminescence, the detection starts at a gated time delay after the excitation pulse. This allows determination of radiative decay times. A tabulation of decay times for 21 centers (ranging from 17 ns to 18 ms) is given in [Per94c].

1.3.4 Raman Scattering

This technique is used to investigate the crystal perfection, which influences the position and linewidth of the principal Raman line at 165 meV (1, 332 cm^{-1}). Also, nondiamond inclusions (graphitic or grain boundaries) can be detected. A review (with a listing of 83 lines or bands) is given in Chap. 4 of [Zai01], see also [Zai00b].

1.3.5 Photoconductivity

If the photocurrent is measured as a function of monochromatic illumination, a photoconductivity spectrum is obtained. A listing of some 60 photoconductivity features is given in Chap. 10 of [Zai01]. In photo-Hall measurements, the type of released carriers (electrons for n-type, holes for p-type) can be determined [Col79a, Col97].

1.4 Organization of the Tables in Chaps. 2–7

The great French scientist René Descartes (1596–1650) proposed a four-step method for the presentation of data “(a) split up the data, (b) put the data in order, (c) establish surveys of the data, and (d) make sure the data are reliable and intelligible.” After several hundred years, this is still a good advice.

A basic idea of how to split up the 2,000 spectral lines in diamond was found for the present book, using two criteria:

1. The type of sample
2. The method of observation

The lines are presented in 150 tables (see Chaps. 2–7).

The five types of samples are:

N = natural diamond (Sect. 1.2.1 and Tables 2.1.1.1–2.4.3)

H = HPHT diamond (Sect. 1.2.2 and Tables 3.1.1.1–3.4.3)