Recent Results on Characterization of Detonation Nanodiamonds

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9.1 Introduction

Main results on the characterization of detonation nanodiamond (DND), accumulated over many years of material production and investigation, were presented in the first edition of this book, *Ultrananocrystalline Diamond* (2006). This (second) edition is mainly focused on new results on DND characterization resulting from recent progress in instrumentation and methodological development of the techniques traditionally used for DND characterization, such as transmission electron microscopy (TEM), X-ray diffraction (XRD), electron spin resonance (ESR) and photoluminescence spectroscopy.

9.2 TEM and electron energy-loss spectroscopy

The focus of this section will be on concrete characterization results on nanodiamond (ND) material by TEM and electron energy-loss spectroscopy (EELS) in an electron microscope. It is by no means a complete reference on TEM or EELS; only a short introduction will be given into each technique. The reader is referred to the many excellent books on scanning TEM (STEM) and EELS in the literature (Ref.s [1–4] amongst many others) for a more in-depth discussion of the techniques presented here.

TEM uses high-energy electrons in combination with electromagnetic lenses to focus the electron beam on a given sample and image the sample on a suitable recording device like a CCD camera. Owing to the high acceleration voltages used in TEM (typically several hundred kilovolts), the wavelength of the accelerated electrons is far shorter than the typical wavelength of light, making the resolving power of an electron microscope far greater than that of its optical counterpart. There are two main modes of operation in an electron microscope; in TEM the whole sample is simultaneously illuminated by a wide electron beam, while in STEM, a fine probe is scanned over the sample, and the scattered electrons are collected in each scan point to create an image.

The limiting factor for (S)TEM image resolution was long not the electron wavelength (~2 pm for a 300 kV acceleration voltage), but rather lens aberrations like spherical and chromatic aberration caused by the use of round electromagnetic lenses in a conventional transmission electron microscope [5]. These aberrations limited resolutions in a typical high-resolution TEM (HRTEM) to a point resolution at optimal defocus of ~1.7 Å (170 pm), far from theoretical resolutions of only a few picometers. Thanks to the recent successful implementation of spherical aberration-correction in electron microscopy, modern instruments are able to reach image resolutions of 50 pm (0.5 Å) in both TEM and STEM mode at conventional acceleration voltages of 300 kV, but can also be operated at lower voltages of 80, 60, or even 40 keV while keeping the atomic resolution [6–10]. Low voltage microscopy has previously been highly used to great success in imaging beam sensitive materials like nanotubes, graphene, and hexagonal BN [11,12], and can allow for prolonged and detailed experiments to be performed while minimizing the risk of knock-on damage or surface graphitization in the case of ND [13].
9.2.1 Bright-field TEM imaging and electron diffraction of ND material

In bright-field TEM, the sample is imaged using a parallel incoming electron beam. In general, only a (small) amount of the electrons that have passed through the specimen are used for imaging in the bright-field imaging mode; an objective aperture can be placed in the back-focal plane of the objective lens to cut out all electrons except the transmitted beam or a selected amount of reflections, providing a bright-field image with enhanced contrast. There are two main contrast regimes in bright-field imaging. For noncrystalline materials, mass-thickness contrast (also known as absorption contrast) is dominant. In crystalline materials like ND, this amplitude-type contrast is in direct competition with diffraction contrast, which originates from elastic Bragg scattering in the crystal and is dependent upon the orientation of the crystalline specimen with respect to the incoming electron beam. In an electron microscope, diffraction and imaging go hand-in-hand. The back-focal plane of the objective lens in a TEM is also the diffraction plane, as the back-focal plane is the Fourier conjugate of the object plane. This means that the microscope operator can switch between the diffraction pattern and the real space image by a simple push of a button.

A typical bright-field TEM image and electron diffraction pattern from an ozone-treated, clean DND sample are displayed in Figure 9.1 [14,15]. The DND particles have primary particle sizes ranging between ~2 and 20 nm, and are in general agglomerated.

**FIGURE 9.1**

Low-magnification image of DND particles [14]. The particles have sizes ranging from ~2 to 20 nm. The inset electron diffraction ring pattern evidences the diamond crystal structure.
into larger structures [16]. The agglomeration of the DND particles is typical for nano-sized material, and is mainly due to Van der Waals attractive forces [17,18].

The crystal structure of the particles can be determined from the inset electron diffraction ring pattern. As the diffraction pattern is taken from many ND particles with varying orientations simultaneously, the angular information is lost leaving only the ring interspacings to determine the crystal phase through Bragg’s law (like an XRD pattern) [19]. In this case, only rings corresponding to the diamond crystal structure (Fd-3m, Space Group number 227) are present. No graphite or n-diamond reflections are visible, an important indication for a high purity of the DND material.

### 9.2.2 Aberration-corrected high-resolution imaging at low acceleration voltage

Unlike X-ray or neutron diffraction, electron diffraction is highly dynamical, meaning that multiple electron scattering with large phase changes occurs frequently in an electron microscope. In HRTEM a large objective aperture (or no aperture at all) is inserted in the back-focal plane of the objective lens, allowing diffracted beams to interfere both with each other and the transmitted beam, forming an interference (fringe) pattern. As a result the contrast in such an image is dependent on the phase of the various beams, giving rise to the name phase-contrast imaging for HRTEM imaging. In some cases these interference patterns or high-resolution images can be directly interpreted, usually however image simulations need to be carried out to interpret the images.

A high-resolution, aberration-corrected TEM image of a typical nanoparticle in the sample is presented in Figure 9.2. To obtain this image, the electron microscope was operated at 80 kV (below the knock-on damage threshold for diamond) with the spherical aberration coefficient ($C_s$) corrected and tuned to $+15 \mu m$. To extend the information limit of the microscope (which is normally limited by chromatic aberration), the monochromator of the microscope was excited to achieve an energy spread of the order of 0.3 eV for the illuminating electron beam. By further extending the information transfer of the microscope, intricate details of the ND surface become visible (see Figure 9.2A). The DND particle is imaged along the [011] zone axis orientation (as evidenced by the inset Fourier transform (FT)), allowing {111}-type surface facets and $\Sigma = 3 \{111\}$ twin boundaries to be imaged edge-on. Two coherent $\Sigma = 3 \{111\}$ twin boundaries run through the particle. This type of twin is typical for DND as it has the lowest defect energy of all diamond defects. This results from the fact that this twin type only demands a small deviation from the ideal lattice, namely only in the fourth neighbor lattice positions. The abundance of these defects has been attributed to the increased growth rate of twinned NDs in comparison to untwinned ND under detonation synthesis conditions [22].

The nanoparticle shows mainly {111}-type surface facets with some {100} truncation, a result of the low surface energy of these low-index facets [19]. The {100} truncation is imaged in more detail in Figure 9.2B. Under the imaging conditions used ($C_s = +15 \mu m$, 4 nm underfocus) the atomic columns are imaged in
FIGURE 9.2
Low voltage, aberration-corrected images of DND particles [14,21]. (A) HRTEM image of a typical DND particle exhibiting two coherent $\Sigma = 3 \{111\}$ twin defects. The diamond surfaces show minimal presence of graphitic material. (B) Enlarged image of the $\{100\}$ truncation in the bottom right of (A). Both $\{100\}$- and $\{111\}$-type surface facets are clean. (C) Image simulation performed for $C_s = 15 \mu m$, $\Delta f = -4 \text{nm}$. The right-hand side has the projected potential overlaid, demonstrating the white image contrast peaks at the atomic positions. (D) HRTEM image of a multiple-twinned DND particle. Inset simulations performed for $C_s = 15 \mu m$, $\Delta f = -4 \text{nm}$, and thickness = 4 and 14 nm.
white, as evidenced by the simulation of a truncated diamond particle in Figure 9.2C. The atomic potential overlay in Figure 9.2C also demonstrates that even though the information transfer of the microscope is extended by use of the monochromator, the 89 pm carbon dumbbells are not directly resolved in the image. An elongation of the column contrast in the dumbbell direction is visible. The combination of the HRTEM image and image simulation allows us to conclude that the surfaces (both the {111}- and {100}-type surfaces are extremely clean. On the region cut out in Figure 9.2B, no graphitic surface material can be made out (although a minimal surface layer is visible on the top two {111} facets in Figure 9.2A as indicated by black arrows).

A second, multiple-twinned nanoparticle is imaged in Figure 9.2D. This type of multiple-twinned nanoparticle was previously reported by our group [23]. As was the case for the particle in Figure 9.2A, this multiple-twinned ND is imaged along the [011] zone axis orientation, with mainly {111}-type and some {100}-type surface facets visible. The [011] zone axis orientation is evidenced by the inset FT. Interestingly, this FT (unlike the FT for the smaller ND) shows the presence of a (400) reflection corresponding to the 89 pm dumbbell spacing. In Figure 9.2E and F two enlarged regions of the particle are imaged, together with their corresponding image simulations. In Figure 9.2E, arising from a thin region of the particle (indicated by a rectangle in Figure 9.2A), the 89 pm dumbbells are imaged as elongated white contrast (as was the case in Figure 9.2A). However, in the thicker region of the particle the dumbbell is clearly resolved, most likely due to dynamical scattering effects. Although the presence of multiple coherent {111} twins was apparent from earlier conventional HRTEM work, several features remained unclear until now. The first is the surface structure, which in this sample exhibits a minimal graphitic presence. Secondly, the details of the multiple twin boundaries are imaged; no indication for an enrichment of amorphous carbon or nitrogen clusters at the twin boundaries can be derived from the HRTEM image. To determine whether amorphous carbon or nitrogen atoms are enriched at the defects and twin boundaries, spatially resolved EELS can be carried out.

9.2.3 Scanning TEM

In STEM the electron beam is focused to an angstrom-sized probe and is scanned over the sample by deflection coils. Depending upon the transmitted electrons that are used to form the image, a bright-field STEM image or dark-field STEM image can be formed [4]. The most-used detector in STEM is by far an annular detector, used to form annular dark-field images. By using the intermediate lenses to change the camera length used in STEM mode, the angular range of electrons falling onto the annular detector can be controlled. In high-angle annular dark-field STEM only the electrons that have been scattered under large angles by the specimen (Rutherford-like scattering) are collected on the annular detector. This type of imaging is also known as Z-contrast imaging, as the Rutherford-like scattering of the electrons scattered to high angles leads to an image intensity that is approximately
TEM and electron energy-loss spectroscopy

9.2.4 Electron energy-loss spectroscopy

When incoming fast electrons are scattered inelastically in a solid, conservation of total energy dictates that the energy transferred in a single-electron excitation or in the excitation of a phonon or plasmon is equal to that lost by the scattered fast electron. In EELS the processes of electron excitation are studied by measuring the energy-loss of the primary fast electrons. EEL spectroscopy is particularly well suited to study light elements like nitrogen, oxygen, boron, and carbon. Heavy elements like gold and platinum are generally not well suited to EELS.
A typical EELS spectrum consists of three major regions:

a. The zero-loss peak at 0 eV from the electrons that are elastically scattered (the majority of the fast electrons) and from electrons that have transferred less energy than the energy resolution of the energy filter and the incoming electron beam.

b. The low-loss region from 1–100 eV showing characteristic peaks from the band gap, interband transitions, and from the excitation of bulk and surface plasmons.

c. The core-loss region from 100 eV onward showing the element-specific ionization edges on top of a decaying background, which can usually be approximated by a power-law function ($A \cdot E^{-r}$). The excitation edges correspond to the energy-loss of inner-shell electrons that are excited to a higher, unoccupied state above the Fermi level.

**Low-loss EELS**

Reference low-loss spectra for diamond, graphite, and amorphous carbon are shown in Figure 9.4, together with low-loss EELS data from three individual clean NDs with different sizes. The low-loss EELS spectra in Figure 9.4B all show a prominent plasmon peak around 34 eV; this is close to the plasmon energy of bulk diamond (33 eV) confirming that the bulk of DND material is diamond [21–27]. A small shoulder is measured around 22 eV, which is attributed to the diamond surface plasmon. The peak does not arise from graphitic or amorphous material, as no $\pi$-plasmon is visible. The smaller the particle, the more prominent the surface

![Figure 9.4](image)


**FIGURE 9.4**

(A) Diamond, graphite, and amorphous carbon low-loss spectra together with (B) low-loss spectra taken from individual DND particles from a clean DND sample [24,25].
plasmon peak becomes, as the surface to volume ratio increases [24]. The band gap around 5–6 eV can also be measured under specific experimental conditions [16].

**Core-loss EELS: ND carbon K-edge ELNES**

In the core-loss EELS region, the shape of the excitation edges is linked to this unoccupied density of states and is called the energy-loss near-edge structure (ELNES). The ELNES therefore contains information about the bonding and electronic state of the probed material and as a result can be used to distinguish between allotropes of the same material and to determine local bonding. A typical example is the difference between the fine structure of the carbon K-edge in the case of diamond (sp$^3$-bonded carbon) and graphite or amorphous carbon (sp, sp$^2$-bonded carbon). Typical EELS spectra taken from cleaned DND samples are displayed in Figure 9.5B [23].

**FIGURE 9.5**

Diamond, graphite, and amorphous carbon K-edge ELNES signatures taken as a reference from a thin diamond film, a thin graphite film, and an amorphous carbon support (top panel) together with background subtracted, normalized core-loss EELS spectra from several cleaned DND samples [23]. Nitrogen is detected in all samples through the K-edge with half maximum at 403 eV. No oxygen is detected at 532 eV (indicated by asterisk). Inset: background subtracted nitrogen K-edge signal from sample S1 showing the nitrogen $\sigma^*$ peaking at 406 eV. The image in (C) indicates a typical investigated area for TEM-EELS.
All ND EELS spectra are aligned to the carbon K-edge onset at 284 eV. The spectra show typical diamond-like ($\sigma^*$) ELNES starting at 292 eV (see diamond reference). The spectra also show a small carbon pre-peak, typical for graphitic material at 285 eV ($\sigma^*$ contribution—see also graphite reference) [28], arising from surface carbon [27]. In many ND samples, a clear signal for nitrogen (nitrogen K-edge) can be measured, with half maximum at 403 eV and peaking at 406 eV. A typical background subtracted nitrogen K-edge is shown in the inset as an example. No oxygen signal (oxygen K-edge at 532 eV) can be detected in the investigated samples.

The area under the ionization edges can be used for elemental quantification. In conventional quantification, the decaying background is removed and the integrated intensity under the edges is measured and quantified using a suitable atomic cross section (effectively a probability for inelastic scattering). Model-based quantification can be used to obtain the most precise and accurate results possible [29]. Typical DND particles can contain up to several at.% of embedded nitrogen [23,30].

**Core-loss EELS: local dopant detection and coordination determination**

Besides confirming the presence of impurities like nitrogen ND particles through core-loss EELS of many particles simultaneously, spatially resolved EELS in a STEM can be used to locally determine the position of, e.g., nitrogen, in the diamond lattice [31,32]. Using STEM-EELS, points analysis, 2D line scans, and 3D “spectrum images” can be carried out by acquiring an EELS spectrum at each probe position. In modern aberration-corrected instruments, probe sizes well below 1 Å are feasible, allowing atomic resolution analysis [8].

An example of a line-scan experiment is displayed in Figure 9.6. The particle is a single diamond crystal, ~13 nm in diameter; the performed line scan is displayed by an arrow in Figure 9.6A. In total 20 EELS spectra were recorded in the line scan of the 13 nm grain. Two typical spectra—one at position A and one at position B on the particle—are displayed in Figure 9.6B. Both spectra show a carbon K-edge with $\sigma^*$ contributions typical for diamond at 292 eV and small $\pi^*$ contributions at 285 eV arising from sp²-hybridized surface carbon. Spectrum B shows a larger graphitic $\pi^*$ contribution than spectrum A, which is to be expected as a larger surface contribution is measured at the thinner position B. The spectrum at position A clearly shows a nitrogen signal at 403 eV (indicated by an asterisk), while the spectrum from position B does not. Using model-based quantification methods, the nitrogen content was determined over the whole line scan. It is plotted in Figure 9.6C as the nitrogen signal strength, together with the carbon signal strength and the HAADF-STEM signal intensity, which may be regarded as a thickness profile. In Figure 9.6D, the normalized sp² and sp³ content is plotted. These values were obtained by modeling the $\pi^*$ and $\sigma^*$ contribution using a Lorentzian at 285 and 292 eV, respectively. To obtain the plot, the area under the modeled Lorentzian peaks was divided by the total intensity of the $\pi^*$ and $\sigma^*$ contribution. In this way the sp² content was determined to be only 5% at the core positions, rising at the edge of the particle to a maximum of 14% sp². It can be seen from the plots in Figure 9.6C and D that there is only a detectable nitrogen signal within the inner
Central nitrogen embedding in a DND nanoparticle [25,33]. (A) HAADF-STEM image of a large DND nanoparticle. The 20 point line scan is indicated by an arrow. (B) Background subtracted, normalized EELS spectra from positions A and B from the large DND particle. Position A on the particle shows a clear nitrogen peak at 403 eV; position B closer to the surface does not. (C) Normalized nitrogen peak strength, carbon peak strength, and HAADF-STEM image intensity for the line scan from (A). (D) Normalized sp² and sp³ content at each scan position modeled by a Lorentzian at 285 and 292 eV for the \( \pi^* \) and \( \sigma^* \) contribution, respectively. The sp³ content at the center is ~95% and at the edge ~86%.

6 nm core of the DND particle. Toward the surface of the particle where the sp² ratio is higher, no nitrogen is detected. The maximum nitrogen content in the core of the particle was measured to be 3.5 at.%. The lack of an N signal toward the surface is not due to noise, as can be seen when comparing spectra A and B in Figure 9.6B.

Similar line-scan experiments were carried out by other groups on high nitrogen-doped DND material. These results also indicated the nitrogen was preferentially embedded in the diamond cores [30].
In a second example, the multiple-twinned ND displayed in Figure 9.7A was investigated using the spectrum imaging method, to determine whether any enrichment of nitrogen at grain or twin boundaries occurs in DND. The HRTEM image of the multitwin again shows the presence of simple $\Sigma = 3$ coherent twin boundaries.
and lamellar multiple-twinned regions, probably containing a large degree of point and planar defects [34]. The particle surface appears to be nearly non-sp$^3$ carbon free. For this particle, a $53 \times 67$ pixel spectrum image (SI) was acquired at 2 Å interspacing. The sp–sp$^2$, sp$^3$, and N maps are displayed in Figure 9.7C–E. As was the case for the line scan in Figure 9.6, the sp$^3$ map follows the annular dark field (ADF) signal nicely, and the intensity in the map can be seen as a thickness fingerprint. Although only minimal graphitic material was visible in the HRTEM image, the sp–sp$^2$ map clearly follows the surface contours of the ND particle. The origin of this signal is therefore attributed mainly to dangling bonds and to some rest non-sp$^3$ material at the surface of the ND particle. A significant sp–sp$^2$ signal is also measured from both the coherent $\Sigma = 3$ twin boundary (example indicated by A) as well as the lamellar twinned regions (example indicated by B). This nondiamond signal must once again arise from dangling bonds, indicating that even the coherent twin boundaries are not sp$^2$ carbon free. The nitrogen K-edge signal is mapped in Figure 9.7E. The nitrogen is embedded in the ND matrix, in good agreement with earlier measurements. Interestingly, an enrichment of nitrogen at the multiple-twinned region is clear from the map. As thickness effects can play a role in the visual interpretation of the nitrogen map, and the map displays a relatively high noise level due to the low nitrogen signal, the nitrogen K-edge from two regions, region 1 being a nondefected diamond region and region 2 being the multiple-twinned region, are plotted in Figure 9.7G. The spectra have been aligned to their continuum level, and it is clear that even though the nondefected region clearly contains nitrogen, the multiple-twinned area is enriched in nitrogen. No such clear nitrogen enrichment was measurable for the coherent twin boundary A.

As mentioned above, the fine structure of EELS edges is known to be related to the local symmetry and environment of the excited atomic species [21,35]. Therefore, the shape of the nitrogen K-edge fine structure should provide clues about the form in which nitrogen is embedded into the ND particles. In previous experiments, the shape and position of the nitrogen K-edge fine structure led our and other groups to the conclusion that nitrogen was tetrahedrally embedded in the diamond particles [23,30].

The averaged experimental nitrogen K-edge fine structure from a diamond core region (both raw data and smoothed) and the experimental carbon K-edge of ND are plotted in Figure 9.8 (left panel). The experimental nitrogen K-edge shows a distinct triangular shape with three pronounced peaks B, C, and D and a less-pronounced pre-peak A (the size of which can vary). This nitrogen ELNES shape was found to be similar in other DND samples, even in samples with very high-nitrogen doping [30]. A striking similarity exists between the nitrogen and the carbon (diamond) K-edge fine structures. Peaks B, C, and D are all present in both ELNES spectra, and in the case of the carbon K-edge the pre-peak A at 285 eV is known to be related to sp- and sp$^2$-hybridized carbon. The striking similarity between the N and C ELNES points to the fact that nitrogen is embedded into an environment that is highly similar to carbon embedded in diamond, namely a dominant sp$^3$ symmetry.
In an attempt to provide more accurate information on type of nitrogen embedding, we performed detailed Density functional theory (DFT) calculations to calculate the nitrogen K-edge ELNES for four possible embedded states of nitrogen, namely:

- Single substitutional nitrogen, Nₜ, or P₁ center
- Two neighboring embedded nitrogen atoms, A-center
- The charge neutral nitrogen-vacancy (NV) center—NV₀
- The negatively charged NV center—NV⁻

The DFT-calculated spectra, performed in the GGA approximation on 2 x 2 x 2 supercells in the full core hole approximation using the code WIEN2k, are plotted in Figure 9.8 (right panel). At first glance, all four calculated N–K-edge spectra look similar, a result of the similarity of the nitrogen coordination in all four cases. However, small differences can be made out. The spectra for NV⁻ and NV₀ centers are near identical, and clearly differ from the experimental nitrogen K-edge. Although
all calculated spectra have been broadened by 1 eV (to correspond to the experimental broadening), the spectra for \( \text{NV}^- \) and \( \text{NV}^0 \) are narrower and display fewer features than the experimental spectra. This appears to indicate that the nitrogen present in as-synthesized ND is not present in large amounts of \( \text{NV}^- \) or \( \text{NV}^0 \) centers, which is in good agreement with literature [34]. These optically active structures are only obtained in large amounts after vacancy creation and sintering treatments [36–38].

The triangular spectrum for single substitutional nitrogen \( \text{N}_s \) shows more similarities to the experimental nitrogen K-edge ELNES, reproducing features B, C, and D as well as a pre-peak to the main feature B. This so-called \( \pi^* \) contribution arises from bond length elongation of one of the CN bonds by \( \sim 30\% \), a result of the energy relaxation step in the calculation, and which is in good agreement with the literature [39]. Due to this elongation, the nitrogen atom is present in a more planar coordination with respect to the other three bonding carbon atoms, giving rise to the \( \pi^* \) contribution. As was the case for the \( \text{NV}^- \) and \( \text{NV}^0 \) spectra, the spectrum is clearly less broadened than the experimental spectrum. The best correspondence is clearly given by the calculated spectrum for two neighboring, substitutional nitrogen atoms (the A-center model). All three peaks at B, C, and D are reproduced in this model, and the peak positions fit well with the experimental positions. The small pre-peak A that is present in the experimental ELNES is however not reproduced by the A-center model, even though it was reproduced in earlier ELNES simulations using multiple-scattering theory [40].

9.3 Near-edge X-ray absorption fine structure spectroscopy

Near-edge X-ray absorption fine structure (NEXAFS) is a type of absorption spectroscopy. The fundamental phenomenon underlying NEXAFS is the absorption of an X-ray photon by a core level of an atom in a solid and the consequent emission of a photoelectron. The resulting core hole is filled either via an Auger process or by capture of an electron from another shell followed by emission of a fluorescent photon. NEXAFS is very sensitive to the bonding environment of the absorbing atom. Often one can use a spectral “fingerprint” technique to identify the local bonding environment.

The nitrogen speciation in DND sample produced from TNT/RDX was assessed by imaging NEXAFS performed at WERA beamline at ANKA synchrotron source, Karlsruhe [41] according to approach described in [42]. Figure 9.9A shows the carbon edge for the DND. The spectra are typical for macro- [43] and ND [41,44,45]. They show the typical features of diamond: an absorption edge representing the conduction band edge, a C 1s core exciton, and a series of structures resulting from a band of \( \sigma^* \) states and the second absolute band gap. The relative intensities of the features around the absorption edge could be slightly different from an ideal diamond due to difficulties in subtraction of the background in this region. Note the presence of a small peak at 285 eV indicating a small amount of \( \text{sp}^2 \) carbon (graphitic), also typical for NDs.
FIGURE 9.9
NEXAFS spectra at carbon (A) and nitrogen (B) absorption K-edges of DND, and (C) NEXAFS spectra of various configurations of nitrogen in cubic (c-dia) and hexagonal (h-dia) diamond lattices calculated using FEFF 8.2. The curves are displaced vertically for clarity; the horizontal axis shows energy relative to the absorption edge. Marked differences between the shapes of the experimental and modeled absorption spectra are obvious.
The nitrogen absorption spectra (Figure 9.9B) are noisier; this clearly results from relatively low concentration of this element. The main absorption edge is observed at 405 eV. This position is indicative of N in sp\(^3\)-bonding configurations (see below). It should be noted that the N NEXAFS spectra of ultrananocrystalline diamond (UNCD) [44] and EELS spectra (DNDs [30]) are similar to those observed by us.

Using the FEFF 8.2 code [46] we have performed theoretical modeling of N NEXAFS spectra in cubic and hexagonal diamond polytypes. Figure 9.9C shows modeled spectra for nitrogen configurations usually encountered in macrodiamonds (substitutional single and paired nitrogen atoms with several values of lattice relaxation), as well as for some other configurations of several N’s and vacancies. They are obviously different from the experimental spectra. Spectra of nitrogen atoms surrounded by various arrangements of vacancies and carbons are characterized by fewer broad spectral features, making them qualitatively more similar to the observations. Results of our modeling are qualitatively similar to earlier calculations of EELS spectra of N in diamonds [40].

The XPS spectra for N in UNCD and DND suggest the presence of two or perhaps three types of N environment [47,48]. Unique interpretation of the N XPS and NEXAFS spectra in the C–N systems is not yet possible, but according to Ref. [48] the observed features originate from nitrogen occupying two- and three-coordinated structures with at least one of the nearest neighbors being also a two- or three-coordinated carbon. This assignment corresponds well to a suggestion that N in UNCD [49,44], in DND [34], and in NDs from meteorites [41] is largely confined to grain and intercrystallite boundaries and other extended defects. This might indicate that the local environment of nitrogen in NDs is closer to that in hexagonal polytypes. Following the XPS results [47,48,50], we suggest that N in NDs is most likely distributed among several main atomic configurations, thus blurring the absorption spectra. However, the set of these configurations is not completely random and/or sample dependent, which is indicated by the consistent shape of the absorption spectra. Anyway, the atomic-level N environment in ND is markedly different from the bulk diamond lattice and, therefore, its manifestations in infrared absorption and luminescence must be different.

Interestingly, controlled oxidation of DNDs and of NDs separated from meteorites shows that peak of nitrogen release coincides with the main peak of carbon, even when small temperature steps (30–50°C) are used. In the same time, during pyrolysis (heating in high vacuum without oxygen) nitrogen release is observed only at temperature of ~1100°C, corresponding to thermal-driven graphitization of diamond structure [51]. These facts indicate that nitrogen impurity is indeed chemically bound to the diamond lattice.

Most likely, the atomic environment of N in NDs can be understood using experimental NEXAFS data and theoretical modeling. However, this approach requires molecular dynamics or Monte Carlo simulation of several plausible configurations as a starting model.
9.4 XRD and small-angle X-ray scattering

XRD and scattering are widely used for investigation of structure of various materials. The most widely used methods are XRD and small-angle X-ray scattering (SAXS). In the last decade, with the advent of modern synchrotron sources with high intensity of hard (i.e. short wavelength) X-rays, high-energy XRD (HEXRD) is becoming an important additional approach to decipher fine details of the structure of nanoparticles and disordered materials.

Very often the X-ray methods are used to infer dimensions of nanoparticles. However, the sizes obtained by diffraction and scattering usually differ. The reason for these differences is due to various aspects of interaction of X-rays with matter revealed by XRD and by SAXS. The XRD pattern results from constructive interference of diffracted X-rays and physical broadening of the diffraction peaks provides information about sizes of so-called coherently scattering domains. In many fields these domains are called crystallites. The SAXS signal comes from heterogeneities of the electron density which, in the case of nanoparticles, usually corresponds to the overall dimensions of the particle. Therefore, in most cases the sizes extracted from the width of X-ray reflections is smaller than those from SAXS. The sizes obtained from electron microscopy are usually similar to the SAXS values. Notice that the sizes obtained from dynamic light scattering are often much larger since this method gives the so-called hydrodynamic radius, which reflects peculiarities of interaction of the particle with the solvent and, in the case of NDs, usually corresponds to aggregates of primary particles.

9.4.1 X-ray diffraction

Intense studies of NDs using X-ray methods give rather consistent results. Already the first diffraction studies of NDs lead to a conclusion that the size of the diamond core is 4–5 nm. Subsequent studies combining XRD, SAXS, and other techniques helped to develop a more elaborate model of a ND grain. The main feature of these models is the hypothesis that the grains are nonuniform and could be described by a core-shell model. The first such model was proposed in 1999 [52]; the subsequent advances aim to explain various fine details of diffraction patterns acquired in very wide angular ranges. One of the two advanced models suggests that the ND grain consists of three shells: a diamond core with a diameter of ~3 nm, surrounded by a sp2/sp3 layer of nongraphitic carbon (probably similar to diamond-like carbon), and 1–2 outermost layers that are onion-like [53]. Partial graphitization of the outermost layers on some faces of the nanograins was suggested in a HEXRD study [54]. Another approach suggests that the “perfect” diamond core is surrounded by a shell of strained diamond material with the lattice parameter different from that of the ideal diamond lattice [55,56]. An interesting observation made in several independent X-ray studies is the hkl-dependence of the physical broadening of diffraction peaks. Such broadening is logically explained by a slight distortion of the cubic diamond structure toward hexagonal. Several other models were suggested, and include,
for example, a model suggesting that the ND grains are hollow [57]. However, these models are not widely accepted.

The nitrogen concentration in NDs is usually below 2–3 at.% [58]. These values are very high in comparison with macroscopic diamonds. Such concentrations of impurities may influence the lattice strongly enough to be observed in diffraction. A good example is considerable increase of the lattice parameters by single substitutional nitrogen atoms in high-pressure high-temperature (HPHT) diamonds (e.g., Ref. [59]). Up to the present, all X-ray-based models of NDs consider only pure carbon grains; impurities such as nitrogen are not accounted for. The correct model of NDs should include impurities-related lattice distortions; this work is currently underway.

An important problem in interpretation of XRD from NDs lies in possible contribution of hexagonal diamond polytypes. The main difficulty results from heavy overlap of principal 111 peak of cubic diamond with the most prominent 002 peak of hexagonal and rhombohedral polytypes; this situation is common to many polytypic substances (e.g., SiC). Although formally the separation of the peaks is sufficient to be reliably measured by modern X-ray diffractometers, the size-strain-related peak broadening and shift makes the task demanding and ambiguous. Moreover, if graphitic carbon is also present in the sample, it will also contribute to the broadening of the main diamond peak.

From a crystallography point of view, certain types of stacking faults in a cubic lattice can be considered as lamellae of a hexagonal polytype. Investigation of pure lonsdaleite would help to decipher the XRD patterns. However, this polytype is not available as a pure phase. Detailed studies of lonsdaleite-rich diamond samples show [60,61] that cubic and hexagonal polytypes are intermixed on nanometer scale. This structure is perfectly compatible with the stacking-fault concept described above.

Reliable observation of diamond polytypes in NDs using XRD requires data acquisition with very high statistics in a broad angular range in order to monitor presence of weak peaks. It would be beneficial to additionally use radiation with wavelengths longer than conventional copper. This would give larger separation of overlapping peaks.

### 9.4.2 SAXS

The first SAXS studies of NDs were performed a long time ago [62]. In general, results of the early studies are consistent with the more recent works. Interpretation of many SAXS studies of UDD is performed in the framework of the fractal model ([63]). However, physics of such approximation remains unclear and, in general, the application of the fractal concept to SAXS from carbons must be performed only after critical assessment of the correctness of background subtraction [64].

One of the most important parameters extracted from a SAXS curve is the size distribution of the scatterers. Mathematically, the extraction of the shape and size of the scatterers from the 1D SAXS curve is an ill-posed problem. Therefore, while working with a polydisperse system (i.e., the particles are not strictly identical) one needs certain assumptions about the shape of the scatterers. In the case of a
polydisperse system the scattering patterns of spheres and of other roughly isometric particles (e.g., cubes) are fairly close to each other. Therefore, unless reliable information from an independent technique is available, spherical shape of nanoparticles is assumed. This hypothesis also applies to disperse NDs.

A typical SAXS curve and size distribution of the scatterers for a conventional DND sample is shown in Figure 9.10C. A common feature of the size distribution for the absolute majority of UDD studied is the presence of the main peak around 4–5 nm, which is in good agreement with XRD data. However, one can clearly see a long “tail” toward large sizes. The origin of this tail is the subject of debates, since several explanations could be proposed. It can be due to presence of (a) large diamond particles [34,64], (b) nondiamond carbon envelope of the grains and other residues of the chemical purification and, finally, (c) the ND particles could be nonisometric and fairly close to a monodisperse system of nonisometric particles with elongation along some directions. The latest suggestion was explored by Ref. [65].

![Figure 9.10](image-url)
The size distribution curve for purified NDs with XRD peaks corresponding only to the diamond phase is rather narrow. Moreover, incorporation of the NDs into polymer matrix gave very similar results. Application of advanced algorithms for shape reconstruction of monodisperse nanoparticles (DAMMIN, [66]) led to the conclusion that the NDs are not strictly spherical, but rather have a V-like shape. SAXS provides information averaged over the whole sample and the V-like shape may indicate high concentration of twinned ND particles. Many TEM studies of UDD are known and twinned grains are not rare. However, the V-like twins apparently are not dominating. This issue clearly requires a more detailed consideration. Imposing symmetry one obtains a more isometric shape, for example, resembling interpenetrant cubes or octahedra, i.e., special types of twins [65]. Our own measurements and calculations gave similar results.

Mikhaylyuk [53] suggested that the SAXS curves of NDs should be treated in the framework of a spherical core with radii of \( \sim 30\,\AA \) and covered by a graphitic sheath with gradually changing electron density. Although such a model seems reasonable from general point of view, its applicability to real ND powders is uncertain, since even a moderate degree of polydispersity of grain sizes may explain the observations. In general, when the system under investigation may be represented as a two-phase system with exponentially changing electron density, one should observe a linear Debye–Bueche plot \( (I(s))^{-1/2} \) versus \( s^2 \), where \( s \) is the scattering vector, determined as \( s \equiv 4\pi \sin(\theta)/\lambda \), which is indeed the case for some carbons [67]. The linearity of this plot is indeed observed for UNCD films grown with high amounts of \( N_2 \) in the growth medium and is explained by contributions from ND rods encased into graphitic carbon sheath [68]. Therefore, the applicability of Mikhaylyuk’s model to disperse NDs should be considered only after thorough investigation of the system.

### 9.4.3 Microstructure of NDs from X-ray data

The first systematical study of the phase composition and size distribution for the main representative classes of NDs using XRD and SAXS has been carried out by Shenderova et al. [32].

The XRD patterns are shown in Figure 9.11. For all samples the diamond phase dominates, which is evidenced by a strong peak at \( 2\Theta \sim 44^\circ \) (the 111 reflection), but minor amounts of graphitic carbon are also observed (002 peak at \( 2\Theta \sim 26.9^\circ \)). The diamond 111 peak is nonsymmetric. The observed shoulder is due to an overlap of the diamond 111 and graphite 101 peaks. In addition, several diffraction peaks (100, 002) of hexagonal diamond (h-dia)—lonsdaleite—likely also contribute to the main peak. However, the lonsdaleite peak is clearly of minor importance.

The overlap of the peaks from diamond and graphite (hexagonal and rhombohedral) polytypes makes a reliable determination of the crystal size of the corresponding phases difficult. Panels A and B of Figure 9.11 show examples of decomposition of the main peak into several components (Pearson VII shape of the peaks is assumed). The dimensions of the diamond crystallites are estimated from the Debye–Scherrer formula and are \( \sim 13.6\,\text{nm} \) for the 111 direction and 9.6\,nm for...
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the 110 peak for the ND-G/RDX150 sample; 8 nm for the ND-G sample; and 4 nm for DNDs produced from explosives. A very rough estimation of the possible lonsdaleite grain size gives 2.4 nm for the ND-G sample. This value is similar to the one reported by Refs. [69] and [60] for h-dia produced by shock-converted graphite and is considerably smaller than the sizes of the cubic diamond crystallites.

In the sample made from graphite precursor a rather strong peak from graphite and of other similar phases is present. This is evidenced by a broad halo centered roughly at $2\Theta \sim 26.9^\circ$, and a number of superimposed sharp peaks. Interestingly, the lonsdaleite peak is also weak, in contrast to some static experiments on HOPG at very high P–T conditions [70].

We have already discussed various approaches to describe the SAXS curves from NDs. In our work, we stick to the model describing the ND sample as a system of quasi-spherical grains and calculate their size distribution using the standard mathematical model for polydisperse spheres [71]. For all samples, the crystal size

![FIGURE 9.11](image.png)

**FIGURE 9.11**

XRD patterns of the NDs. (A) NDs from graphite precursor; (B) from graphite-hexogen mixture; and (C) DND of wet synthesis. Decomposition of the main peak at $2\theta = 44^\circ$ is shown; Pearson VII shape is assumed for all components.
of the dominant fraction determined by SAXS is larger than the size determined from the broadening of the Bragg peaks. The discrepancy in the crystal size determined by both techniques reflects the fact that many ND particles consist of several crystallites within a single grain.

The SAXS data for the ND-G sample (Figure 9.10A) show a bimodal size distribution of the particles with peaks (diameters) at ~6 nm and at ~23 nm. Unfortunately, the SAXS curves do not allow one to unambiguously determine whether the “small” and “large” particles represent different phases or not. The size distribution of the NDs produced from explosives (Figure 9.10C) is typical for DNDs: the main peak shows diameters around 6 nm and a broad tail stretching out to larger sizes. It should be noted that the fraction of particle crystal sizes exceeding 6 nm is larger for ND of dry synthesis as compared to ND of wet synthesis (Figure 9.10C). The secondary peaks at larger sizes in DND of dry synthesis most probably belong to a graphite phase, since ND particles with grain sizes larger than 10 nm were not observed by HRTEM for this sample.

Finally, the size distribution for the ND-G/RDX sample (Figure 9.10B) differs considerably from the majority of the NDs studied within this work, since this sample possesses a relatively broad size distribution centered at ~34 nm. Moreover, this is the only ND sample for which linearity of the Debye–Bueche plot may be present. Notice that for this work polycrystalline, i.e., not deagglomerated, powder was used. The comparison of the SAXS and TEM data for this sample shows that the sample consists of particles with fairly broad size distribution and with various shapes (isometric and elongated). Therefore, it is uncertain whether the suspected plot linearity reflects the existence of the electron density fluctuations or results from polydispersity of the particles.

### 9.5 ESR spectroscopy

ESR spectroscopy is commonly used for a detection of nitrogen-related impurities in synthetic diamonds with a very low detection limit (~10^{12} spins). Nitrogen mostly incorporates in the synthetic diamonds in the form of single substitutional atoms that are paramagnetic. For a long time the ESR analysis in its traditional continuous-wave (CW) version was not informative in DND characterization. Strong background signal from presumably surface structure defects [72,73] of DND particles dominated the ESR spectra, preventing detection of paramagnetic nitrogen (P1 center) in a diamond core. An advanced pulse ESR approach, in particular the electron spin echo (ESE) technique, allows efficient time selection for spins having different relaxation times. Using the ESE at liquid helium temperatures, P1 centers were discerned for the first time from the strong background signal in DND produced from TNT/RDX mixture [74]. Later, Fionov et al. [75] estimated the concentration of paramagnetic nitrogen in DND to be 2 ± 1 ppm, by modeling and subtracting the broad background in CW ESR spectra. A strong increase of ESR signal from paramagnetic N has been
observed using pulsed EPR in DND sintered under HPHT treatment (800°C and a pressure of 6 GPa) [38]. A new approach for efficient depletion of the strong background ESR signal in DNDs was suggested by Orlinskii et al. [76]. ND of dynamic synthesis with an average grain size of ~30 nm (based on SAXS measurements) was studied in that work. The ND was produced from a mixture of graphite and RDX. The ND powder was dispersed in ice and subsequently analyzed by the ESE technique. That allowed an essential decrease of the spin relaxation time of dominant nonnitrogen defects, while keeping the P1 spin relaxation time unchanged. Observed effect was able to assign the dominant signal in the ESR spectra of the NDs to surface defects.

The systematical pulse ESR study of the main representative classes of NDs produced by detonation shock-wave conversion of different carbon precursor materials, namely, graphite and a graphite/RDX mixture into ND, as well as ND produced from different combinations of explosives using different cooling methods (wet or dry cooling) has been carried out by Shenderova et al. [32]. ESE technique in the X-band of microwave frequencies has been used to detect single substitutional P1 centers and to estimate their concentration in the studied ND samples. The measured ESE spectra are shown in Figure 9.12. The ESR signal from substitutional N was easily separated from the background in the TNT/RDXw (spectrum 2) and graphite/RDX (spectrum 4) samples. The estimated concentrations of P1 centers in the samples are given in Table 9.1.
Photoluminescence spectroscopy

Photoluminescent (PL) spectroscopy is used to inspect structural perfection of a diamond lattice, revealing impurities and structural defects emitting in a wide range of diamond transparency under their photo-excitation. For the last decade, an interest in the PL characterization of ND has increased. This is explained by promising results on the use of luminescent NDs as a source of a single-photon emission for quantum information technologies [77] or, alternatively, as a bright light source applicable for biolabeling [78].

For a long time, PL characterization of DNDs was confined to broad-band PL registration in the range 400–700 nm. The typical PL spectrum recorded for DND at 488 nm excitation is shown in Figure 9.13 [79].

As this broad PL starts to dominate with decreasing of ND grain sizes [80] when the fraction of surface carbon became essential (about 0.1 for 5 nm diamond grain), it makes sense to relate this PL band with surface defects enabling them to create continuously distributed energy states in the band gap of diamond [81]. One more piece of evidence in favor of PL band identification with surface defects is strong

<table>
<thead>
<tr>
<th>Sample</th>
<th>ND-G</th>
<th>ND-G/RDX</th>
<th>ND-TNT/RDXw</th>
<th>ND-TNT/HNSw</th>
<th>ND-TNT/RDXd</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (ppm)</td>
<td>–</td>
<td>0.6</td>
<td>0.02</td>
<td>&lt;0.006</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 9.1** Nitrogen Concentration Estimated by ESE Analysis for Different Classes of NDs

**FIGURE 9.13**

Typical RT PL spectrum of DND recorded at 488 nm excitation. Two narrow lines in the range 520–530 nm are characteristic of Raman scattering in the DND [79].

**9.6 Photoluminescence spectroscopy**

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variations of the PL intensity with ND surface functionalization [78,82–84]. The strong “surface” PL of DND powder interferes with detection of luminescent defects formed in an ND core. In the first place it concerns the detection of nitrogen-related centers as it was found that nitrogen impurities are present in a large amount in a DND core [79,85]. NV centers are one of the structural forms of optically active N-related defects, formation and control of which in the ND is one of the most actual task for modern nanotechnologies. It was demonstrated that NDs containing NV centers represent an advanced material platform for production of quantum information bits and/or fluorescent biolabels [77,78]. Two types of luminescent NV centers are distinguished: the negatively charged (NV⁻) and the neutral (NV⁰) ones, characterized by zero-phonon lines (ZPLs) at 638 and 575 nm, respectively.

Recently, two main approaches were applied to detect the NV PL in DND with high sensitivity efficiently depleting the “surface” PL. In the first approach, a time-resolved PL spectroscopy was used [86]. The approach is based on the fact that radiative relaxation times from excited electronic states are much shorter for the surface defects (<0.5 ns) [86,87] than for the NV centers (~10 ns) in NDs. In the second approach, a confocal PL spectroscopy of a single nanoparticle was used [32,88]. Much higher quantum yield of NV PL as compared to that of “surface” PL allows the detection of even single NV centers in individual 5–10 nm diamond particles [89,90]. Recently, an innovative approach for strong enhancement of NV PL in DND using sintering treatment was suggested in Ref. [38].

### 9.6.1 Time-resolved PL of DND

PL from NV centers was found in DND for the first time under use of time-resolved PL spectroscopy [86]. Experiments on time-resolved PL detection were held for typical DND produced from a mixture of TNT and RDX explosives. A pulsed excitation was realized by laser with 531 nm light emission and a pulse width of 0.6 ns. A standard technique on increasing the NV concentration in the diamond doped with nitrogen was applied: the DND powder was irradiated with high-energy particles (protons) followed by sample annealing. Featureless “surface” PL was observed for the DND sample before and after the sample treatment (Figure 9.14, two bottom lines marked with triangle and two diamonds) when no time delay was applied under PL registration. When the proton-irradiated sample was measured using time-gating with a delay time of 3.5 ns after the excitation pulse (third line, single diamond) ZPLs of NV⁻ and NV⁰ color centers become visible at 637 and 575 nm, respectively (marked with arrows).

### 9.6.2 Confocal PL spectroscopy of single DND particles

Contrary to time-resolved PL experiments that do not require a special preparation of the DND powder for testing, a thorough dispersion of the aggregated DND particles in a solution is required at sample preparation for the confocal PL analysis of single DND particles. Well-dispersed low-concentrated DND solution then is either dropped or spin-coated onto a glass coverslip (or other convenient substrate).
To distinguish between neighbor ND particles during laser beam scanning of glass substrate, the density of the ND particles should be less than 5 μm². As long as all analyzed ND particles can be placed in a focal plane of an objective used for laser beam focusing, then a collection of the PL from only a thin volume layer adjacent to the focal plane (a confocal collection) supplies the highest signal/noise ratio for single ND PL detection.

The first direct observation of NV centers in discrete 5 nm NDs at room temperature using confocal PL spectroscopy was reported in Ref. [88]. The NDs were produced from TNT/RDX mixture. Figure 9.15 presents data from the analyzed sample, collected with the combined confocal scanning luminescence and atomic force microscope (AFM). The AFM-based measurements clearly show areas of the sample with a sparse spatial distribution of nanoparticle (Figure 9.15A) with a typical size in the 5 nm range (Figure 9.15C). As shown, some isolated nanoparticles (1%) were luminescent (Figure 9.15B), and their spectra (Figure 9.15D) were consistent with those reported for NVs in ND [89,90]. Furthermore, the second-order correlation function $g^{(2)}(t)$ confirmed that the emission originated from a single center (Figure 9.15D, inset).
During confocal PL study of the isolated DND [88], a new property of NV centers, luminescence intermittency or “blinking,” was found for some luminescent ND particles (for about 25%). Possible reasons for the appearance of this property are discussed in detail in Chapter 10 of this book.

To this date, most PL research of DND material has been limited to a study of NDs produced from TNT/RDX detonation mixture. The first and still only systematical PL study of the main representative classes of NDs produced by detonation

![FIGURE 9.15](image_url)
Photoluminescence spectroscopy

shock-wave conversion of different carbon precursor materials, namely, graphite and a graphite/RDX mixture into ND, as well as ND produced from different combinations of explosives using different cooling methods (wet or dry cooling) has been carried out by Shenderova et al. [32]. It was demonstrated that (i) ND particles larger than \( \sim 20 \) nm may contain \textit{in situ} produced optically active NV centers, (ii) in ND produced from explosives, NV centers are detected only in ND produced by wet synthesis, and (iii) ND synthesized from a mixture of graphite/RDX (G/RDX) contains the largest amount of NV centers formed during synthesis among all studied NDs.

Confocal luminescent and topographical images of the G/RDX sample are shown in Figure 9.16A. From the measurements of photon statistics (second-order intensity correlation function), the maximum concentration of \( \sim 3 \) NV centers per particle (Figure 9.16B) was estimated. NV PL was observed in more than 20\% ND particles.

The concentration of the NV centers in G/RDX ND is so high that it is detected even by conventional PL spectroscopy used for the ND powder, as shown in

FIGURE 9.16

(A) Confocal fluorescent and topographical images of sample G/RDX. (B) Photon antibunching curve, measured for the emitting point marked with white line on the topographical image [32].
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Figure 9.17. ZPLs of NV\(^0\) and NV\(^-\) centers are resolvable at, respectively, 576 and 639 nm. NV PL is so strong for the G/RDX ND that no “surface” PL is enough to overshadow it, contrary to the typical DND produced from TNT/RDX mixture for which the “surface” PL dominates the spectrum (Figure 9.17).

G/RDX ND has larger typical primary grains (34 nm) and lower N concentration (<0.5%) as compared to TNT/RDX ND (grain size is 6 nm, N concentration is 2–3%). Still it is not clear which of these two characteristics play a crucial role in the increased NV concentration for G/RDX ND as compared to that for TNT/RDX ND. The N atoms at high concentrations are possibly prone to the formation of complexes that are not optically active. In addition, at high concentrations, N atoms can suppress an optical activity of neighboring NV defects. Alternatively, a decrease of ND particle size results in an efficient interaction of the NV centers with surface defects including a charge interaction between them. As a result, the NV\(^0\) and NV\(^-\) could be transferred into optically inactive NV\(^+\) centers in small NDs. The NV interaction with ND surface defects will be discussed in more detail in Chapter 10.

9.6.3 PL spectroscopy of HPHT-sintered DND

Baranov et al. [38] have presented the first results on an observation of a strong increase of NV PL by an HPHT sintering (800°C and 6 GPa for 11 s) of DND particles, which were produced from TNT/RDX mixture. Figure 9.18A shows the
room temperature 532 nm laser-induced luminescence spectrum measured on a single 12 μm ND cluster. A quite well-distinguished NV⁻ ZPL at 637 nm followed by prominent vibronic sidebands is observed in the spectrum. The low-temperature PL spectrum (Figure 9.18B, solid line) demonstrates narrowing of 637 nm ZPL as well as reveals the presence of neutral NV (ZPL at 575 nm) inside the sintered DND cluster. For comparison the low-temperature PL spectrum of irradiated and annealed 50 μm HPHT diamond crystal with estimated concentration of NV⁻ centers of order of 10 ppm is shown in Figure 9.18B (dashed line). No reasonable explanation of the strong increase of NV PL in sintered DND was suggested. In our opinion, removing of NV centers–ND surface interaction accompanied by recovering of NV⁻ from NV⁺ could be one of the possible explanations of the observed phenomenon.

9.7 Conclusion

Essential progress in the characterization of DND has been made over the past few years. The main achievements are related to the study of nitrogen impurities in DND. The presence of nitrogen within the “core” of DND grains has been unambiguously proven. Two configurations of nitrogen defects have been detected in the DND particles: single paramagnetic nitrogen centers and NV complexes. Difficulties in the study of the nitrogen in DND arise from the small sizes of the diamond crystallites and from the presence of a non-negligible fraction of surface atoms. Progress in spatial resolution of nanoscale analysis techniques and the development of new methodologies is helping investigators to gain a step-by-step understanding of the peculiarities of nitrogen incorporation in NDs.
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