Luminescence of negatively charged single vacancies in diamond: ND1 center

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ABSTRACT

Strong photoluminescence (PL) of ND1 radiation center with zero-phonon line (ZPL) at 393.5 nm has been excited in irradiated diamonds with a laser working at a wavelength of 355 nm. Emission of the ND1 center consists of ZPL and vibrational replicas related to quasilocal vibrations of an energy 76 meV. PL and absorption spectra of ND1 center exhibit very close mirror symmetry. The energies of the quasilocal vibrations are the same in luminescence and absorption. The interaction with the lattice phonons at the ND1 center is very weak. In luminescence of the irradiated diamonds, ND1 center behaves like one related to simple primary radiation defects in negative charge state. PL of the ND1 center is stimulated by nitrogen donors and suppressed by boron acceptors. It is assumed that the luminescence of the ND1 center is effectively excited only in the spectral range of its intrinsic absorption from 340 to 390 nm.

1. Introduction

Single vacancies are the simplest and the most common radiation defects in diamond crystal lattice. Isolated single vacancies can be easily detected spectroscopically. When in neutral charge state, they give rise to the well-known GR1 center (ZPL at 741 nm). GR1 center is active equally well in absorption and luminescence. When charged negatively, single vacancies are detected as the ND1 center (ZPL at 393.5 nm at liquid nitrogen temperature). The ND1 center was reported for the first time in [1]. It was studied and labeled as ND1 in [2]. Based on the piezospectroscopic analysis, the ND1 center was ascribed to point defects of Td symmetry [3]. The assignment of the ND1 center to negatively charged single vacancy was proposed in [4,5]. Decades ago, ND1 center was believed to be active in absorption, photoconductivity and EPR, but not in luminescence [3,6–8]. Although a weak center with ZPL at a wavelength of 393 nm was occasionally seen in PL spectra of electron-irradiated diamonds, the lack of a clear spectrum of its electron-phonon sideband did not allow to confidently identify it as the ND1 center. The communication of Steeds and co-workers [9] was probably the first one where the radiation center with the ZPL at 393.5 nm and

vibrational replica of energy 80 meV recorded in PL spectra was ascribed to the ND1 center. Their arguments were based on the well matching positions of ZPLs of the 393.5 nm center in PL and the ND1 center in absorption, the same energy of the vibrational replica forming the electron-phonon side bands and the reduction in the luminescence intensity of the 393.5 nm center with the increase in the excitation laser power. The latter was explained by the de-ionization of the negatively charged vacancies.

To clarify this uncertainty and to find out whether the ND1 center can be indeed excited in luminescence we performed detailed measurements of PL, cathodoluminescence (CL) and absorption of several irradiated natural and synthetic diamond samples with different concentration of nitrogen and boron. As a result, we confirm that ND1 center can be well excited in PL. Some new features of ND1 center are reported.

2. Experimental

The samples used in this research were plates cut from natural type Ia diamonds with high A-defect concentration, natural type IIa diamonds

with low A-defect concentration, synthetic HPHT-grown type Ib diamonds with low (colorless) and high (yellow) C-defect concentration, synthetic HPHT-grown boron-doped type IIb diamonds and low nitrogen CVD diamonds. Parameters of the samples are summarized in Table 1 below.

The irradiation was performed with electrons of energy in the range from 0.7 MeV to 8.3 MeV in a dose range from 2.5×10^{16} to 3.0×10^{19} cm^{-2} and with Xe ions of energy 167 MeV in a dose range from 1.0×10^{10} to 8.1×10^{14} cm^{-2} [10].

PL was measured with two spectrometers. One of them was Nanofinder HE (LOTIS TII) equipped with a 3D scanning confocal microscope. Its spectral resolution was 0.1 nm. Lasers working at wavelengths 355 nm and 532 nm at a power of 4 mW were used for the excitation. The laser beam was focused on the sample surface with $20^{\times}$ (NA 0.4) objective in a spot about 1 μm. Another spectrometer was Renishaw inVia Raman Microscope with 325 nm laser. The laser beam was focused with a $15^{\times}$ objective (NA 0.32) to a spot of 1.2 μm. Spectral resolution was about 0.5 nm. CL was measured with a home-made instrument equipped with a 10 kV electron gun and a spectrometer working in a spectral range from 200 to 900 nm with a resolution of 0.2 nm. Current density of the electron beam was about 50 μA/cm^2. Optical absorption was measured with a home-made spectrometer working in a spectral range from 200 to 1000 nm with a resolution of 0.4 nm. The probed area on the sample surface was about 0.8 mm for CL and absorption measurements. All the measurements were performed at room temperature (RT) and liquid nitrogen temperature (LNT).

3. Experimental results

PL spectra obtained from different samples are shown in Fig. 1. Before irradiation, none of the samples revealed in their spectra any primary radiation centers (not shown). After the irradiation, spectra of the nitrogen-containing diamonds show the presence of several primary radiation centers including the intrinsic GR1, 3H and TR12 centers and the nitrogen-related center with ZPL at 389 nm [11]. In addition, a strong center with ZPL at 393.5 nm accompanied by electron-vibrational band spreading from 390 to 450 nm appears in all spectra. The spectra taken from type IIb sample are "empty" before and after irradiation. The only their feature is a very weak broad band with a maximum at 475 nm.

Intensity of the 393.5 nm center, relative to the intensity of other centers, depends on the nitrogen concentration. In natural type IIa diamond with low A-defect concentration, the intensities of the 393.5 nm and GR1 centers ae comparable. In type Ia diamond with high content of A-defects, intensity of the 393.5 nm center is about 5 times higher than that of the GR1 center. In colorless low nitrogen Ib synthetic diamond, the 393.5 nm center exceeds in intensity the GR1 center, whereas in high nitrogen yellow Ib diamond, the GR1 center intensity is negligibly small compared with that of the 393.5 nm center.

The 393.5 nm center shows strong electron-phonon interaction with vibrations of energy 76 meV. In the spectra recorded at LNT (Fig. 1b), five distinctive vibronic replicas at wavelengths 403.2, 413.0, 423.4,

Table 1
Samples used in this research. Types and impurity content.

Diamond samples	Main impurity	Concentration, ppm
Natural type Ia	Nitrogen, A-defects	280
Natural type IIa	Nitrogen, A-defects	12
Synthetic HPHT (colorless)	Nitrogen, C-defects	5–10
Synthetic HPHT type Ib (yellow)	Nitrogen, C-defects	200
Synthetic HPHT type IIb (blue)	Boron	Not measured
CVD diamond type IIa (colorless, LPHT annealed at 2000 °C)	Intentionally undoped	<1

433.8 and 444.4 nm are identified. These replicas form a broad band with a maximum at about 430 nm. Although in some spectra this vibronic band strongly overlaps with other centers, e.g., with 389 nm center, N3 center and an unknown center with ZPL at 454 nm, the 393.5 nm ZPL and its most intense vibronic replicas are always discernible.

We have studied the distribution of the luminescence centers though the depth of the Xe-irradiated samples and CVD diamond sample irradiated with 1 MeV electrons. It has been found that the 393.5 nm center has been created in the areas showing the presence of GR1 center. Combining the data obtained on all Xe-irradiated samples we have found that the intensity of the 393.5 nm center increases linearly with the irradiation dose (Fig. 2). The strong scattering of the data points in the dose dependence is caused most likely by the non-homogeneity in the nitrogen distribution over the samples.

We have performed thorough CL measurements of all samples and found that the 393.5 nm center is not active in CL. The laser excitation at wavelength 325 nm is not effective too. Detailed studies of the 393.5 nm center excited with laser 325 nm over cross-section of one of the CVD samples irradiated with 1 MeV electrons (Fig. 3a) reveal that in some areas the absorption of this center was stronger than its emission resulting in a reverse (absorption) signal in the luminescence spectrum (Fig. 3b). Interestingly, in some places, the 393.5 nm center was detected simultaneously in the regimes of luminescence and absorption.

In absorption spectra, intense ND1 center with ZPL at 393.5 nm accompanied by equidistant phonon replicas of an energy 76 meV is the dominating feature. Comparison of the spectra of the ND1 center in absorption and the 393.5 nm center in PL reveals their close mirror symmetry relative to ZPL (Fig. 4a,b). Table 2 summarizes the spectral data obtained from both spectra taken at LNT. It is remarkable that the energies of the vibrations in the PL and absorption spectra of both centers are practically equal.

We have simulated PL spectrum of the 393.5 nm center and absorption spectrum of the ND1 center using Lorentzian-shaped lines for ZPLs and Gaussian-shaped bands for vibrational replica and achieved a good match between the simulated and experimental spectra (Fig. 4b). Unfortunately, we do not know the real shape of the base line underlying the spectra, so for the base line we simply took a straight line between the bottom of ZPL and the end of the most distant visible vibronic replica. This simplification is obviously the reason of some discrepancy between the experiment and the simulation. In both spectra, no vibronic features can be identified as originating from the lattice phonons. This finding is in stark contrast with the electron-vibrational sideband of the GR1 center, which shows substantial presence of quasilocal vibrations of energy 37 meV and the lattice phonons, both acoustic and optical (Fig. 4c).

The 393.5 nm center has much more developed electron-vibrational band as compared with the GR1 center (Fig. 5a). For comparison, the electron-phonon spectra of neutral NV^0 and negatively charged NV$^-$ centers are shown to reveal the same behavior (Fig. 5b).

Electron-vibrational interaction at the 393.5 nm center does not increase noticeably with temperature (Fig. 6a). Debye-Waller factor (integral intensity of ZPL relative to the total intensity of ZPL and vibrational sideband) of the 393.5 nm center is about 0.004 at RT and 0.005 at LNT. The same behavior is observed for GR1 center (Fig. 6b). Debye-Waller of GR1 center remains at a level of 0.2 at RT and LNT.

4. Discussion

The experimental data of our research confirm the assumption made in [9] that the radiation center with ZPL at 393.5 nm is the ND1 center. From now on we refer to the 393.5 nm center as the ND1 center. Comparing PL and absorption spectra of the ND1 center one can see their close mirror symmetry relative to ZPL (Fig. 4b, Table 2). In both cases the electron-vibrational bands are formed by quasilocal vibrations of energy 76 meV. Practically identical energies of the quasilocal vibrations in PL and absorption suggest that the atom positions and the
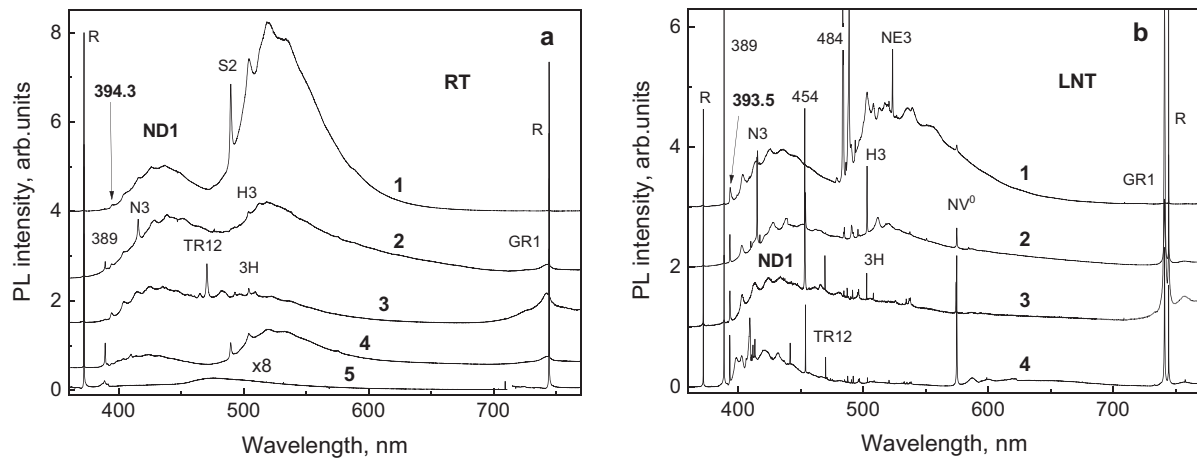
Fig. 1. PL spectra of irradiated diamonds recorded at RT (a) and LNT (b): 1 – Ib yellow, electron irradiation dose 1.1×10^{17} cm^{-2}, 2 – Ia, electron irradiation dose 2.7×10^{17} cm^{-2}, 3 – IIa, Xe ion irradiation dose 6.0×10^{12} cm^{-2}, 4 – Ib colorless, electron irradiation dose 1.1×10^{17} cm^{-2}, 5 – IIb, electron irradiation dose 2.7×10^{17} cm^{-2} (intensity of spectrum is multiplied 8 times for clarity; not shown for LNT). The spectra are adjusted to equal intensity of Raman line (R) and shifted vertically for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
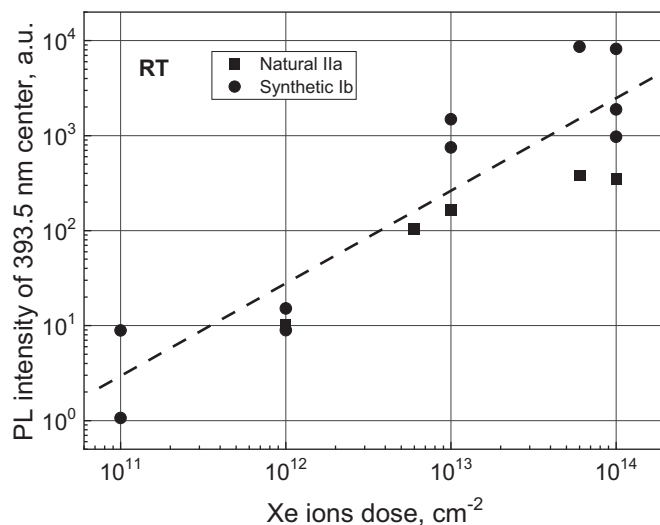

Fig. 2. PL intensity of the 393.5 nm center versus dose measured at RT in Xe-ion irradiated synthetic Ib (circles) and natural (squares) diamonds. Intensities are adjusted to equal intensity of Raman line.

strength of the interatomic bonding in the negatively charged vacancy remain the same in the ground and excited states.

The electron-phonon sidebands of the ND1 center in absorption and PL can be well simulated by superposition of the quasilocal vibronic bands only (Fig. 4b). No features can be identified as the interactions with the acoustic and/or optical lattice phonons. In contrast, the GR1 center reveals considerable interaction with the quasilocal vibrations and with almost the whole phonon spectrum of the diamond lattice (Fig. 4c). It is an observation suggesting that the optically active electronic orbitals of single vacancy in negative charge state are strongly localized within the vacancy core and do not spread over the surrounding lattice atoms. When vacancy is in neutral charge state, its optically active electronic orbitals are more diffuse expanding over the surrounding lattice atoms and thus resulting in substantial coupling with the lattice phonons.

The strength of the electron-vibrational interaction at the ND1 center in luminescence is almost two orders of magnitude stronger than at the GR1 centers: Debye-Waller factors are about 0.004 and 0.2 for these centers respectively (Fig. 5). Both centers reveal minor increase in the

electron-vibrational interaction with temperature. However, the intensity of anti-Stokes luminescence of the GR1 center increases with temperature much stronger as compared with the ND1 center (Fig. 6b). This increase is driven by the enhancement of interaction with the low energy acoustic lattice phonons and by the increase in population of the quasilocal vibrations. Since the energy of the quasilocal vibrations of GR1 center is small (37 meV), its anti-Stokes luminescence is substantial at RT. This feature is seen as a broad hump at a wavelength of 725 nm in room temperature spectrum (Fig. 6b). In case of ND1 center, the interaction with lattice phonons is negligible and the quasilocal vibrations are much more energetic (76 meV). Thus, the anti-Stokes luminescence of ND1 center remains weak even at RT (Fig. 6a). Estimations of the probability of activation of quasilocal vibrations at RT using Bose-Einstein statistics result in 0.32 for 37 meV vibrations and only 0.056 for 76 meV vibrations.

The stark differences in the electron-vibrational interaction of ND1 and GR1 centers are probably common for the centers related to vacancy-containing defects in negative and neutral charge states. An example is NV$^-$ center (negatively charged NV defects) and NV^0 center (neutral NV defects) (Fig. 5b). NV$^-$ center has a stronger electron-vibrational coupling than NV^0 center. Contribution of lattice phonons in the electron vibrational coupling of NV$^-$ center is lesser than for NV^0 center. The energy of the qusilocal vibrations interacting with NV$^-$ defects (64 meV) is greater than the energy of the quasilocal vibrations interacting with NV^0 defects (44 meV). As a result, anti-Stokes luminescence of NV$^-$ center is weaker than that of NV^0 center. Research on the anti-Stokes luminescence of NV centers is in progress and the details will be published elsewhere.

Linear dependence of the ND1 center intensity on the irradiation dose (Fig. 2) and the fact that the center is created directly during irradiation agree with the assignment of the ND1 center to simple primary radiation defects - single vacancies. Response of the intensity of ND1 center to doping is typical for the centers related to negatively charged defects. ND1 center is strong in type Ib diamonds, but undetectably weak in type IIb diamonds.

The fact that the ND1 center is not excited in cathodoluminescence and not readily excited at wavelength 325 nm suggests that the effective excitation of this center occurs in the spectral range of its intrinsic absorption from 340 to 390 nm. In this respect, the excitation of the ND1 center resembles the excitation of the NV$^-$ center: they both are well excited only within the spectral ranges of their intrinsic absorption. In contrast, GR1 and NV^0 centers are excited practically at any wavelength and in cathodoluminescence. Another factor, which may be important
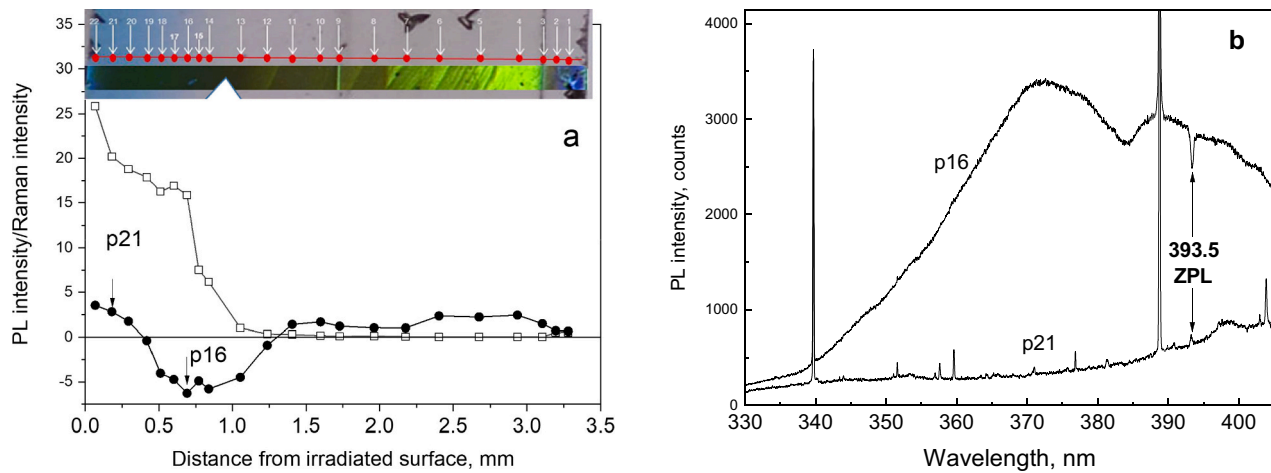
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Fig. 3. (a) Distribution of intensity of GR1 (open squares) and 393.5 nm (full circles) centers over the depth in low-nitrogen CVD diamond irradiated with 1 MeV electrons at a dose of 3×10^{18} cm^{-2}. Intensities are measured relative to the intensity of Raman line. Negative PL intensity means absorption. Intensity of the 393.5 nm center is multiplied 100 times for clarity. The picture on top shows the optical image of the sample and the places (red dots) of PL measurements. The greenish stripe is the fluorescence image obtained with DiamondView microscope. (b) PL spectra taken in points p16 and p21. Intensities of the spectra are adjusted to equal intensity of Raman line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
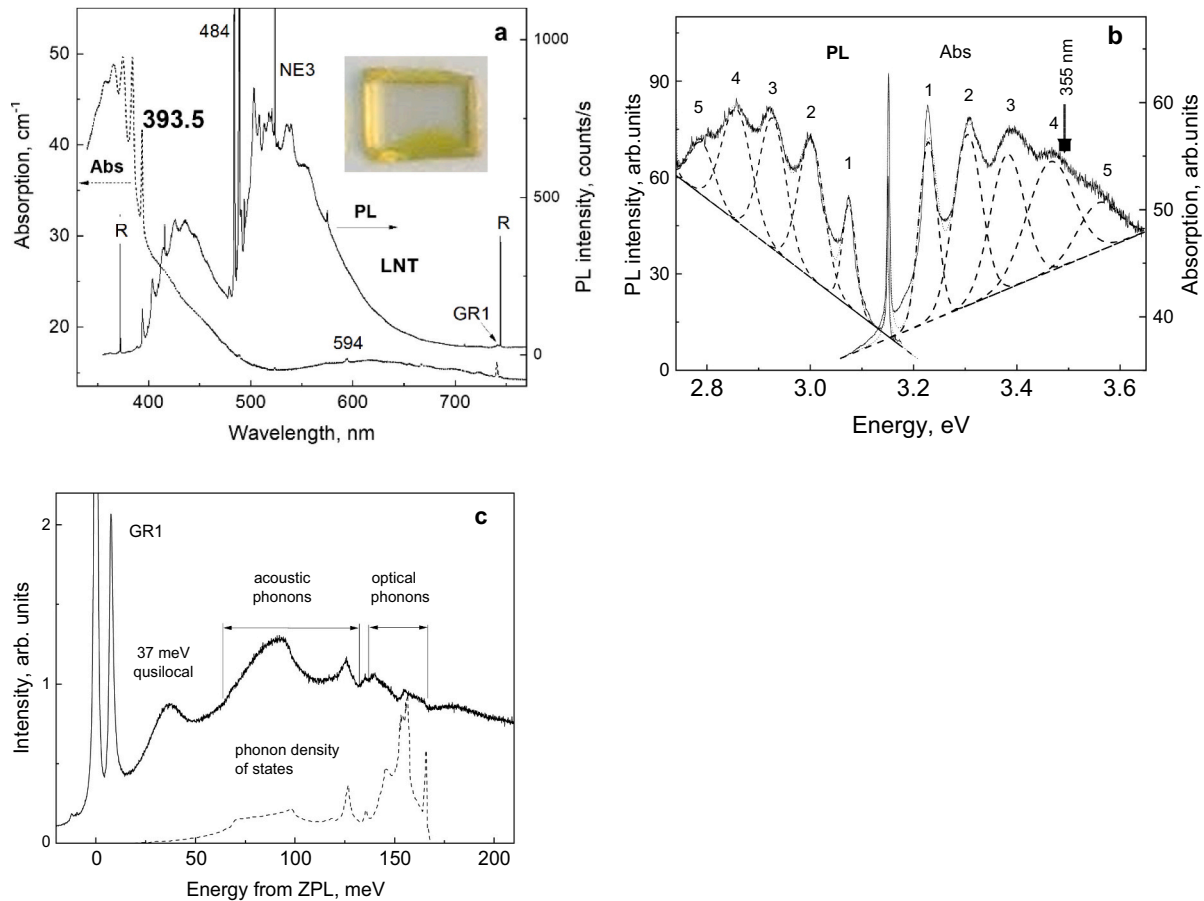

Fig. 4. (a) PL (solid trace) and absorption (dashed trace) spectra taken at LNT from HPHT-grown diamond (shown in insert) irradiated with 6 MeV electrons at a dose of 1.1×10^{17} cm^{-2}. (b) Detailed PL spectrum of the 393.5 center and absorption spectrum of ND1 center measured at LNT: solid traces - experimental spectra; dashed and dotted traces – simulation. (c) Structure of the electron-vibrational band of the GR1 center in PL spectrum of electron-irradiated CVD diamond. The features related to the quasilocal vibration and lattice phonons are labeled. For comparison, the phonon density of states in diamond [6] is shown with dashed line.

for PL excitation of ND1 center, is the excitation density. An attempt to excite ND1 center with UV light of a mercury lamp (wavelength 365 nm) failed [3]. However, we have achieved very efficient excitation with

355 nm laser. These wavelengths are close to each other and they both are well within the absorption range of the ND1 center. We see only one substantial difference between the two excitations – the excitation

Table 2

Electron-phonon structure of 393.5 nm center in PL and ND1 center in absorption spectra measured at LNT.

Replica	PL (393.5 nm)				Absorption (ND1)			
	λ, nm	E, eV	Shift from ZPL, meV	FWHM, meV	λ, nm	E, eV	Shift from ZPL, meV	FWHM, meV
0	393.5	3.151	0	3.45	393.4	3.152	0	3.18
1	403.2	3.075	76	30.7	384.1	3.228	76	41.9
2	413.0	3.002	149	58.0	375.3	3.304	152	64.9
3	423.4	2.928	223	60.3	366.7	3.381	229	77.2
4	433.8	2.858	293	67.4	357.9	3.464	312	105.9
5	444.4	2.790	361	56.2	348.5	3.558	406	92.6
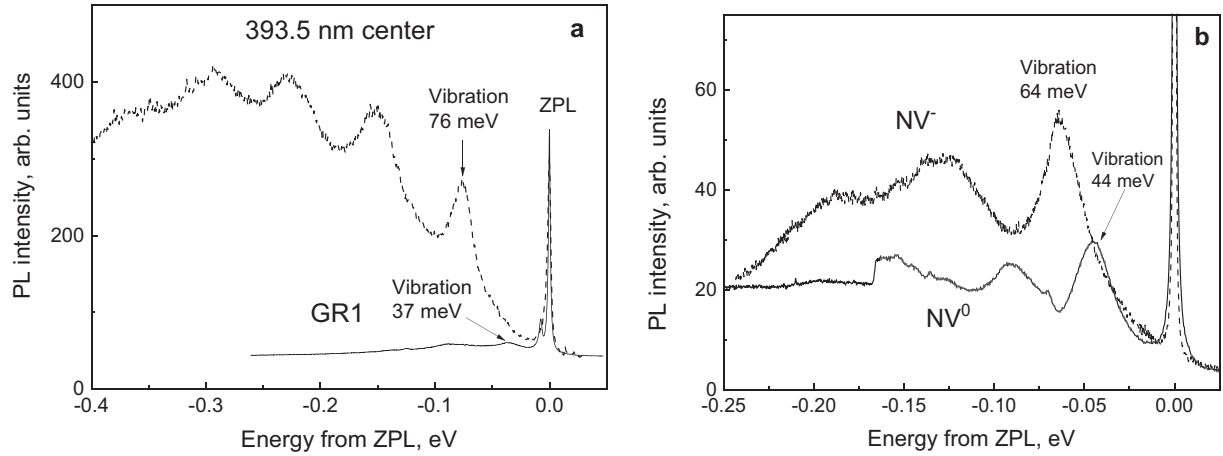
Fig. 5. Comparison of electron-vibrational bands of neutral and negatively charged centers at LNT: (a) GR1 (solid trace) and 393.5 nm (ND1, dashed trace) centers; (b) NV^0 (solid trace) and NV$^-$ (dashed trace) centers. Intensities of spectra are adjusted to equal integral intensity of ZPLs.
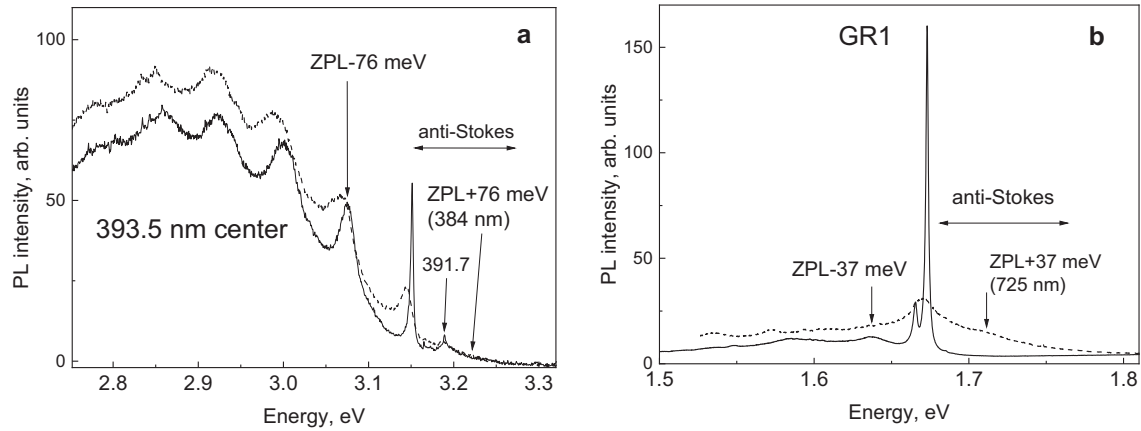
Fig. 6. Electron-vibrational sidebands of 393.5 nm (a) and GR1 (b) centers recorded at RT (dashed traces) and LNT (solid traces). Anti-Stokes replica of the 76 meV quasilocal vibration (ZPL + 76 meV) is expected at a wavelength 384 nm. No feature is seen at this wavelength. A weak band at wavelength 725 nm is the first anti-Stokes replica of the 37 meV quasilocal vibration. Spectra in both graphs are adjusted to equal integrated intensity of ZPLs.

power density. For the laser it is about 10^5 W/cm^2, while for the mercury lamp, we estimate it was not more than 0.1 W/cm^2.

The absorption signal of ND1 center observed in PL spectra (Fig. 3) is not a unique feature. Some other centers may also produce absorption signals in luminescence spectra, or/and luminescence signals in absorption spectra. We have no clear explanation of this effect yet. However, one of the essential conditions for the absorption signal in luminescence spectrum is the strong luminescence background in the spectral range of the center absorption. In case of the ND1 center, it is the spectral range from about 350 nm to 394 nm (Fig. 3b). If the luminescence intensity in this spectral range is low, then the center is detected in the regime of PL only.

5. Conclusion

We confirm that ND1 center with ZPL at 393.5 nm can be effectively excited in PL. Our main argument is a very good mirror symmetry of PL spectrum of the 393.5 nm center and the absorption spectrum of the ND1 center. All other properties of the 393.5 nm center discussed above support this conclusion.

In luminescence ND1 center behaves like a simple primary radiation defect in negative charge state: the center is formed directly by irradiation, its intensity linearly increases with the irradiation dose, its intensity is strong in the presence of nitrogen donors, and the center in not detected in the spectra of boron-doped diamonds.

The ND1 center interacts predominantly with quasilocal vibrations of energy 76 meV. This energy is the same in luminescence and absorption implying that the atomic structure of single vacancy in diamond does not change with electron excitation. The interaction of the ND1 center with the lattice phonons is negligible suggesting that the electronic orbitals of the negatively charged vacancy are well confined within its core.

Our results suggest that PL of ND1 center is effectively excited at wavelengths within the spectral range of its intrinsic absorption from 340 to 390 nm. In PL spectra excited at shorter wavelengths, e.g. at 325 nm, the ND1 center can be detected in the regimes of emission (positive luminescence), or absorption (negative luminescence), or both emission and absorption simultaneously. The absorption signal can be especially pronounced in the spectra with substantial luminescence background in the range from 340 to 395 nm.

We attract attention of the reader to the stark differences in the electron-vibrational coupling of ND1 and GR1 centers in luminescence and assume that these differences could be common for other centers related to vacancy-containing defects in neutral and negatively charged states. The negatively charged defects tend to have strong electron-vibrational interaction with quasilocal vibrations and weak interaction with lattice phonons, while the neutral defects reveal comparable contributions from the interactions with quasilocal vibrations and lattice phonons. The energy of the quasilocal vibrations of negatively charged defects is greater than the energy of quasilocal vibrations of neutral defects.

Finding the way of the effective excitation of ND1 center in photoluminescence substantially expands the capabilities of the luminescence techniques in the research of irradiated diamonds and in the studies of the defects in different charge states.

CRediT authorship contribution statement

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N. M. Kazuchits – measurements, writing manuscript.

V. N. Kazuchits – preparation of samples, measurements.

M. S. Rusetsky - measurements.

A. V. Mazanik - measurements.

V. A. Skuratov – preparation of samples, measurements.

K. S. Moe - measurements.

A. M. Zaitsev – writing manuscript.

Declaration of competing interest

Authors of the mentioned above manuscript declare no conflict of interests.

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