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Excitonic absorption and emission in diamond near the edge of fundamental absorption

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ABSTRACT

The study of optical absorption of CVD diamond near the fundamental absorption edge was performed in the temperature range of 87-296 K. At temperatures lower than 195 K the absorption was practically constant. At higher temperatures the sharp increase of absorption took place. This sharp increase was attributed to the sharp enrichment of the phonon spectrum. Same phonon modes have different contributions to the negative and the positive branches of free-exciton absorption. For the negative branch (phonon absorption) the TA-mode dominated. For the positive branch (phonon emission) the TO-mode dominated. The possibility of diamond-based cathodoluminescent UV-sources at 235 nm was demonstrated.

Keywords: diamond, absorption, exciton, cathodoluminescence, UV-source, fundamental edge, band gap, phonon

1. INTRODUCTION

Diamond is a one-component semiconductor with an indirect band gap $E_g \sim 5.49$ eV [1]. The binding energy of a free exciton (FE) in diamond is 80.5 meV [2]. At room temperature, the FE binding energy is twice larger the thermal energy of the diamond lattice vibrations $E_x/2 \sim 3/2 k_B T$, i.e. under normal conditions, nonequilibrium electron-hole pairs (EHP) form FEs that are not thermally ionized. FEs in diamond can exist up to temperatures of ~ 350 °C.

In the spectra of optical absorption and luminescence, FEs show the continua of absorption and bands of recombination radiation at photon energies

$$h\nu_{h\nu} = E_g - E_x \pm h\omega, \quad (1)$$

where E_g is the band gap, $h\omega$ is the energy of the phonon emitted (+) or absorbed (-) during the absorption or emission of the photon, $h\nu_{h\nu}$ is the cutoff energy for the absorption continuum or the maximum energy for the recombination radiation band, respectively. In these processes in diamond the phonons of TO-, TA-, LO- and LA-modes take part with energies of 141, 87, 163 and 127 meV, respectively. Besides, two- and three-phonon components can be observed with the participation of additional optical phonons (O^Γ) with an energy of 156-160 meV [3, 4].

When describing optical transitions in a diamond near the fundamental absorption edge, in addition to the contribution of different phonon modes it is necessary to take into account the fine splitting of the FE state.

Initially, excitonic states were observed in natural diamonds of IIa and IIb types, which demonstrated the fundamental absorption edge at 225-226 nm. In [5], the energy values of the TO-, TA-, LA-, and O^Γ -phonons were determined from the optical absorption (OA) spectra of natural diamonds at different temperatures. In cathodoluminescence (CL) spectra of natural diamonds the FE radiative recombination was three orders of magnitude less intense than the impurity-defective luminescence in the visible range [6, 7]. The FE recombination radiation was observed in the form of bands associating with phonons of TA- (~ 5.325 eV) and TO- (~ 5.27 eV) modes. The TO-mode was split into two components at 5.268 and 5.276 eV.

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In [8] the exciton state splitting in 4 levels (EX1-EX4) of bound excitons (BEs) on boron atoms was observed in the high resolution CL spectra of high-pressure high-temperature (HPHT) diamond of IIb type at 100 K. In [9], the boron BE splitting into 4 levels was observed for HPHT diamonds with different content of the ^{13}C isotope. In [10], the FE radiative recombination was observed in CL spectra of a single crystal chemical-vapor-deposited (CVD) diamond. At 80 K it was sufficient to take into account 2 levels of FE (EX3 and EX4) to simulate the FE band shape, which included the TO- and LO-phonon modes of the emission. In [11], a splitting of the FE state into four levels in the PL spectra of HPHT diamond was observed. To explain the fine splitting, the joint action of the electron-hole exchange and spin-orbit interactions was assumed. In [12], to analyze the PL spectrum of HPHT diamond at temperature of 1.8 K, it was necessary to take into account the only first two of FE states (EX1 and EX2), since higher states could not be populated thermally. In [13], the EX1-EX4 states of TA-mode were observed in OA spectra of the CVD diamond. The PL spectra of the same sample contained the FE radiative recombination of phonon TO-, LA-, and LO-modes. Each of the modes was split into 4 levels, separated from the EX1 energy level by 3.6, 6.7 and 13.6 meV, respectively. Analysis showed the joint action of the spin-orbital and the exchange interactions, as well as mass anisotropy of holes (light/heavy holes).

The theory suggests the possibility of existence of a bigger number of FE levels than EX1-EX4 [13]. Perhaps some of these transitions are forbidden in radiative transitions, but in absorption this forbiddance can be partially removed. Thus, the study of FE states in diamond is an actual fundamental task.

From a practical point of view, the FE radiative recombination in diamond is of interest as the basis of optoelectronic devices emitting in the UV-C spectral region. A number of papers reported the creation of p-n and p-i-n transitions and their electroluminescence in the diamond FE band [14-16]. However, the efficiency of such devices is still low. In part, this is due to the insufficient quality of the diamond layers [15].

In general, low efficiency of LEDs of the UV-C range is typical for devices, based on other materials. For example, LEDs based on GaN are also far from perfect [17]. For this reason, the search for other principles for the creation of UV-C emitting optoelectronic devices is in progress. Recently it was reported on the cathodoluminescent UV-source based on the lithium tetraborate luminophore doped with copper and silver [18]. The use of diamond as a luminophore can have prospects for creating a LED alternative – diamond cathodoluminescent UV-sources.

In this paper, we report on the study of OA spectra of diamond in the temperature range of 87-296 K. Preliminary results on the use of diamond as a luminophore in a cathodoluminescent UV-source with a wavelength of 235 nm are reported.

2. EXPERIMENTAL

The OA spectra of high quality CVD diamond sample (#C10) were studied at different temperatures. The sample dimensions were $5 \times 5 \times 0.25 \text{ mm}^2$. The setup for the optical transmission spectra measurements is shown in Fig. 1.

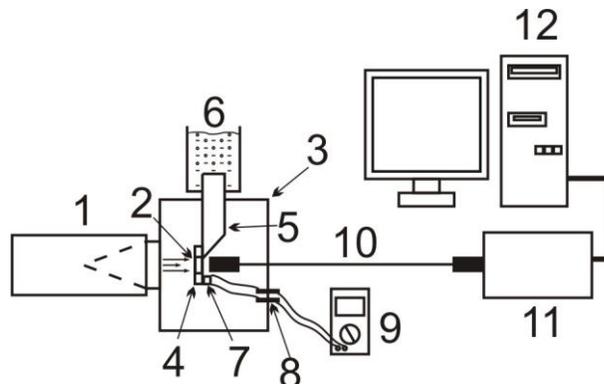


Figure 1. The setup for the optical transmission spectra measurements. 1 - light source, 2 - diamond sample, 3 - vacuum chamber, 4 - copper sample holder, 5 - hollow copper heat sink, 6 - jar with liquid nitrogen, 7 - thermistor, 8 - vacuum-tight electric bushings, 9 - ohmmeter, 10 - optical fiber, 11 - spectrometer, 12 - PC.

The combined light source SL5 (deuterium and halogen lamps, Stellar-Net Inc.) 1 emitted the continuous spectrum in the range of 200-850 nm. The diamond sample 2 was placed in the sealed chamber 3. The chamber 3 was evacuated by a 2NVR-5DM forepump. Sample 2 was mounted with the copper holder 4 on the hollow copper heat sink 5. The heat sink 5 went out with the heat/vacuum seal into the jar 6 with liquid nitrogen. The thermistor 7 (Pt1000, Heraeus) was

mounted on the copper holder 4. Its resistance was measured through vacuum-tight bushings 8 by the digital ohmmeter 9. The light passed through sample 2, undergoing absorption and reflection on the sample faces. Then, the light from the source fell into the spectrometer 11 (HR 2000, Ocean Optics) through the optical fiber 10. After the signal was accumulated, the measured spectrum was captured by the personal computer 12. Before measurements, the emission spectrum of the source 1 was measured without mounting of sample 2 in the holder 4. The light source spectrum measured this way was used as the reference spectrum. The thermal contact between sample 2, holder 4, heat sink 5 and thermistor 7 was provided by KPT-8 thermal paste. The temperature of sample 2 was assumed equal to the temperature of thermistor 7 and was calculated from the temperature dependence of its resistance. In the temperature range of the measurements, the resistance of the thermistor 7 varied in the range 252-1088 Ohm, which corresponded to a temperature of 87-296 K.

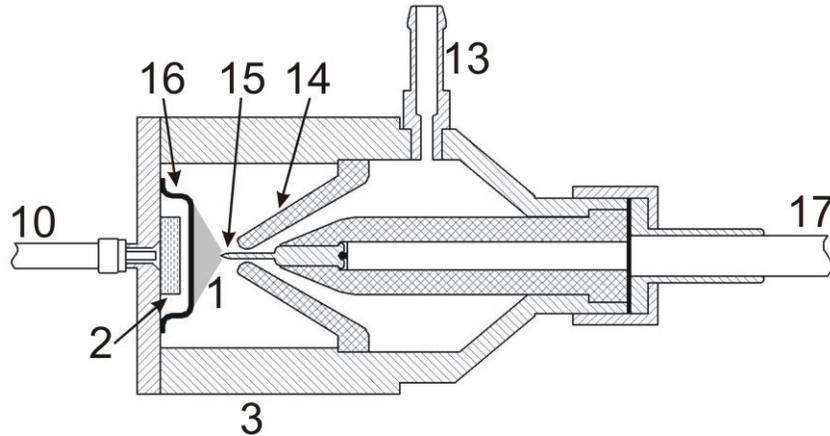


Figure 2. The prototype of diamond-based cathodoluminescent UV-source. 1 - electron beam, 2 - diamond sample, 3 - vacuum chamber, 10 - optical fiber, 13 - pump-out pipe, 14 - insulator, 15 - cathode, 16 - mesh anode, 17 - high voltage input.

The prototype of the diamond cathodoluminescent UV-source is shown in Fig. 2. The runaway electron beam of 100-ps duration was generated in the volume discharge 1 [19]. The electron beam, incident on the diamond sample 2 (#C12), excited the CL in it. Sample 2 was hermetically mounted on the flange of the mini-camera 3. The CL emission after passing the sample 2 entered the optical fiber 10 and further into the spectrometer 11 (similarly Fig. 1a). The mini-chamber 3 of stainless steel was pumped through the pipe 13 and filled with nitrogen or argon at a pressure of up to 60 Torr. The chamber 3 was divided into two compartments by an insulator 14 (polyamide), which had a special shape for matching the wave impedance and ensured the uniform gas discharge (in other experiments). A volume discharge occurred between the needle/tube cathode 15 and the mesh (optical transmission of 64%) anode 16, which was mounted with spot welding. Voltage pulses with an amplitude of 10 kV, a duration of 12 ns, and a repetition rate of 100 Hz were applied to the cathode 15 through the high voltage input 17 from the pulse voltage generator NPG-18/3500N. The pulse voltage formed the volume discharge 1. At the ionization wave front, the electron beam (in the cathode-anode direction) with duration of 100-ps at half-maximum was generated with a peak current density of $\sim 1 \text{ A/cm}^2$. Passing through the mesh anode 16, the electron beam excited the CL in the diamond sample 2. After the optical signal was accumulated in the spectrometer 11, the CL spectrum was captured by the personal computer 12. Further, the spectral sensitivity of the spectrometer and the transmission of the optical fiber were taken into account by software processing. The measurements were carried out at room temperature. In general, the measurement procedure was similar to [20, 21].

3. EXCITONIC ABSORPTION IN DIAMOND

Figure 3 shows the transmission spectra of a diamond sample #C10 at various temperatures. As the temperature decreases from room temperature to 195 K, the transmission spectrum changes drastically: in the spectral range 223-237 nm, the transmission of a diamond grows rapidly (irregularly in this spectral range). With a further temperature decrease below 195 K, the transmission spectrum remains practically unchanged. In addition to the spectra of the diamond sample #C10, Fig. 3 shows the theoretical spectrum of non-absorbing diamond.

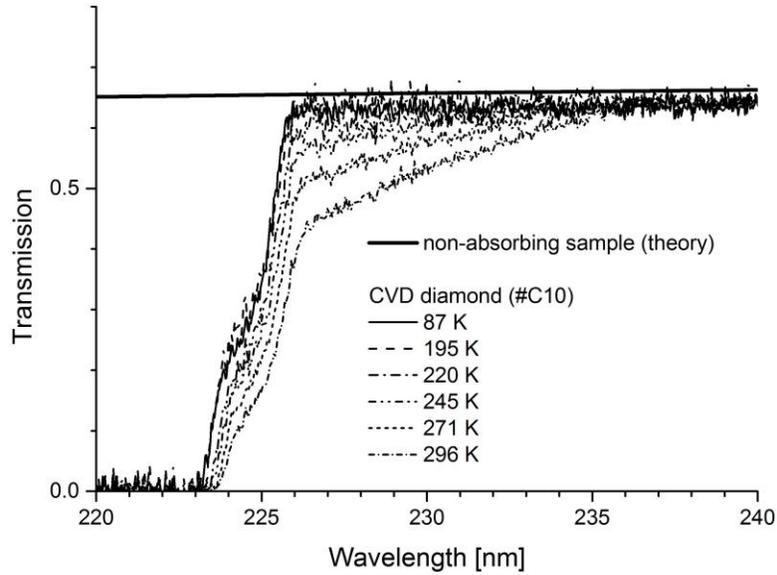


Figure 3. Transmission spectra of the theoretical non-absorbing diamond and the CVD diamond sample #C10 at different temperatures.

At zero absorption ($\alpha(\lambda) \equiv 0$), the transmission of the diamond is by the formula:

$$T(\lambda) = \frac{(1 - r(\lambda))^2}{1 - r(\lambda)^2}, \quad (2)$$

where $r(\lambda)$ is the reflection coefficient of the diamond, which in the case of Fresnel reflection is written as

$$r(\lambda) = \frac{(1 - n(\lambda))^2}{(1 + n(\lambda))^2}, \quad (3)$$

here $n(\lambda)$ is the refractive index of a diamond, which is described in the optical range by the empirical formula [22]:

$$n(\lambda) = \sqrt{\frac{\lambda^2}{0.21413 \cdot \lambda^2 - 0.002678} + 1}. \quad (4)$$

The theoretical spectrum in Fig. 3 shows the maximum possible transmission for a diamond.

To calculate the OA spectra, we used the quadratic equation solution for the transmission of a plane-parallel sample with taking into account for multiple Fresnel reflections from both faces:

$$T(\lambda) = \frac{(1 - r(\lambda))^2 \cdot e^{-\alpha(\lambda)d}}{(1 - r(\lambda)^2) \cdot e^{-2\alpha(\lambda)d}}, \quad (5)$$

where d [cm^{-1}] is the thickness of plane-parallel sample.

Figure 4 shows the OA spectra of sample #C10 at various temperatures, calculated from formula (5) using the experimental transmission spectra from Fig. 3. The photon energy interval was 5.2-5.551 eV. At lower photon energies, the spectra did not practically change with temperature. At higher energies, because the transmission was too small, the calculated absorption index exhibited significant oscillations.

It is seen from Fig. 3 and Fig. 4 that in the photon energy range of 5.24-5.49 eV (236.6-225.8 nm) at 87-195 K, the absorption (transmission) index practically does not change. With an increase in temperature from 195 K to 296 K, a significant increase in the absorption in this spectral region occurs. The cutoff energies of FE absorption continua of the negative branch ("−" in formula (1), phonon absorption) are located in the photon energy range of 5.242-5.49 eV. The cutoff energies of FE absorption continua of the positive branch ("+" in formula (1), phonon emission) are located in the range of 5.49-5.581 eV.

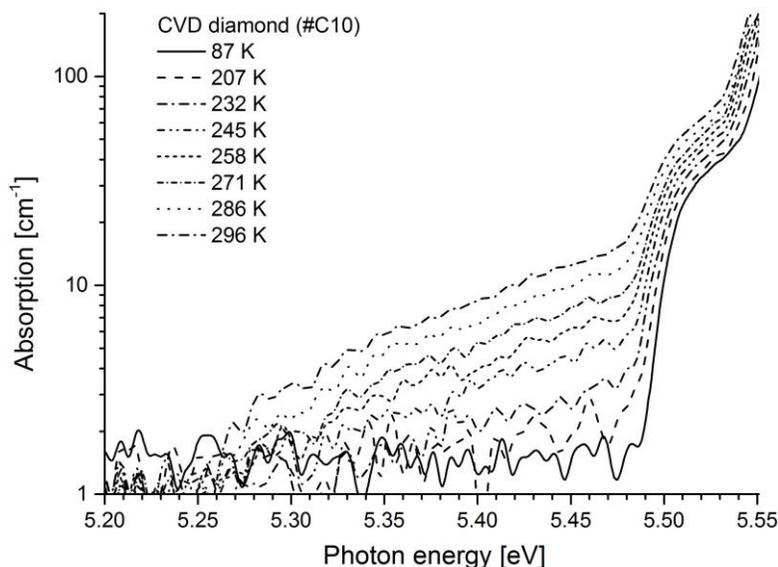


Figure 4. The optical absorption spectra of the CVD diamond sample #C10 at different temperatures, calculated from Fig. 3 using formula (5).

Table 1 shows the cutoff energies of the absorption continua for four FE transitions (EX1-EX4) of the negative and positive branches of the phonon modes ("-"LO, "-"TO, "-"LA, "-"TA, "+"TA, "+"LA, "+"TO, "+"LO) calculated from the data of [13].

As it was said above, when the diamond sample is cooled from room temperature to ~ 195 K, the absorption decreases for the FE negative absorption branch. With further cooling by liquid nitrogen, the value of the absorption coefficient in the photon energy range of 5.24-5.49 eV remains practically unchanged. Since in this spectral region there is absorption to the FE state of negative branch only, we can conclude that at temperatures above 190-200 K the phonon spectrum in the diamond is sharply enriched.

Table 1. The cutoff energy [meV] of interband optical absorption into the FE state, which undergoes a fine splitting, for the positive and negative branches of phonon "±"TA-, "±"LA-, "±"TO-, "±"LO-modes.

The negative branch of FE absorption							
"-"LO1	"-"LO2	"-"LO3	"-"LO4	"-"TO1	"-"TO2	"-"TO3	"-"TO4
5.2424	5.2451	5.2488	5.2541	5.262	5.2656	5.2687	5.2756
"-"LA1	"-"LA2	"-"LA3	"-"LA4	"-"TA1	"-"TA2	"-"TA3	"-"TA4
5.2759	5.2795	5.2821	5.2894	5.3177	5.3208	5.3237	5.3311
The positive branch of FE absorption							
"+"TA1	"+"TA2	"+"TA3	"+"TA4	"+"LA1	"+"LA2	"+"LA3	"+"LA4
5.4917	5.4948	5.4977	5.5051	5.5299	5.5335	5.5361	5.5434
"+"TO1	"+"TO2	"+"TO3	"+"TO4	"+"LO1	"+"LO2	"+"LO3	"+"LO4
5.544	5.5476	5.5507	5.5576	5.5684	5.5711	5.5748	5.5801

Figure 5 a-d shows the temperature dependences of the absorption coefficient at cutoff energies of the FE negative absorption branch for the phonon LO- (a), TO- (b), LA- (c), and TA- (d) modes. In the temperature range of 87-182 K, the absorption coefficient varies only slightly for all phonon modes at an average absorption level of 1.3-1.8 cm⁻¹. For the LO-mode (Fig. 5a) at the temperature of 86 K, the absorption coefficient for the exciton levels increases from levels with lower energy to levels with a higher one (LO1 < LO2 < LO3 < LO4). With increasing temperature, the dependences for these mode change monotonically in such a way that at the temperature of 182 K, the values of corresponding absorption coefficients practically converge to 1.4-1.5 cm⁻¹. For the TO- and LA-modes (Fig. 5 b and c, respectively), the absorption values for each transition to FE states exhibit the maximum at 150 K. For the TA-mode, this maximum is

shifted to 160 K. For all phonon modes (LO, TO, LA, and TA) and FE state levels (EX1-EX4), the absorption coefficient minima take place at temperatures of 195 and 232 K. At temperatures above 195 K, the general tendency for the LO-mode is a slight decrease in the absorption coefficient (1.2 times in the interval temperatures of 207-296 K). For the TO-, LA-, and TA-modes, an increase in the absorption index is taken place (in 1.7, 2 and 3 times, respectively). In this case, the contribution of each FE levels to the increase in the absorption coefficient was minimal for the LO-mode and maximal for the TA-mode. In general, for the FE absorption of negative branch, the following tendency of increment of the absorption index for each FE levels was observed: LO<TO<LA<TA.

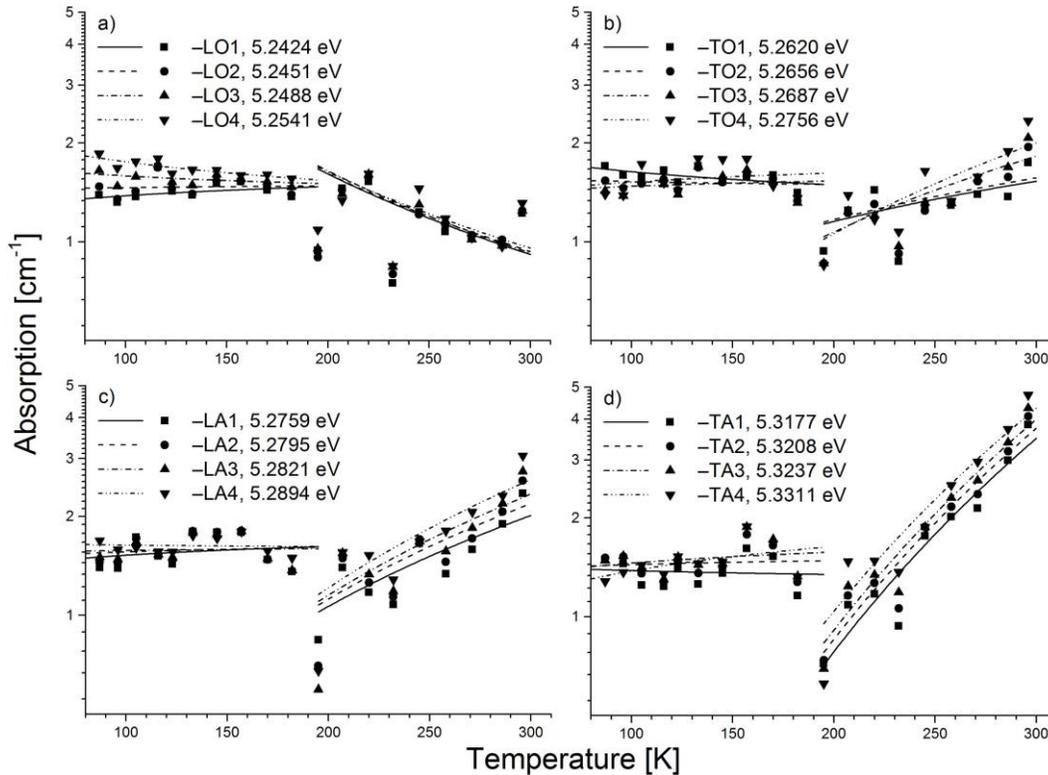


Figure 5. The temperature dependences of the absorption coefficient at cutoff energies of the FE negative absorption branch for the phonon LO- (a), TO- (b), LA- (c), and TA- (d) modes.

Figure 6 a-c shows the temperature dependences of the absorption coefficient at cutoff energies of the FE positive absorption branch for the phonon TA- (a), LA- (b), and TO- (c) modes. The dependencies for the LO-mode and for the transition to the fourth exciton state (EX4) for the TO-mode (TO4) have not been shown, since for them, the cutoff energies are located at photon energies above 5.555 eV. At such photon energies, the absorption coefficient takes values above 200 cm⁻¹, which for the C10 sample, according to formula (5), gives the transmission $T < 0.5\%$. Such transmission values could not be measured correctly under our conditions. Calculation of the absorption coefficient from formula (5) for a range above 5.551 eV produced chaotic oscillations (from 200 to 400 cm⁻¹).

As it can be seen from Fig. 6 a-c for the FE positive absorption branch in the temperature range of 86-182 K, the absorption coefficient also slightly changed for the TA-, LA-, and TO-modes. Starting from temperature of 195 K, the dependencies increased more rapidly. The monotonic increase in the absorption was observed for all phonon modes and for each levels of the FE state. For the TA-, LA-, and TO-modes, the increase in the absorption coefficient in the temperature range of 207-296 K was 2-4, 2, and 1.7-2 times, respectively. The contribution of each FE levels to an increasing in the absorption coefficient was minimal for the TA-mode and is maximal for the TO-mode. Those, for the FE positive branch of absorption, the intensity of the phonon interaction had same tendency as for the recombination radiation of free excitons: the TO-mode is dominating, then the LA- and TA-modes are in decreasing order.

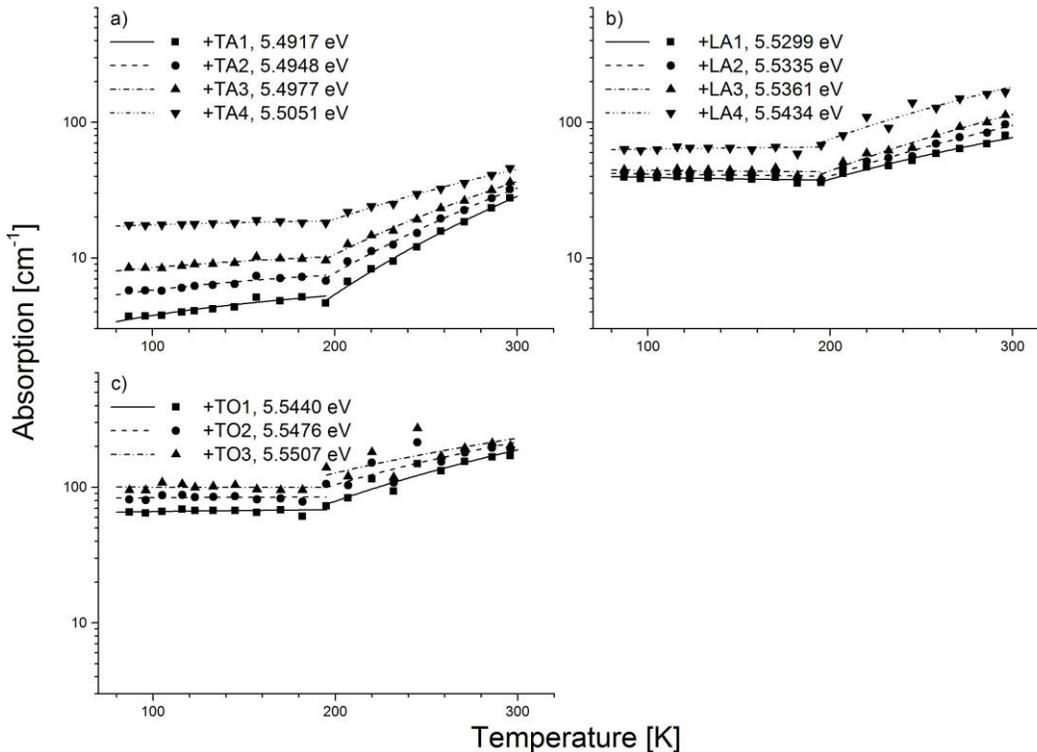


Figure 6. The temperature dependences of the absorption coefficient at cutoff energies of the FE positive absorption branch for the phonon TA- (a), LA- (b), and TO- (c) modes.

Thus, the OA spectra of diamond near the edge of fundamental absorption contain the information about the structure of FE fine-splitting levels. The study of the OA spectra of 0.25-mm thickness diamond sample as function of temperature revealed the sharp enrichment of the phonon spectrum at temperatures of 190-200 K, the different contribution of phonon modes to the negative and positive branches of the OA (dominance of the TA- and TO-modes, respectively). A study of thinner samples will allow us to establish temperature dependences for the positive branch of the LO-mode. The study of thicker samples will allow us to verify the conclusions for the FE negative branch of absorption and, possibly, to reveal the cutoff energies of additional fine-splitting levels that are forbidden in radiative transitions.

4. EXCITONIC EMISSION IN DIAMOND

As it was said in the introduction, because of the difficulties of creating diamond-based LEDs (p-n or p-i-n diodes), diamond cathodoluminescent UV-sources could become an alternative version of light emitting devices in UV-C region (at 235 nm). Recently, attempts are being made to create cathodoluminescent UV-sources based on lithium tetraborate [18]. At the same time, the development of CVD diamond synthesis technologies makes it possible to obtain inexpensive samples of a few square millimeters of high quality. In [23] it was reported about the achieved diamond PL efficiency of 13% in the band of FE radiative recombination. The use of diamond as a luminophore in the CL-UV-sources will allow to ensure long-term operation of such sources without cooling thanks to the high radiation resistance, the highest thermal conductivity and the high FE binding energy. Accumulation of radiation defects can be monitored by absorption at a neutral vacancy (vibronic system GR1 with a zero-phonon line at 741 nm). The low-temperature annealing in a vacuum will allow the diamond luminophore to be restored by annealing/recombining vacancies and interstitial atoms.

To excite the CL in diamond, it is sufficient to use a technical vacuum and a standard cathode-mesh anode circuit. As cold cathode, it is also possible to use the hydrogen-terminated diamond layer. Such cathode will be characterized by a negative electron affinity.

Figure 2 shows the simplest prototype of diamond cathodoluminescent UV-source emitting at wavelength of 235 nm. Figure 7 shows the CL and PL spectra of C12 diamond sample at room temperature, obtained by using it as the luminophore in the prototype in Fig. 1b (CL) and by exposing it to pulsed laser radiation at 222 nm with FWHM

duration of 8 ns (PL) [21]. It can be seen that in the spectra, the TO-mode dominates at 235 nm. The two-phonon component at 240 nm is also observed. We can note the poor signal-to-noise ratio in Fig.7 because the CL intensity was weak. It is required to optimize the configuration of the electrodes and the CL excitation system. The PL spectrum is given for comparison.

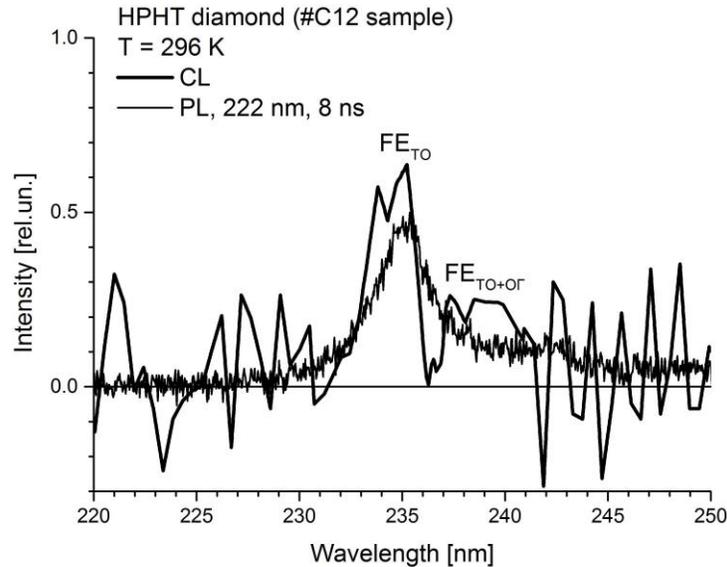


Figure 7. Emission spectra of HPHT diamond sample #C12 in CL measurements of diamond-based CL-UV-source prototype (#C12 as luminophore) and laser-induced PL measurements [21].

5. CONCLUSION

The optical absorption of CVD diamond sample at the fundamental absorption edge is investigated in the temperature range of 87-296 K. The sharp increase in absorption with the increase in temperature above 195 K is shown, which is attributed to the sharp enrichment of the phonon spectrum and, as a consequence, to the increase of absorption into the free exciton negative branch. Different contributions of phonon modes for the negative and positive FE absorption branches is shown. Thus, for the negative branch the transitions with phonon absorption of the TA-mode dominated. For the positive branch the transitions with phonon emission of the TO-mode dominated. The possibility of using the HPHT diamond as the luminophore in cathodoluminescent UV-sources emitting at a wavelength of 235 nm is demonstrated.

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