Excitonic states in diamond in the spectra of optical absorption and luminescence

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Abstract. The optical absorption and photoluminescence spectra of two synthetic diamonds in the temperature range of 80-300 K were measured. It is established that the free exciton state in a diamond is split by at least 12 sublevels. The "negative" branch of interband transitions makes the main contribution to the temperature dependence of the optical absorption spectrum near the fundamental edge. For the "negative" branch of interband transitions with the transverse optical (TO) phonon absorption, the transition probability falls from $9 \times 10^8$ to $1.8 \times 10^5$ cm$^{-1}$ eV$^{-1}$ with an increase in temperature from 83 to 202 K. With temperature increase up to 294 K, the value of transition probability shows practically no changes. For the "positive" branch, the probability of interband transitions with the generation of TO phonons in diamond is $2 \times 10^8$ cm$^{-1}$ eV$^{-1}$ in the temperature range 83-227 K. As the temperature rises from 227 to 294 K, the probability of these transitions increases to $2 \times 10^9$ cm$^{-1}$ eV$^{-1}$. The fine splitting of the free exciton state leads to an additional broadening of the radiative recombination bands of free excitons in diamond.

1. Introduction

Generation of runaway electron beams negatively affects the efficiency of controlled thermonuclear reaction in devices of the TOKAMAK type [1-3]. To register runaway electrons, various detectors are created, including ones on the basis of diamond because of their high radiation resistance and the transparency window up to the vacuum ultraviolet range. These detectors are known as "Cherenkov detectors" and usually consist of a diamond crystal, a lightfiber and a photoelectric multiplier (PMT). It is believed that such detectors measure Vavilov-Cherenkov radiation (VCR), but the spectral characteristics of radiation in known works are not given [4, 5]. On the other hand, it is well known that when the diamond samples are excited by electron beams with electron energies of tens to hundreds of keV, pulsed cathodoluminescence (CL) is detected [6, 7]. Including CL was recorded when excitation by beams of runaway electrons obtained in gas diodes [8, 9].

For diamond, the electron energy threshold for excitation of the VCR is ~50 keV. VCR in diamond shows exponential growth for wavelengths less than 300 nm [10]. Low-nitrogen diamonds synthesized by the methods of chemical vapor deposition (CVD) and high-pressure high-temperature growth (HPHT) show the fundamental absorption edge at 225 nm (5.49 eV). Radiative recombination of free excitons (FEs) in diamond is observed in the region of 232-242 nm, which should be taken into account when registering VCR. Because of the high binding energy ~80 meV, the FEs in diamond is stable up to temperatures of ~350°C. In recent studies it was shown [11, 12] that the FE state
undergoes a fine splitting. Using measurements of the optical absorption (OA) and photoluminescence (PL) spectra in the region of the fundamental edge, it was established that the FE state is split into at least 4 sublevels.

In this paper, we present the results of approximating the fundamental absorption edge in diamond. It is shown that 4 sublevels of the FE state are insufficient for an adequate approximation of the absorption edge. It is necessary to take into account both "positive" and "negative" branches of transitions. It is suggested that the fine splitting of the FE state causes the appearance of at least 12 sublevels, and its effect on the envelope, width, and spectral position of the FE radiative recombination bands. The temperature dependence of the OA spectrum of the "negative" and "positive" branches of the interband transitions is investigated. The spectra of the edge PL are described.

2. Experimental methods, absorption spectrum approximation and diamond samples

To measure the OA spectra, the we used the combined light source SL5 (deuterium and halogen lamps, Stellar-Net Inc.) with spectrum in the range of 200-850 nm. Light passed through the sample, via the light fiber and was received in the spectrometer HR4000 (Ocean Optics). Before starting the measurements of the optical transmission spectra, the reference spectrum of the light source emission was measured. The OA spectra were found by the method described in [13].

To excite PL in the samples, we used a KrCl-laser "Photon-2" [9]. The laser provided UV radiation at 222.2 nm (5.58 eV) of duration 18 ns at FWHM with a peak intensity up to 13 MW/cm². The diamond sample was placed in the evacuated chamber and was fixed by a copper holder on the hollow copper heat sink, which was cooled down with liquid nitrogen. A thermistor Pt1000 (Heraeus) was attached to the copper holder. Luminescence passed through the sample and the optical fiber is fed to the spectrometer. The spectral sensitivity of the spectrometer and the transmission of the light guide were taken into account by software processing.

The optical characteristics of two synthetic diamond samples C10 and C12 were studied. The single crystal C10 (5×5×0.25 mm³) was synthesized by the CVD method and nominally did not contain impurities. The single crystal C12 (5×5×0.25 mm³) was synthesized by the HPHT method from a nickel-containing charge with a nitrogen getter. The samples demonstrated the fundamental absorption edge at ~225.8 nm (~5.49 eV) and the absence of the OA bands or lines of impurities or defects.

Approximation of diamond OA spectra $\alpha(h\nu) [\text{cm}^{-1}]$ in vicinity of fundamental edge made according to the expression for edge absorption in indirect semiconductors [14]:

$$\alpha = \sum_{p} \left( n_{y} + 0.5 \pm 0.5 \left[ \sum_{i} A_{p,i} \left( h\nu - \left( E_{g} - E_{x,i} \pm h\omega_{p} \right) \right) \right]^{1/2} + B_{p} \left( h\nu - \left( E_{g} \pm h\omega_{p} \right) \right)^{2} \right),$$

where

$$n_{y} = \left( e^{h\omega_{p}/k_{B}T} - 1 \right)^{-1}$$

– Bose-Einstein distribution of phonons in energy; "-" in the symbol "±" means "negative" branch of absorption, i.e. absorption of a photon with phonon absorption; "+" in the symbol "±" means "positive" branch of absorption, i.e. absorption of a photon with phonon generation; $p$ – phonon modes (TA, LA, TO, LO); $i$ – sublevels of the FE split state; $A_{p,i}$ are the elements of the transition matrix to the $i$-th sublevel of the split FE state for different phonon modes $p$; $B_{p}$ are the elements of the interband transition matrix for different phonon modes $p$; $E_{g}$ is the indirect band gap in diamond; $E_{x,i}$ is the binding energy for the $i$-th sublevel of the FE state; $h\omega_{p}$ is the phonon energy of the $p$-th phonon mode; $k_{B}$ is the Boltzmann constant; $T$ is the temperature. The following constants were taken: $E_{g}=5.49 \text{ eV}$, $h\omega_{TA}=87 \text{ meV}$, $h\omega_{LA}=123 \text{ meV}$, $h\omega_{TO}=141 \text{ meV}$, $h\omega_{LO}=157 \text{ meV}$, $h\omega_{\Gamma}=165 \text{ meV}$ (for
two-phonon processes). Elements of the transition matrices $A_{p,i}$ and $B_p$ acted as variable parameters. The determination of the binding energies of the FE states is given in the next paragraph.

3. Results and discussion

In [11, 12], a fine splitting of the FE state in diamond into four sublevels was reported due to the spin-orbit and exchange interactions, and the anisotropy of charge carriers effective mass. It was noted that up to 12 sublevels can exist, of which only 4 are optically bright. According to the difference ($E_{g} - E_{x_i}$) for the 4 sublevels given in [11], the binding energy of the FE states indicated in table 1.

| Sublevel sign | Sublevel binding energy (meV) |
|---------------|-------------------------------|
| Ex1           | 85.3                          |
| Ex2           | 82.2                          |
| Ex3           | 79.3                          |
| Ex4           | 71.9                          |

Table 1. Notation and binding energy for sublevels of the split state of free excitons in diamond on the basis of data from [11].

Figure 1a shows an example of the approximation of the absorption spectrum of sample C12 at a temperature of 294 K using formulas (1) and (2) for binding energy of sublevels from table 1. Here, figure 1a shows the averaged curve of the OA spectrum of the sample C12 and the measured absorption coefficient (black circle) at the wavelength of 222.2 nm (5.5799 eV) [13]. Note that no values of the variable parameters $A_{p,i}$ and $B_p$ make it possible to achieve the complete correspondence between the measured and the calculated OA spectra by the formulas (1) and (2) using the data from table 1. In the spectral regions 5.250-5.290 eV, 5.320 eV, 5.360-5.450 eV, 5.475-5.495 eV, and 5.535-5.550 eV, there are significant deviations in the measured and calculated OA spectra.

Figure 1. The measured and calculated optical absorption spectra of the C12 diamond sample at 294 K. The calculated spectrum is given for four sublevels of the free exciton split state from [11] (a) and for 12 sublevels (b). The inserts show the same spectra, but on an enlarged scale. The absorption coefficient of sample C12 measured with a KrCl laser (222.2 nm) in [13] was marked with a black circle.

It was reported the observation of four sublevels of the split FE state, with 12 states being theoretically considered [11]. We assumed that the fine splitting of the FE state occurs on 12
sublevels, but all of them show themselves only in the OA spectra, while only 4 of them are optically bright. Using the second derivative of the absorption, we established the presence of 27 kinks in the OA spectrum of the sample C12 in the region of the "positive" branch of absorption into the FE state with the TA-phonon. However, before publishing the binding energies of the sublevels of the split FE state corresponding to these kinks, we plan to conduct additional measurements on the high-resolution spectral instrument with a much lower level of thermal noise than one for the spectrometers in this work.

Figure 1b demonstrates an example of spectrum approximation of sample C12 at 294 K (the same spectrum as in figure 1a). It is obvious that a much larger number of sublevels of the split FE state makes it possible to ideally approximate the spectrum of diamond OA near the fundamental edge. The inset on figure 1(b) shows the same OA spectrum on an enlarged scale. Dashed lines denote areas of single-phonon transitions. Solid vertical lines denote the cutoff energies for interband "negative" transitions with a parabolic dependence of the absorption coefficient on the photon energy. Such transitions make a significant contribution in the spectral range 5.35-5.47 eV. At the same time, in the range 5.40-5.45 eV, deviations of the measured and calculated OA spectra were observed, which required additional transitions to the FE state, which corresponded to energy of phonons of 8–30 meV in energy. Due to it's impossible for phonons in a diamond to have such energies, we assumed the existence of two-phonon processes like ones in the radiative recombination of FEs. One of the optical phonons (LO or TO) is absorbed during the optical transition, and the other is generated (OΓ).

Figure 2a shows the measured OA spectra of a diamond sample C12 in the temperature range from 83 to 294 K. The inset shows spectra of a sample of C12 on an enlarged scale. There was a strong dependence of the OA spectra on temperature in the temperature range 202-294 K. In the temperature range 83-202 K, the change in the spectra with a change in temperature was less pronounced.

Figure 2b shows the dependences of the best values (for approximating the OA spectrum) of the matrix element of the interband transition \( B_p \) for the TO mode of the "negative" branch (squares) and the "positive" branch (circles) obtained by approximating the spectra of the C12 sample for different temperatures. We note that for the "positive" OA branch, the values of \( B_{p,TO} \) did not practically change
in the temperature range 83-227 K and amounted to \((1.5-2.0) \cdot 10^8\ \text{cm}^{-1}\cdot\text{eV}^{-1}\). With a further increase in temperature to 294 K, the \(B_{r_{\text{TO}}}\) values increased by an order of magnitude. For the "negative" OA branch, the values of \(B_{r_{\text{TO}}}\) decreased from \(9.0 \cdot 10^8\) to \(1.8 \cdot 10^5\ \text{cm}^{-1}\cdot\text{eV}^{-1}\) with an increase in temperature from 83 to 202 K, i.e. almost 4 orders of magnitude. With a further increase in temperature to 294 K, the \(B_{r_{\text{TO}}}\) values remained practically unchanged \((1.8-3.0) \cdot 10^5\ \text{cm}^{-1}\cdot\text{eV}^{-1}\). The fall of \(B_{r_{\text{TO}}}\) by 4 orders of magnitude with a rise in temperature from 83 to 202 K is of a fundamental nature. For a confident interpretation of this effect, we plan to carry out measurements and calculations for several additional diamond samples.

In our calculations we neglected the band gap width temperature dependence for diamond, and used its constant value \(E_g=5.49\ \text{eV}\). Usually for indirect semiconductor, the gap width temperature dependence is determined as the cumulative effect of exciton processes and thermal expansion of the lattice. Diamond has the highest packing density and rigidity of chemical bonds and characterizes by a small coefficient of linear expansion \(k_\alpha\) (see the inset in figure 2), which is 5-20 times smaller than for typical metals. So we assume that the optically measured band gap dependence of a diamond in [16] is determined to a greater extent by exciton processes than by thermal expansion of the lattice.

The temperature dependence of the diamond OA spectra near the fundamental edge is primarily determined by the interband transitions of the "negative" absorption branch (see figures 1a,b and 2a,b). The contribution of transitions to the split FE state of the "negative" branch is significant, but much less. Actually, as the "edge of fundamental absorption" in the diamond OA spectra, the edge of transitions to the split FE state of the "positive" branch is represented.

![Figure 3](image)

**Figure 3.** Photoluminescence spectra of a diamond sample C10 excited by a KrCl laser at 222.2 nm for the peak intensities of laser radiation of 7, 10 and 13 MW/cm\(^2\) at 81 K (a) and 298 K (b). In the photoluminescence spectra of sample C10, the bands of radiative recombination of free excitons (FE\(_{TA}\), 5.323 eV; FE\(_{TO}\), 5.272 eV; FE\(_{TO+O\Gamma}\), 5.115 eV) and droplets of electron-hole liquid (EHL\(_{TO}\), 5.219 eV; EHL\(_{TO+OF}\), 5.067 eV) are distinguished.

The large number of split FE state sublevels is reflected in the luminescence spectra. Figures 3a,b show the pulsed PL spectra of a diamond sample C10 at 81 K (a) and 294 K (b), measured upon excitation by a KrCl laser at 222.2 nm (5.5799 eV) at peak intensities of 7, 10 and 13 MW/cm\(^2\).

At 81 K and 7 MW/cm\(^2\), there were three spectral components of FE radiation with a TA generation (FE\(_{TA}\), 5.323 eV), TO (FE\(_{TO}\), 5.272 eV) and TO+O\(^\Gamma\) (FE\(_{TO+O\Gamma}\), 5.115 eV) of phonons. Increasing of the laser radiation intensity led to additional spectral components of the recombination
radiation of droplets of electron-hole liquid (EHL) with the generation of TO (EHL$_{TO}$, 5.219 eV) and TO+$\Gamma$ (EHL$_{TO\Gamma}$, 5.067 eV) phonons. At 298 K and 7 MW/cm$^2$, i.e. at a temperature much higher than the EHL critical temperature [13, 17], the FE recombination bands underwent temperature broadening. A further increasing of the laser radiation intensity led to a significant broadening of the FE$_{TO}$ and FE$_{TO\Gamma}$ components, which is not explained in the terms of temperature broadening.

Despite of a significant increase in temperature, the change in the position of the FE$_{TO}$ does not exceed 5 meV, whereas in [16] the optical band gap change with temperature rise from 80 to 300 K was ~15 meV. On the one hand, this effect can be a proof to our assumption of a weak temperature dependence of the diamond band gap due. On the other hand, this may indicate a change in the sublevels population of the split FE state as a function of temperature. In the latter case, the statement can be valid if all sublevels of the FE state are optically bright, which contradicts the results of measurements [11, 12]. Perhaps some high-energy sublevels of the split FE state (with a low binding energy) can be optically bright. This can explain the spectral components broadening in FE$_{TO}$ and FE$_{TO\Gamma}$ with increasing intensity of the laser radiation.

In [18] it was reported the radiative recombination of a dense electron-hole plasma (EHP) at high concentrations of charge carriers, but at a temperature above the EHL critical value. The appearance of EHP components led to a broadening of FE bands under similar excitation conditions like on figure 3b.

Optical excitation generates "cold" electron-hole pairs or FE (excitation by a KrCl laser with a photon energy of 5.58 eV). When carriers are generated by an electron beam, each electron of e-beam with energy of tens to hundreds of keV generates thousands to tens of thousands of "hot" electron-hole pairs (for each pair of carriers an average of 11-17 eV is expended). During the thermalization each of them generates dozens-hundreds of acoustic phonons, thereby warming up the diamond lattice. It can be assumed that the process leads to a redistribution of the split FE state sublevels population, which is reflected in the luminescence spectra. We plan to carry out the CL spectra measurements with high spectral resolution for various single and polycrystalline natural and synthetic diamond samples, excited by electron beams of various energies and durations, including subnanosecond ones.

4. Conclusion

Optical absorption and photoluminescence spectra were measured for two synthetic diamonds for temperatures of 80-300 K. Optical absorption spectra were approximated for edge absorption in the split free-exciton state and interband transitions for the "negative" and "positive" branches.

It is established that for adequate approximation of the diamond fundamental absorption edge it is necessary to take into account at least 12 sublevels of the split free-exciton state. A "negative" branch of interband transitions and, to a lesser extent, a "negative" branch of absorption into the split free-exciton state make a significant contribution to the temperature dependence of the optical absorption spectra of a diamond near the fundamental edge.

By the results of approximation, it was found that the probability of interband transitions with the generation of TO phonons (the "positive" branch) in diamond practically does not change in the temperature range of 83-227 K. As the temperature rises from 227 to 294 K, the probability of these transitions increases by an order of magnitude.

For a "negative" branch of interband transitions with an absorption of TO phonons, the transition probability falls by 4 orders of magnitude with an increase in temperature from 83 to 202 K. With further increase in temperature to 294 K, the value of this quantity remains practically unchanged.

The presence of a large number of split free-exciton state sublevels leads to broadening of the free-exciton radiative recombination bands in diamond.

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References
[1] Pourshahab B, Abdi M R, Sadighzadeh A and Rasouli C 2016 Phys. Plasmas 23 072501
[2] Zeng L, Chen Z Y, Dong Y B, Koslowski H R and Liang Y 2017 Nucl. Fusion 57 046001
[3] Zhou R J, Hu L Q, Zhang Y, Zhong G Q, Lin S Y, et al 2017 Nucl. Fusion 57 114002
[4] Sadowski M J 2011 Nukleonika 56 85
[5] Zebrowski J, Jakubowski L, Rabinski M, et al 2018 J. Phys.: Conf. Series 959 012002
[6] Zaitsev A M 2001 Optical properties of diamond: A data handbook (Berlin: Springer-Verlag)
[7] Solomonov V I, Mikhailov S G 2003 Pulse cathodoluminescence and its application for analysis of condensed matter (Ekaterinburg: Ural Branch of RAS) (In Russian)
[8] Baksht E Kh, Burachenko A G, V.F. Tarasenko 2010 Tech. Phys. Lett. 36 1020
[9] Lipatov E I, Lisitsyn V M, Oleshko V I, et al 2012 (Pulsed cathodoluminescence of natural and synthetic diamonds exited by nanosecond electron beams, Cathodoluminescence ed. N Yamamoto) Rijeka: InTech p 324
[10] Sorokin D A, Burachenko A G, Beloplotov D V, et al 2017 J. Appl. Phys. 122 154902
[11] Hazama Y, Naka N, Stolz H 2014 Phys. Rev. B 90 045209
[12] Morimoto H, Hazama Y, Tanaka K, Naka N 2015 Phys. Rev. B 92 201202(R)
[13] Lipatov E I, Genin D E, Tarasenko V F 2015 Opt. Spectrosc. 119 918
[14] Grivickas P, Grivickas V, Linnros J, Galeckas A 2007 J. Appl. Phys. 101 123521
[15] Vecherin P P, Zhuravlev V V, Kvaskov V B, et al 1997 Natural diamonds of Russia ed Kvasov V B (Moscow: Polyaron) p 302 (In Russian)
[16] Clark C D, Dean P J, Harris P V 1964 Proc. R. Soc. London, Ser. A 277 312
[17] Lipatov E I, Genin D E, Grigor’ev D V, Tarasenko V F 2016 Russ. Phys. J. 59 131
[18] Murayama K, Sakamoto Y, Fujisaki T, et al 2007 Diamond Relat. Mater. 16 958