

Temperature dependences of the 603/700/787 nm system photoluminescence in natural diamond

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The study was carried out on temperature dependences of the 603/700/787 nm system photoluminescence in a natural diamond crystal at range from 80 to 470 K. It was found two zero phonon lines 584 nm (2.124 eV) and 603 nm (2.054 eV) are electronic transitions from sublevels of the split excited state with activation energy of 70 meV. Temperature behavior of the zero-phonon lines 656 nm (1.888 eV) and 700 nm (1.770 eV) also corresponds to the split excited state with activation energy of 118 meV.

Keywords: 603/700/787 nm system, diamond, photoluminescence, temperature dependences.

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Introduction

More than three hundred optically active centers (OACs) have been identified in natural diamond, but only a few of them have been studied in detail with a reliably established crystal structure defect (CSD) model. One of the little-studied centers is the 603/700/787 nm photoluminescent system, which is often observed in the spectra of natural type Ia crystals [1–3]. The system is normally localized in sectors $\langle 100 \rangle$, which are characterized by increased (relative to sectors $\langle 111 \rangle$) dislocation density and impurity content levels.

The features of zero-phonon lines (ZPLs) at 603, 700, and 787 nm at different temperatures were discussed in earlier studies [1,4]. It is believed that the 603 and 700 nm lines have similar temperature dependences: rapid quenching with an increase in temperature and vanishing at room temperature. The 787 nm ZPL intensity decreases monotonically with increasing temperature, and photoluminescence (PL) is quenched completely at 400 K. The relation between the 700 nm and 656 nm ZPLs observed in the PL spectra at temperatures of 80 and 290 K, respectively, was noted in [5]. A resonance mechanism of energy transfer from the sensitizer (700 nm OAC) to the activator (656 nm OAC) is assumed.

According to the results of our research [6], the 603/700/787 nm system consists of five radiative (2.124 eV (584 nm); 2.054 eV (603 nm); 1.888 eV (656 nm); 1.770 eV (700 nm); and 1.575 eV (787 nm)) and three excited energy levels: 2.86 eV for 656 and 700 nm, 2.680 eV for 584 and 603 nm, and 2.49 eV for 787 nm. The 584/603 and 656/700 nm line pairs may be interpreted as spin-allowed and spin-forbidden electronic transitions, respectively. Thus, a study of temperature dependences is needed to clarify

the PL features of the 603/700/787 nm system and to verify the proposed model of 584/603 and 656/700 nm electronic transitions.

Sample and research methods

The study of temperature dependences of PL of the 603/700/787 nm system was carried using a plate of natural diamond 123-76. The crystal was found in alluvial placers of the Krasnovishersky District in the Urals. The specifics of internal structure and distribution of OACs in the crystal were discussed in [7,8]. According to the results of infrared (IR) spectroscopy, the total nitrogen content in the crystal varies from 800 to 1400 ppm with most nitrogen atoms (67%) found in the (N_4V) form. The coefficient of absorption of the 3107 cm^{-1} band of the (N_3VH) hydrogen center varies from 1.1 to 37.9 cm^{-1} in sectors $\langle 111 \rangle$ and $\langle 100 \rangle$, respectively.

PL spectra were recorded with a Horiba Lab RAM HR 800 Evolution spectrometer with $\lambda_{\text{ex}} = 488 \text{ nm}$ laser excitation at the „Geoanalitik“ common use center of the Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences. A Linkam THMS 600 system was used to adjust the plate temperature from 80 to 470 K in 10 K increments. The obtained temperature dependences were processed using a specialized program written in Mathcad 15.

Results and discussion

The variation of the 603 nm ZPL in the PL spectra of natural diamond with an increase in temperature is presented in Fig. 1. In the course of heating from 80 K, the line shifts smoothly to the red region (Fig. 1, b) by

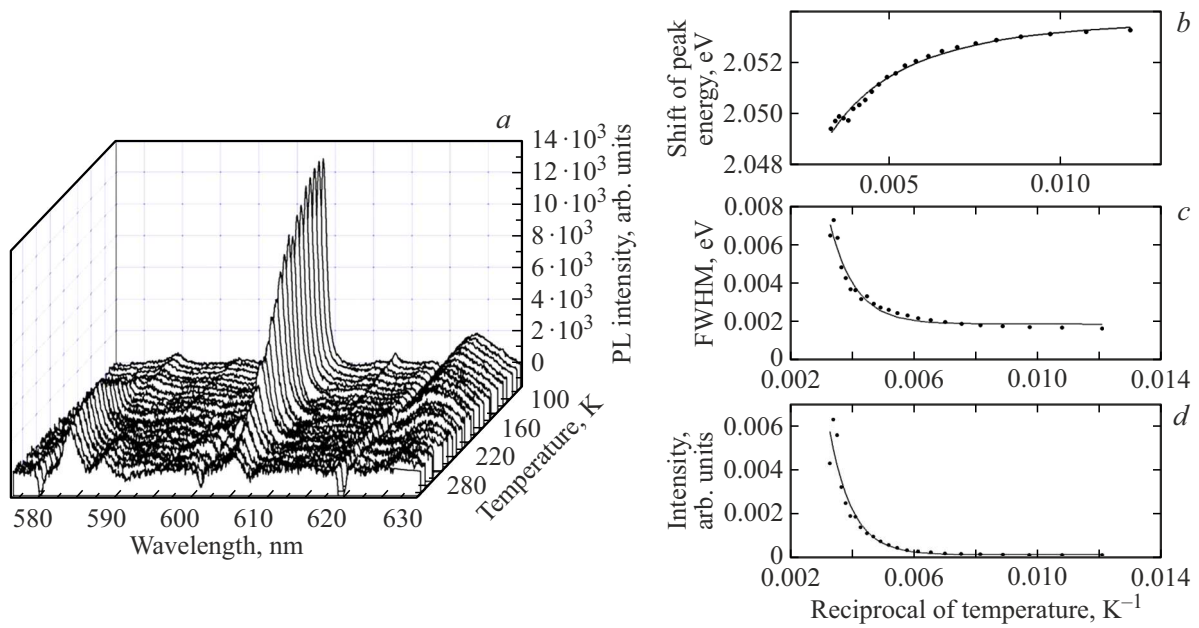


Figure 1. Photoluminescence spectra of the 584 and 603 nm ZPLs at temperatures ranging from 80 to 300 K (*a*); temperature dependences of the 603 nm ZPL parameters: energy (*b*), full width at half maximum (*c*), and intensity (*d*). Points denote experimental data, and curves are the results of approximation of temperature dependences.

1.2 nm and gets broadened (Fig. 1, *c*) by 0.7 nm. Complete quenching of the 603 nm line in the PL spectra is seen at 310 K (Fig. 1, *d*).

Figure 2 shows the spectra and characteristics of the 700 nm ZPL obtained by heating the crystal from 80 to 410 K. As the temperature increases, the 700 nm ZPL shifts smoothly to the red spectral region by 2.1 nm (Fig. 2, *b*) and gets broadened by 1.9 nm (Fig. 2, *c*). The 700 nm ZPL is quenched at a temperature of 310 K (Fig. 2, *d*).

The temperature dependences of the 787 nm ZPL are shown in Fig. 3. In the course of heating from 80 K, the line shifts smoothly to the red region (Fig. 3, *b*) by 1.9 nm and gets broadened (Fig. 3, *c*) by 1.4 nm. Its quenching is seen at a temperature of 450 K.

It should be noted that the spectra of phonon repetitions of the 603, 700, and 787 nm system lines decay uniformly at higher temperatures along with the corresponding ZPLs (Figs. 1, *a*, 2, *a*, 3, *a*).

The smooth shift of the 603, 700, and 787 nm ZPLs to the red spectral region with increasing temperature is indicative of a reduction in energy of the radiative transition levels and may be characterized using the Fan expression [9,10]:

$$E_g(T) = E_g(0) - A \frac{1}{\exp\left(\frac{hw_S}{k_B T}\right) - 1}, \quad (1)$$

where $E_g(0)$ is the energy (position) of the peak maximum at 0 K; hw_S — energy of phonons inducing the shift of electronic levels; T — temperature in the process of spectrum measurement; k_B — Boltzmann constant ($8.61 \cdot 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), $A = 2Shw_S$ — Fan parameter; and S — Huang–Rhys factor.

The broadening (FWHM) of the 603, 700, and 787 nm ZPLs with an increase in crystal temperature characterizes the OAC–lattice interaction and follows the expression

$$\Gamma = \Gamma_{\text{inh}} + \Gamma_{LO} \frac{1}{\exp\left(\frac{hw_{LO}}{k_B T}\right) - 1}, \quad (2)$$

where Γ_{inh} is the width of an inhomogeneous line that does not depend on temperature; Γ_{LO} is the electron–phonon interaction constant; and hw_{LO} is the energy of phonons causing the broadening of electronic levels.

The variation of intensity of the 603, 700, and 787 nm ZPLs with increasing crystal temperature follows Mott's law, which is written as follows:

$$I = \frac{I_0}{1 + A \exp\left(-\frac{\Delta E}{k_B T}\right)}, \quad (3)$$

where I_0 is the PL intensity at 0 K, A is a constant, and ΔE is the activation energy of thermal quenching.

The results of approximation of temperature dependences of the shift, broadening, and quenching of the 603, 700, and 787 nm ZPLs are summarized in the table.

According to the results of approximation of temperature dependences of the 603 nm ZPL, the energy of phonons inducing its broadening ($hw_{LO} = 55.5 \text{ meV}$), is higher than the energy of shift phonons $hw_S = 42.3 \text{ meV}$. This indicates that the shift and broadening of the 603 nm ZPL at higher temperatures are attributable to the interaction of the center with phonons having different wave vectors. The ratio of energies of phonons inducing the shift and broadening of the 700 nm ZPL is inverse ($hw_{LO} < hw_S$),

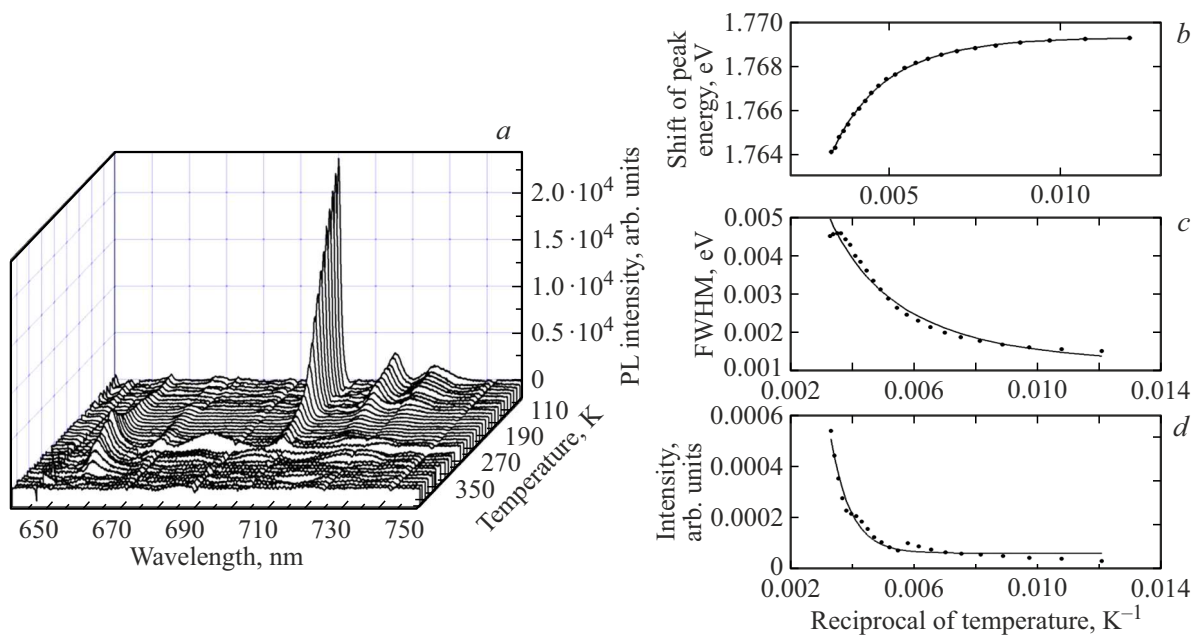


Figure 2. Photoluminescence spectra of the 656 and 700 nm ZPLs at temperatures ranging from 80 to 410 K (a); temperature dependences of the 700 nm ZPL parameters: energy (b), full width at half maximum (c), and intensity (d). Points denote experimental data, and curves are the results of approximation of temperature dependences.

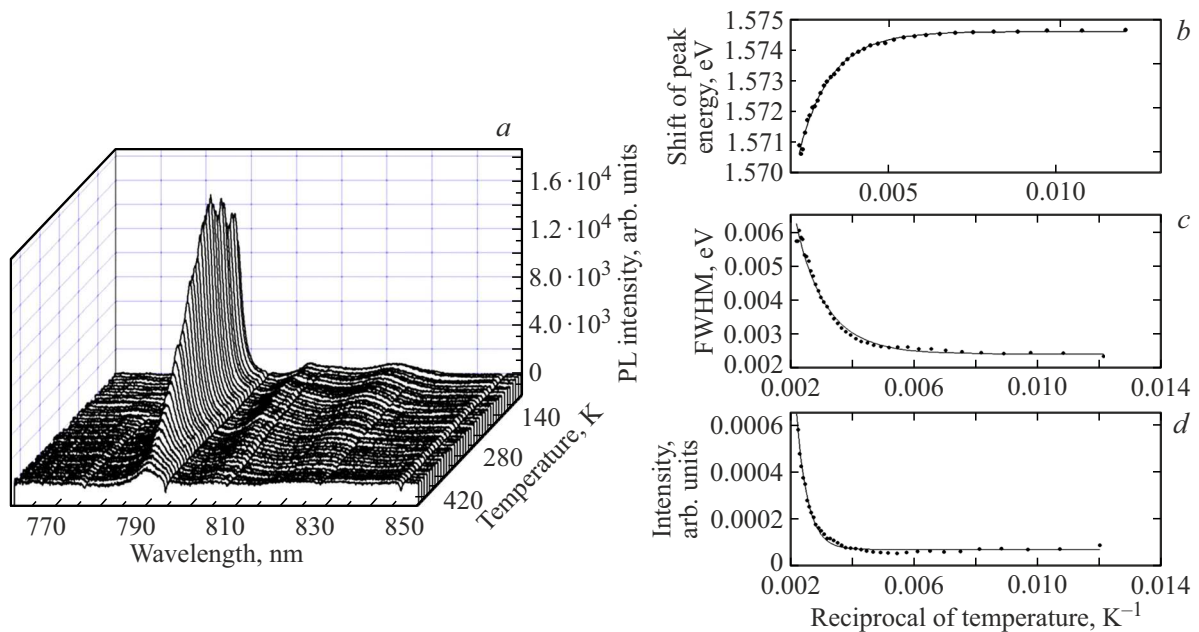


Figure 3. Photoluminescence spectra of the 787 nm ZPL at temperatures ranging from 80 to 470 K (a); temperature dependences of the 787 nm ZPL parameters: energy (b), full width at half maximum (c), and intensity (d). Points denote experimental data, and curves are the results of approximation of temperature dependences.

which is also explained by the interaction of the center with different vibrations. As for the 787 nm ZPL, the energies of phonons inducing its shift and broadening are $hw_S \approx hw_{LO} \approx 70$ meV, which is close to the energies of branch $\Lambda 3(A)$ of acoustic dispersion curves of diamond [11].

At a temperature of 150 K, two ZPLs (584 and 656 nm) grow more intense in the PL spectra of diamond with the

603/700/787 nm system (Figs. 1, a, 2, a). Their intensity reaches its maximum at 290–300 K (Figs. 4, a, d). The 656 nm line vanishes from the PL spectra at $T = 410$ K. The 584 nm ZPL is quenched at a temperature of 370 K. At temperatures of 160–260 K, the intensity ratio of the 584 and 603 nm ZPLs is exponential in nature and is approximated by a straight line (Fig. 4, c) in Arrhenius coor-

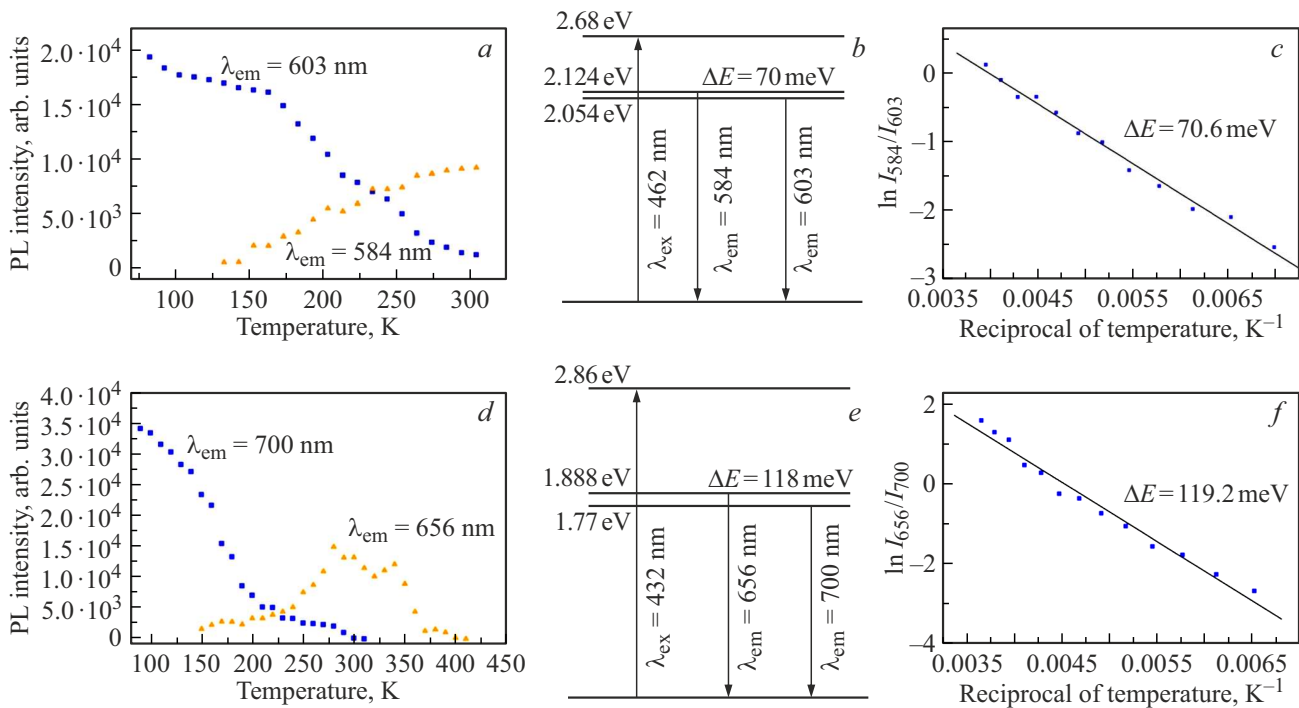


Figure 4. Temperature dependences of the integral intensities of the 584 and 603 nm ZPLs (a) and the 656 and 700 nm ZPLs (d); energy level diagrams (b, e); and temperature dependences of the intensities of the 584 and 603 nm ZPLs (c) and the 656 and 700 nm ZPLs (f) in Arrhenius coordinates. Points denote experimental data, and curves in panels c and f are the results of approximation of temperature dependences.

Results of approximation of temperature dependencies

Parameters	Zero-phonon lines of system 603/700/787 nm		
	2.054 eV (603 nm)	1.770 eV (700 nm)	1.575 eV (787 nm)
$E_g(0)$ (eV)	2.053	1.769	1.575
S	0.24	0.29	0.15
hw_S (meV)	42.3	48.5	69.4
Γ_H (meV)	1.75	1.35	2.05
Γ_{LO} (meV)	22.7	10.3	16.7
hw_{LO} (meV)	55.5	33.0	70.4
I_0 (arb. units)	6318	18904	12963
ΔE (meV)	116	121	235

dinates ($\ln I_{584}/I_{603} = f(1/T)$). As for the 656 and 700 nm ZPL pair, linearity in Arrhenius coordinates (Fig. 4, f) is preserved within the temperature range of 150–270 K.

The results of approximation of the ZPL intensity ratio in Arrhenius coordinates allow one to estimate activation energy ΔE of the transition between split sublevels:

$$\ln \frac{I_h}{I_l} = -\frac{\Delta E}{k_B T}, \quad (3)$$

where I is the integral ZPL intensity, T is the spectrum measurement temperature, and k_B is the Boltzmann con-

stant. Subscripts h, l denote the high and low radiative sublevels of the split energy level, respectively. The transition activation energy for the 584 and 603 nm ZPLs is 70.6 meV, which is consistent with the energy value of spectral separation of lines (70 meV). The transition activation energy for the 656 and 700 nm ZPLs is 119.2 meV and is close to the spectral separation energy of 118 meV.

Thus, the temperature behavior of the 584 and 603 nm ZPLs suggests a redistribution of intensities between the sublevels of the excited state with a splitting energy of 70 meV. The features of temperature variation of the 656 and 700 nm ZPLs correspond to a split excited state with a distance between sublevels of 118 meV. The 787 nm ZPL reveals no splitting of excited or ground states; it is likely that a different photoluminescence mechanism is at work here.

Splitting of energy levels is a fairly common phenomenon for diamond OACs [4,11]. For example, splitting of the ground state is observed for the GR1 center [4]. Nitrogen-vacancy centers H3 and H4 are characterized by splitting of excited levels [11]. The SiV center [12] and the CSD with a germanium impurity [13] feature two sublevels of the ground and excited states. Splitting of energy levels is typical of a number of nickel OACs, including S2 and S3 centers [14]. Our previous research experience suggests that the temperature behavior of the 584/603 nm and 656/700 nm ZPLs is consistent with the model of spin-allowed and spin-forbidden transitions proposed in [6]. The

excited state for the 584/603 nm and 656/700 nm centers is split with energy distances of 70 meV and 118 meV, respectively. At a temperature of 80 K, the upper energy sublevels at 2.124 eV (584 nm) and 1.888 eV (656 nm) are weakly populated and spin-forbidden electronic transitions proceed from the sublevels at 2.054 eV (603 nm) and 1.770 eV (700 nm). As the temperature increases, sublevels get repopulated, and the short-wavelength 584 nm and 656 nm ZPLs, which correspond to spin-allowed transitions, become more intense.

Conclusion

The temperature behavior of photoluminescence of the 603/700/787 nm system in natural diamond was examined within the range from 80 to 470 K. The 603, 700, and 787 nm ZPLs broaden uniformly and shift to the red region with increasing temperature. The 603 and 700 nm lines are quenched at a temperature of 310 K, while the 787 nm ZPL vanishes much later (at 450 K). The shift and broadening of the 603 and 700 nm ZPLs are attributable to the interaction of centers with phonons having different wave vectors. As for the 787 nm ZPL, the energies of phonons inducing its shift and broadening are close to the energies of branch $\Lambda_3(A)$ of acoustic dispersion curves of diamond.

At a temperature of 150 K, two ZPLs (584 and 656 nm) grow more intense in the PL spectra of natural diamond crystals with the 603/700/787 nm system. The specifics of variation of ZPL intensity ratios 584/603 nm and 656/700 nm with temperature indicate a redistribution of energy sublevels of the split excited state and is consistent with the model of spin-allowed 2.124 eV (584 nm) and 1.888 eV (656 nm) and spin-forbidden 2.054 eV (603 nm) and 1.770 eV (700 nm) transitions. The obtained new data on the structure of impurity defects in diamonds may be used to identify the indicators of thermal evolution of the diamond-bearing lithospheric mantle.

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Conflict of interest

The authors declare that they have no conflict of interest.

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