

Vibrational anharmonicity of A-band related optical center and its temperature dependence studied by femtosecond laser excitation in bulk natural diamond

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Abstract. *Unusual A-band spectra with well-resolved quasi-periodical phonon progressions of multiple peaks ($N \sim 9$) were excited in a natural diamond by 515 nm, 300-fs laser pulses at variable pre-heating temperatures of 24-200°C. The non-radiative multi-phonon part of the relaxation path was comparable with the total relaxation energy (zero-phonon line energy), pointing out some extended defects (e.g., dislocations) as the recombination centers of the A-band emission. The derived temperature dependences of the peak intensities, separations and half-widths of the separate spectral peaks in the A-band phonon progressions indicate the different trends for vibration-free zero-phonon electronic transition and vibration-related lower-energy electronic transitions to high vibrational levels of the ground electronic state – lower thermal damping and more softened phonon for the zero-phonon transition, also implying the extended defect origin of the A-band photoluminescence.*

Keywords: natural diamond; A-band; femtosecond laser; photoluminescence; temperature effect; dislocations.

Classification numbers: 78.55.Ap, 81.05.ug, 78.47.J-.

1. Introduction

Photoluminescence is the most sensitive spectroscopic method for characterization of intrinsic (non-equilibrium carriers, interstitial-vacancy pairs [1]) and extrinsic (impurity atoms or clusters [2]) imperfections in the ultra-hard regular diamond lattice. Optically-active impurity

centers are broadly characterized spectroscopically [3], while their corresponding atomistic structure frequently remains unknown. Specifically, despite the numerous previous studies (see the broad bibliography review in Ref. [3]), the origin (or a few of them) of characteristic so-called A-band (maximum at 435 nm/2.88 eV, half-width \approx 0.22-0.45 eV, Fig. 1), the most characteristic luminescence feature of natural, chemical-vapor deposited (CVD) and high-pressure, high-temperature (HPHT) synthesized diamonds, is still remaining a subject of controversies [4]. To note, recombination of free carriers via an excitonic mechanism in the form of ultraviolet (UV) emission (237 nm) or via trapping in some, still unknown defect centers in the form of UV-green A-band emission are the main relaxation paths for electronic excitations in synthetic and natural diamonds [3], correspondingly. Hence, insights into the structure and optical properties of A-band related optical center is of high importance in controllable characterization and electronic modification of natural diamonds.

The first line in considering the origin of A-band and its underlying color (defect) center is related to radiative recombination at dislocations, typical for the relatively narrow A-bands peaked at 440 nm and usually observed in low-nitrogen II-type diamonds. The underlying optical centers could be donor (D)-acceptor (A) pairs, decorating dislocations [4] (the non-decorated ones appear non-luminescent [5] and vacancies bound to dislocations [6]. There is a purely dislocation-related model of the A-band peaked at 415 nm [7], related to electronic transitions from deep-lying acceptor centers (e.g., electronic levels of dislocations) to the valence band [8] and strongly supported by electron-energy loss spectroscopy measurements [5]. The A-band is believed to be related to the 4-eV band, as a transition from the conduction band to the dislocation band localized at about 1.8 eV above the valence band [9]. In natural diamonds the spectral position of the maximum of the dislocation-related A-band may range from 2.8 eV (445 nm) to 2.99 eV (415 nm) [3].

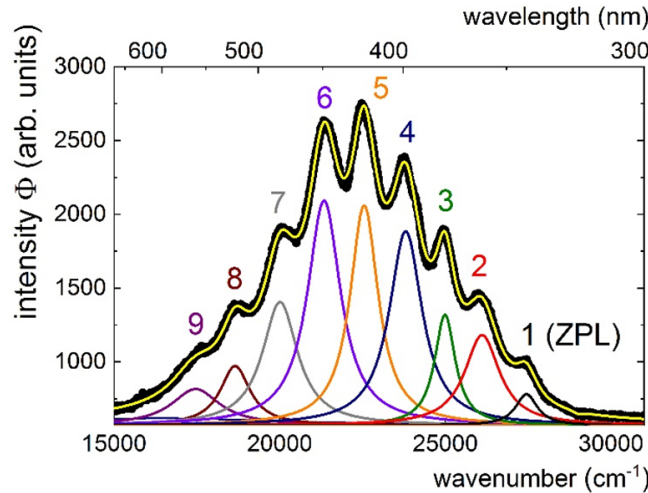


Fig. 1. Typical room-temperature photoluminescence (PL) intensity spectrum of femtosecond (fs)-laser excited A-band with its multi-peak ($N=1-9$) phonon progression series fitted by corresponding Lorentzian curves (see below).

The other line in visualizing the A-band related luminescent center is based on intra-center transitions of B1 centers (platelets), observed for the broad A-band with a maximum at 480 nm in natural type I diamonds. Alternatively, the A-band is also considered as an electron-hole recombination at deep centers, the energy levels of which lie in the middle of the bandgap (width E_g) near $E = E_g/2 - 0.75$ eV [10]. The A-band emission was also thought as formation of free excitons [11], could be a two-stage process for the 2.75 eV (450 nm) PL band [12], with the spatial distribution of the A-band luminescence in CVD diamond films similar to that of the free-exciton emission [13].

Phenomenologically, the A-band is the main cathodeluminescence (CL) feature of low-nitrogen diamonds, e.g., IIa-diamonds of mosaic texture [14]. In synthetic diamonds the A-band is particularly strong around macroscopic inclusions distorting the surrounding lattice [15]. The dislocation-related A-band can be observed in CL only in IIa-diamonds of relatively high purity [16], since low-nitrogen (<20 parts per million, ppm) natural diamonds appear to be always rich in dislocations. The nitrogen impurity strongly quenches the dislocation-related A-band luminescence [17] – for example, the dislocation A-band with a maximum at 440 nm can be detected in natural diamonds with a concentration of the A (2N, where N is the substitutional nitrogen atom N) and B1 (4NV, the four substitutional nitrogen atoms surrounding the carbon vacancy V, also - so-called N9) centers below 3×10^{17} cm⁻³ [18]. The B1 centers, however, do not strongly suppress the A-band in CL, whereas the A centers quench it considerably [18]. There is a trend that straight dislocations are more efficient in the A-band emission than curved ones, implying that the dislocation kinks may be efficient non-radiative recombination centers [4]. The A-band luminescence observed from individual dislocations is strongly polarized with the electric-field E-vector parallel to the dislocation lines regardless of the dislocation type and is independent of the Burgers vector [4].

Moreover, the A-band reveals no fine-line structure even at low temperature in very perfect diamonds. However, the dislocation-related A-band is thought to be a vibronic side-band of a center with its zero-phonon line (ZPL) energy position at about 3.0 eV, while the ZPL is not observed due to the very large Huang-Rhys factor of the luminescent defect and the strong nonhomogeneous stress around dislocations [19]. However, recently a well-resolved multi-peak A-band phonon progression with its maximum at 420-430 nm was observed in a IaA-diamond (predominating A-centers) upon its 515 nm femtosecond laser excitation, proceeding via two-photon absorption, with its strong thermal damping even at moderate above-room temperatures [20].

Overall, the intrinsic atomistic structure and related electronic energy spectrum of the important A-band related color (defect) center in natural and synthetic diamonds appear controversially and ambiguously understood, requiring more detailed, novel insightful experimental multi-parametric research to be performed to shed light on its rather exotic origin. In this study, the quantum structure of vibrational energetic states, underlying the characteristic A-band phonon progression excited by 515 nm femtosecond laser pulses as a function of temperature, was explored in a natural IaA-type diamond by analyzing thermal effects on the corresponding intensities, positions and half-widths of separate spectral peaks in the band.

2. Experiment

In this work we used a nitrogen-doped (>700 ppm) natural colorless IaA-type diamond plate (dimensions $2 \times 2 \times 1$ mm³), containing about 650 ppm of non-luminous low-aggregation

A-centers (substitutional doublets 2N), identified by their infrared (IR) absorption peak at 1282 cm^{-1} , minor concentration ($\approx 50\text{ ppm}$) of B1-centers (4NV, peak at 1175 cm^{-1}) and marginal B2-centers (platelets, peak at 1365 cm^{-1}) [3].

Ultrashort-pulse laser photoexcitation of the diamond plate occurred at the maximal fs-laser intensity $I_0 \approx 16\text{ TW/cm}^2$ at the 300-micron depth by 10 kHz train of 300 fs, 515 nm ($\approx 19000\text{ cm}^{-1}$) pulses from Yb-doped fiber laser Satsuma at different pulse energies $E = 20\text{--}400\text{ nJ}$ were focused by a Nikon micro-objective (numerical aperture $NA = 0.3$) into a 3-micron (1/e-intensity level) focal spot inside the diamond through its polished side window (Fig. 2). The resulting photoluminescence (PL) emission was collected sideways by a 0.2-NA UV-transparent quartz/fluorite objective and then focused, as a luminous track, onto an input slit of a broadband spectrometer ASP-150F (spectral resolution – 0.5 nm, non-gated charge-coupled device (CCD) array).

In temperature-dependent PL studies the laterally thermally-isolated diamond sample was resistively heated in 5°C steps from 24°C till 200°C , with the stationary sample temperature measured both by a built-in thermocouple and a remote directional-sampling digital infrared thermometer CA380 (CASON, operation range: $-32^\circ\text{C} - 380^\circ\text{C}$) with accuracy $\approx 0.3^\circ\text{C}$.

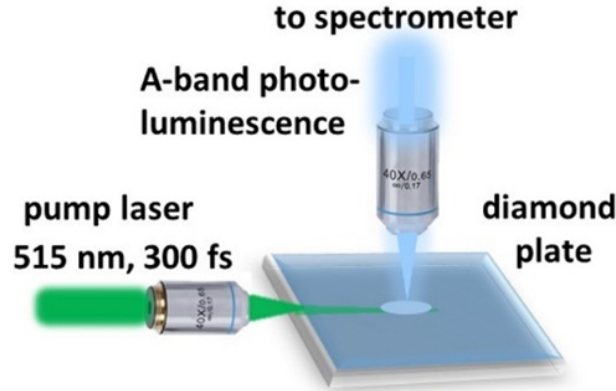


Fig. 2. Schematic of experimental setup for PL studies under fs-laser excitation.

3. Results and discussion

3.1. Spectral analysis of A-band PL yield

Thermo-luminescence of dislocation-related A-band with its maximum at 440 nm could be effectively excited in natural diamonds over the direct minimum of the conduction band and localized states located in the bandgap at energies about 3.3, 4.1 and 5 eV above the valence band [21], while the transitions from the indirect minimum of the conduction band are not effective. The corresponding photoluminescence excitation (PLE) spectrum of the dislocation-related A-band consists of a band ranging from 3 to 4 eV (intrinsic absorption of the A-band) and sample-dependent UV-range bands: a broad continuum above 4.6 eV (substitutional atomic nitrogen C-centers in Ib-diamonds), a structured band above 5.2 eV (B1-center) [3]. Commonly, this band was observed as structureless one even at low temperature in very perfect diamonds, but was thought, e.g., to

be a vibronic side-band of a center with ZPL at about 3.0 eV, where the ZPL is not observed due to the very large Huang-Rhys factor of the center and the strong nonhomogeneous stress around dislocations [22].

In this study, the A-band spectra range in Fig. 3 from 350 nm (ZPL, $N = 1$) till 550 nm ($N = 9$), exhibiting 9 well-resolved peaks ($N = 1 - 9$) and its maximum at about 440 nm. Each peak or the whole series could be fitted versus wavenumber (17 000 -28 000 cm^{-1}) by Lorentzian curves with the intensity Φ_{1-9} (Fig. 4), Lorentzian full-width at half maximum (FWHM) Γ_{1-9} (Fig. 5), and inter-peak spacing Ω_{ij} (Fig. 6). Here, the inter-peak spacing represents the phonon energy in the local mode associated with the A-band recombination center, following the emission sequence for the excited state to the different high vibrational levels of the ground state (Fig. 7). Then, the multi-peak PL band spectrum can be approximated by a standard intensity distribution for phonon progression with the peak number N (single-mode coupling) [23]

$$\Phi_N \propto \frac{e^{-S} S^N}{N!}, \quad (1)$$

where the Huang-Rhys factor $S \approx 6$, evaluated for the three most intense peaks $N = 4 - 6$, using Eq. (1), since high- N ($N = 8$) and low- N ($N = 0$) peaks are too low in their intensity and noisy to be accurately acquired. Here, Eq. (1) works in the case of identical force constants for vibrations in the ground and excited states, where the excited state potential is shifted along the configurational coordinate by the magnitude a , thus defining the Huang-Rhys factor S in terms of a , phonon frequency and mass, Ω and m ,

$$S = \frac{a^2 m \omega}{2 \hbar}. \quad (2)$$

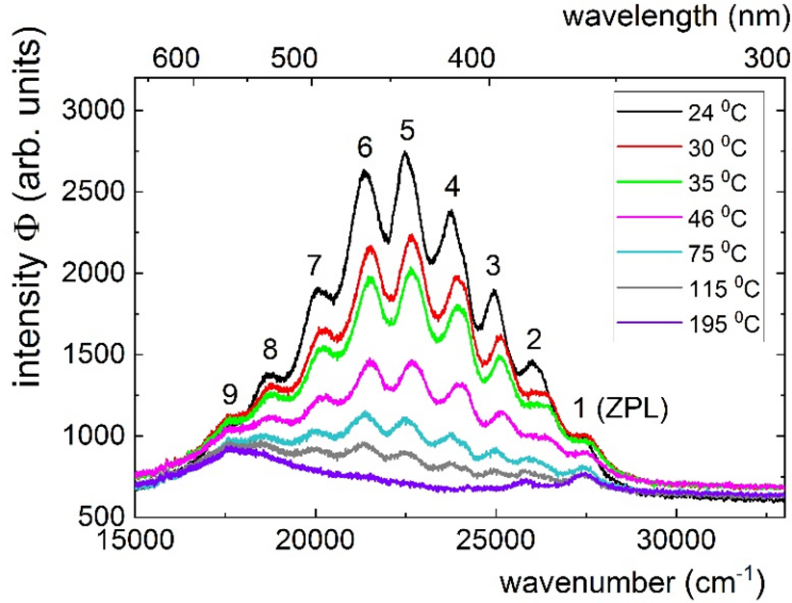


Fig. 3. Spectra of the selected A-band PL region upon fs-laser excitation at different temperatures of 24-200°C.

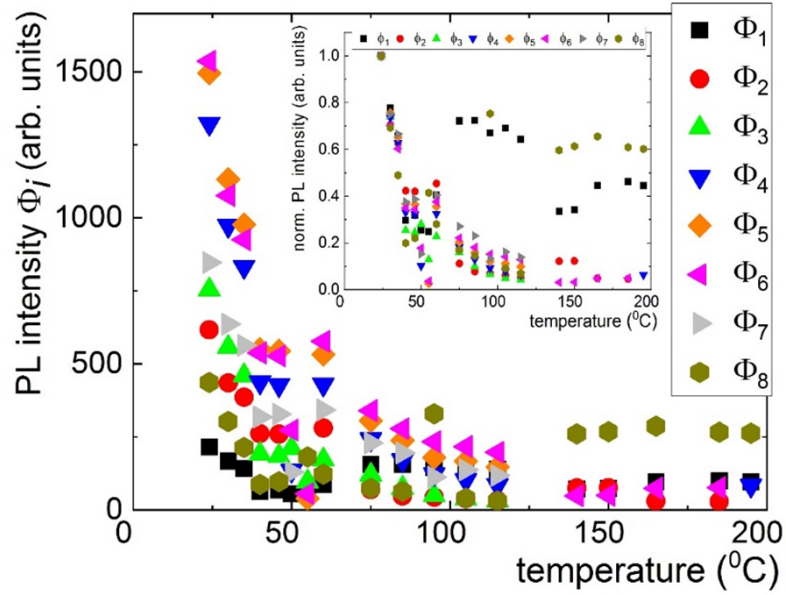


Fig. 4. PL intensities Φ_i of separate A-band peaks versus temperature. Inset: normalized PL intensities Φ_i .

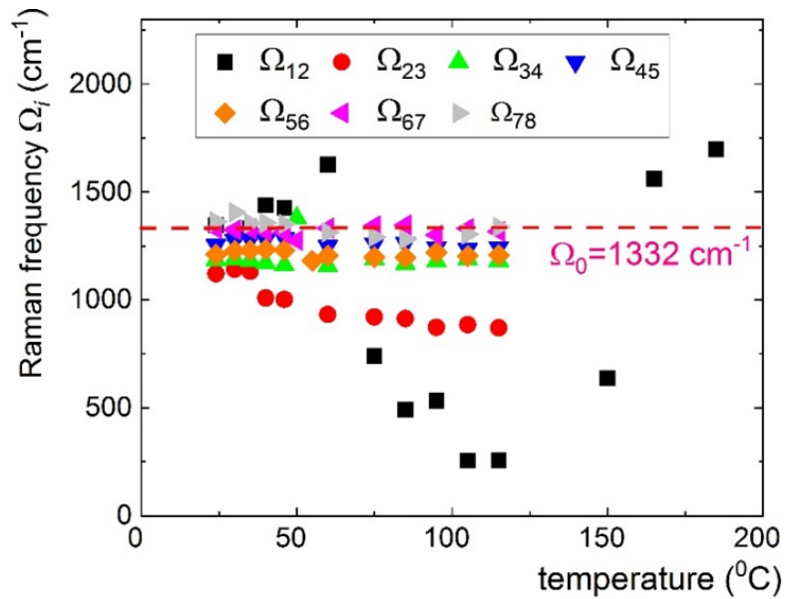


Fig. 5. Raman frequencies (inter-peak spacings) Ω_{ij} in the phonon progression series as a function of temperature. The reference center-zone optical-phonon phonon frequency Ω_0 of diamond is shown by the pink horizontal dashed line.

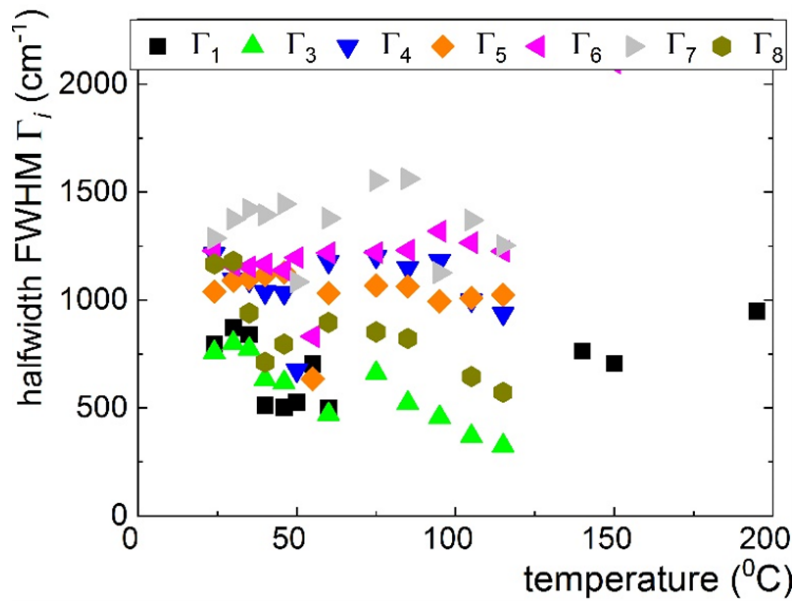


Fig. 6. Lorentzian peak half-widths (FWHM) Γ_{1-8} as a function of temperature.

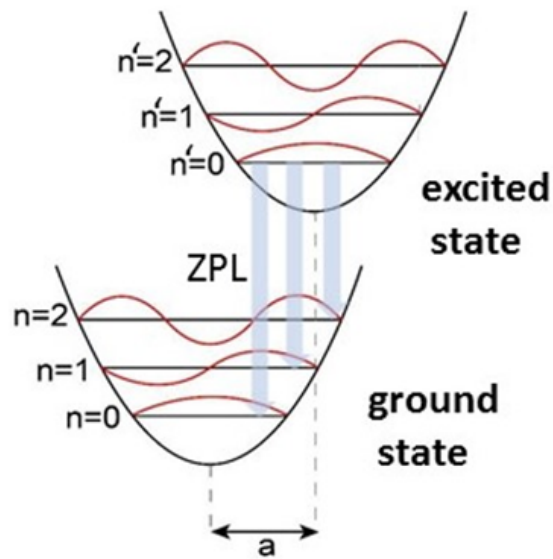


Fig. 7. Energetic scheme of PL emission from the excited state to the ground state, showing the pure electronic transition at the zero-phonon line (ZPL).

3.2. Temperature dependences of PL characteristics

Usually, *temperature dependence* of the spectral A-band parameters varies versus diamond types and excitation conditions. The A-band PL is temperature-independent at temperatures up to

250K [24]. In natural diamonds the A-band intensity falls almost to zero by a temperature above 400 K [25]. In CVD diamond films the A-band intensity attains its maximum at temperature about 170 K and then falls rapidly with a temperature increase above 200 K [26]. The activation energy of the thermal quenching of the dislocation-related A-band in natural IIb-diamonds and CVD-diamonds is about 0.3 eV, implying the considerable room-temperature effect on A-band PL yield [19].

In this study, the main visual thermal effect on the A-band spectra in Fig. 3 appears to be total damping of the most intense peaks ($N = 2 - 7$), with the ZPL peak and the neighboring peak at $N = 1$ decrease considerably, while persisting in the spectra. Moreover, the all intermediate peaks related to vibrationally-excited levels, fall in their intensity similarly (Fig. 4), comparing to the purely electronic transition at $N = 0$ (ZPL). The opposite peak at $N = 8$ minorly decrease in its intensity versus temperature and appears to be converted to some other, much broader PL band.

Usually, dislocations are favorable for non-radiative recombination, filling the bandgap by defect states with minor gaps, comparable with phonon energies, which could be overcome via multi-phonon transitions. In the case of the A-band, the non-radiative multi-phonon part ($N = 0 \rightarrow N = 8$) of the relaxation path in Fig. 1, $\approx 1.5 \times 10^4 \text{ cm}^{-1}$, is comparable with the total relaxation energy of $\approx 3 \times 10^4 \text{ cm}^{-1}$ (ZPL energy), thus potentially indicating some extended defects (e.g., dislocations) as the recombination center underlying A-band PL, in agreement with the previous suggestions [4–9].

In more details, the wavenumber/frequency of the local phonon, Ω_N , representing the high vibrations levels of the ground state involved into A-band PL phonon progression series (Fig. 7), were found to increase versus N toward the normal frequency $\Omega = 1332 \text{ cm}^{-1}$ (Fig. 5), thus contradicting the common trend for phonon softening due to anharmonicity. This could be related to phonon hardening at the higher vibrational levels of the ground state, if it is impurity – donor or acceptor – center, softening the phonon alike photoexcited center or free carrier. In this case, the decreased localization of the phonon near the center at the high vibrational levels makes it hardening. In the same trend, the temperature dependence of the phonon frequency exhibits the pronounced minimum at $N = 0, 1$ near 50°C (Fig. 5), while at higher N the minimum appears less and less distinct. Likewise, damping constant Γ_N appears rather high, but minimal at $N = 0$ (ZPL), while considerably increase versus N , remaining almost temperature-independent (Fig. 6). This could indicate some strong stabilizing interactions of the phonon at the high vibrational levels.

4. Conclusions

In conclusion, a well-resolved multi-peak A-band was detected in photoluminescence spectra of a natural diamond excited by 515 nm femtosecond laser pulses at variable ambient temperatures of 24-200°C. The non-radiative multi-phonon part of the relaxation path was found to be comparable with the total relaxation energy (zero-phonon line energy), thus potentially indicating some extended defects (e.g., dislocations) as the recombination center underlying A-band PL, in agreement with the previous suggestions. The derived temperature dependences of the peak intensities, separations and half-widths indicate the different trends for vibration-free zero-phonon transition and vibration-related lower-energy transitions to high vibrational levels of the ground state – lower thermal damping and more softened phonon for the zero-phonon transition, also in agreement with the extended defect origin of the A-band photoluminescence.

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