UDC 537.311.33:548.25

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PERSISTENT HIGH-TEMPERATURE SPECTRAL HOLE BURNING IN A NEUTRON-COLOURED DIAMOND

(Presented by G. Liidja)

A spectroscopic investigation of a neutron-irradiated IaB-type natural diamond crystal was carried out. Spectral hole burning in the absorption lines of defect aggregates at 649.5, 655 and 681 nm was performed. By virtue of the high Debye temperature of the diamond the holes burnt-in at LHeT were observable in the spectra up to ~ 200 K.

1. Introduction

For a successful application of the spectral hole burning (SHB) new materials are needed, where HB (or at least recording of the written-in at low temperature spectral modulations) would be performable at liquid nitrogen or at room temperature. In reality, it means finding compromise between two conditions which are in some respect contradictory: on one hand, the photochromic defect (impurity) has to be in weak interaction with the surrounding to ensure minimal homogeneous width of the optical transition, on the other hand the defect must "feel" quite well the non-regularities of the surrounding crystal to achieve an as-large-as-possible inhomogeneous width of the spectral line.

Some progress has been made in using inorganic defective crystals as materials for SHB. In Sm^{2+}: BaClF crystal SHB has been performed, while the recorded holes have been stored at room temperature [1]. In Sm^{2+}: $BaFCl_{0.5}Br_{0.5}$ compound HB has been carried out at LN temperature [2], and in Sm^{2+}: $SrFCl_{0.5}Br_{0.5}$ even at room temperature [3]. In the neutron-irradiated sapphire at LHeT the burnt-in spectral holes reveal extremely high thermoresistance and can be restored even after warming the specimen up to 670 K [4].

The purpose of this investigation was to study the possibilities of using neutron-irradiated diamond crystals as material for high-temperature SHB.

The classification of natural diamond crystals is based on the spectroscopic methods. Ia-type crystals are defined as containing nitrogen atoms in an aggregate form (in IaA-type nitrogen atoms exist mostly in pairs; in IaB_1- or IaB_2-type they constitute large aggregates). Ib-type crystals contain nitrogen in the form of isolated defect atoms (here belong most of synthetic and very few natural crystals). Due to the importance of diamond in industry, much attention has been paid to investigations of electronic and optical processes in such crystals (see,

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e. g. reviews [5, 6]). Here only investigations of radiation-coloured crystals will be reviewed briefly. In [7], the absorption and emission spectra in the visible spectral region have been measured by varying the irradiation doze of neutrons and the regime of annealing. In [8], a comparison of aggregation of defects in neutron-irradiated Ib-type synthetic and IaA-type natural crystals has been carried out.

SHB in diamond crystals has been investigated at 415 nm absorption line [9] (N3-type defect containing 3 nitrogen atoms [10]). In samples prepared by means of electron irradiation SHB has been performed in the 496 nm spectral line (H4-type defect consisting of a vacancy and an aggregate of nitrogen atoms); in the 638 nm line (N-V-type defect consisting of vacancy+nitrogen atom); in the 741 nm line (GR1-type defect consisting of a single vacancy) [9, 11]. All the above-mentioned spectral holes have been burnt in at helium temperature and exist several tens on minutes [9, 12]. The burning process has been best understood in the case of N-V defect. It has been cleared up that the 638 nm line corresponds to the $^3E \leftarrow ^3A$ electron transition and that optical excitation leads to the redistribution of defects between the spin levels of the ground state. The relaxation rate in the spin ensemble determines the lifetime of spectral holes [12, 13]. In this work a piece of IaB-type natural diamond (linear dimensions ~ 3 mm), was prepared by irradiating with a neutron flux 10^{19} neutrons/cm^2 and subsequently annealing at 950 °C. In the experiments an XeCl-excimer-laser-pumped pulse dye-laser (spectral width of pulses ~ 0.4 Å) or an Ar$^+$-ion-laser-pumped Coherent CR-599 single-frequency dye laser were used. In the first case holes were detected in transmission spectra by using an incandescence lamp in combination with a double monochromator. By using the single-frequency laser, after burning the reduced-intensity laser beam was scanned several times over the actual spectral range and the transmittivity of the sample was recorded. HB experiments were carried out in the temperature range 5 K to 200 K, the sample being placed in the cold flux of helium vapours.
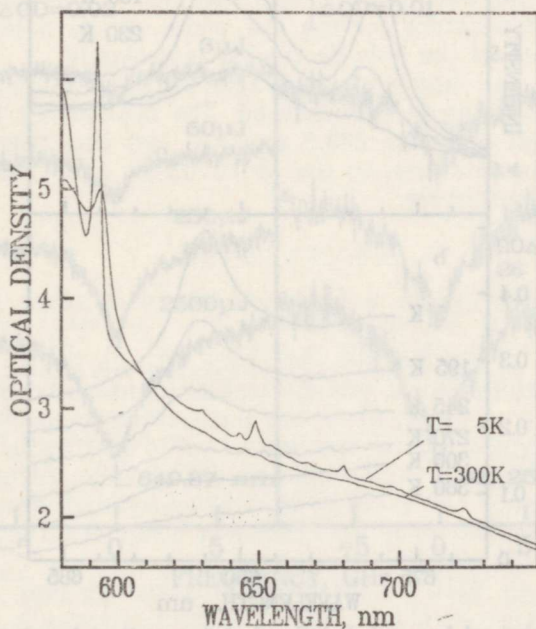

Fig. 1. Absorption spectrum of the neutron-irradiated diamond in the red spectral range at room and LHe temperatures, respectively.
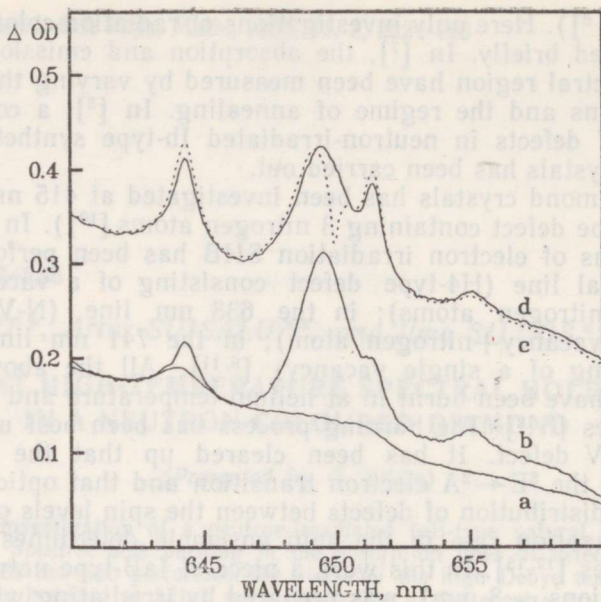
Fig. 2. Phototransformation of the spectrum on pulse-laser irradiation. *a* — initial spectrum at room temperature, *b* — the same spectrum at LHeT; *c* — spectrum after irradiating by 644.2 nm dye laser pulses for 20 min at the average power of 1.5 W/cm², *d* — the same spectrum after irradiating by 650 nm pulses for 12 min at the average power of 0.5 W/cm². Irradiation and measuring at 5 K. For better observation the curves *c, d* are shifted from *a, b*.
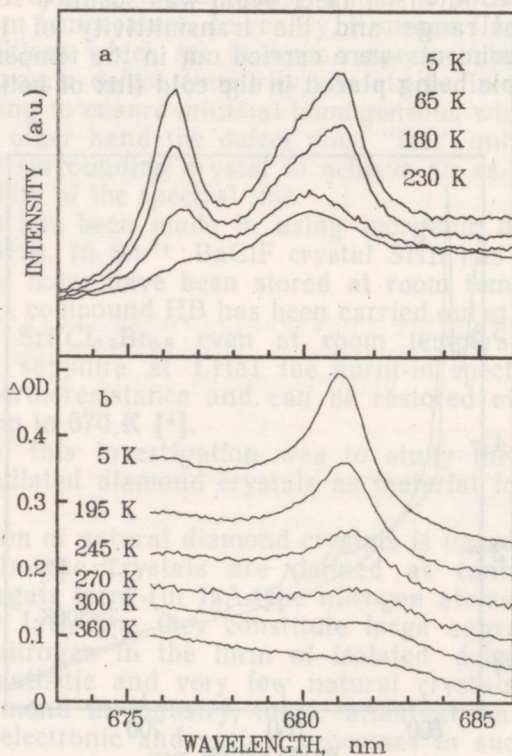

Fig. 3. *a* and *b* — Temperature dependence of the 681 nm line in absorption and luminescence spectrum, respectively. Luminescence was excited by a He-Ne laser at the power of 1 W/cm².
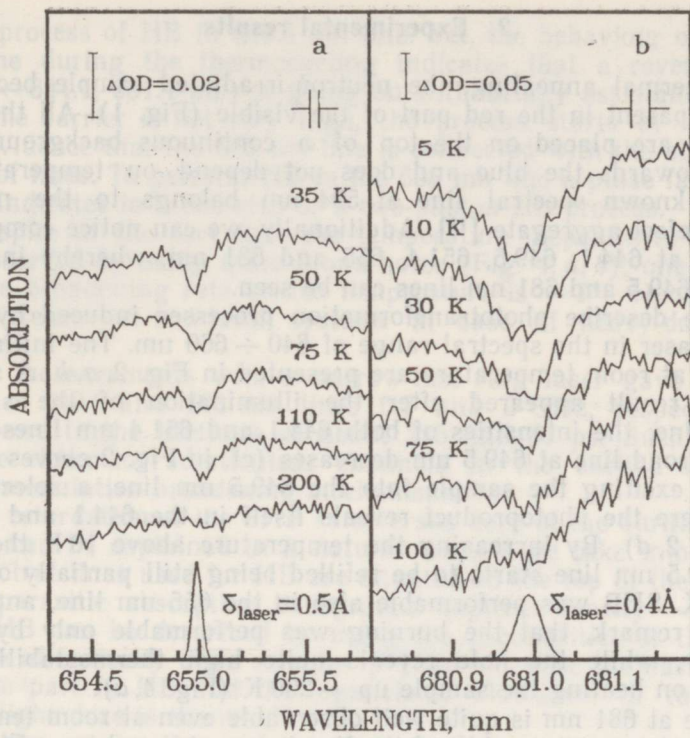
Fig. 4. *a* and *b* — Temperature behaviour of the spectral holes burnt in at 5 K in 655 and 681 nm lines, respectively.
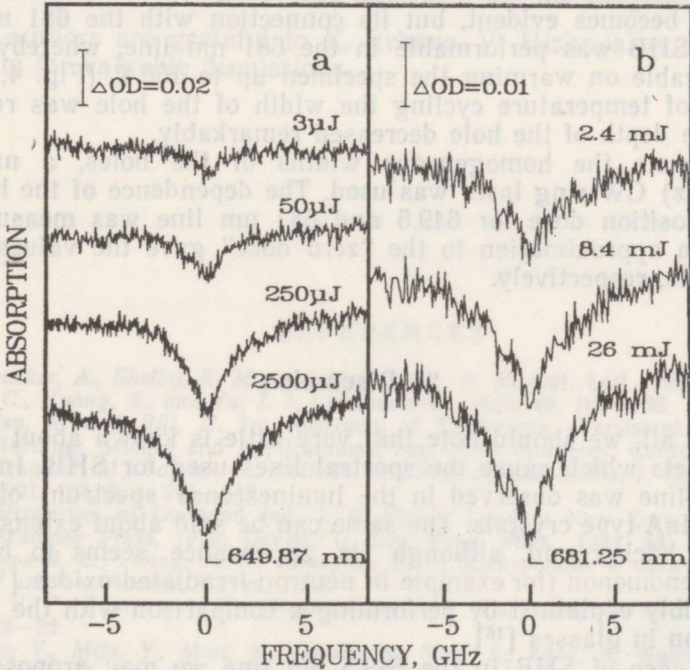
Fig. 5. Spectral holes burnt in the neutron-irradiated diamond by using single-frequency dye laser (linewidth 2 MHz). *a* — Dependence of the width of hole in 649.5 nm line versus on the exposition doze; *b* — the same for hole burnt in 681 nm line. In both cases the laser beam was focussed into the pinhole with diameter 0.5 mm.

2. Experimental results

After thermal annealing, the neutron-irradiated sample became partially transparent in the red part of the visible (Fig. 1). All the lines in the spectra are placed on the top of a continuous background, which increases towards the blue and does not depend on temperature. The quite well known spectral line at 594 nm belongs to the nitrogen+ radiation defect aggregate [11]. Additionally, we can notice comparatively week lines at 644.1, 649.5, 651.4, 655 and 681 nm, whereby in luminescence only 649.5 and 681 nm lines can be seen.

Now we describe phototransformation processes induced by using a pulse dye laser in the spectral range of 640 ÷ 660 nm. The initial spectra at 5 K and at room temperature are presented in Fig. 2, a, b. A somewhat surprising result appeared after the illumination of the sample in 644.1 nm line: the intensities of both 644.1 and 651.4 nm lines increase, while the broad line at 649.5 nm decreases (cf. in Fig. 2 curves b and c). In case of exciting the sample into the 649.5 nm line, a selective SHB occurs, where the photoproduct reveals itself in the 644.1 and 651.4 nm lines (Fig. 2, d). By increasing the temperature above 10 K the spectral hole in 649.5 nm line starts to be refilled being still partially observable up to 100 K. SHB was performable also in the 655 nm line, and running ahead, we remark, that the burning was performable only by using a pulse laser, while the hole reveals quite high thermostability, being observable on heating the sample up ~ 200 K (Fig. 4, a).

The line at 681 nm is quite well observable even at room temperature, whereby the temperature shift of the line is proportional to ~ T^4, which is in good agreement with the classical point defect model [14]. The resonance luminescence of this defect, which consists of two components (where at high temperature the component at 680 nm prevails), can be excited by using either an Ar^+ or a He-Ne laser (Fig. 3, b). An additional line at 676 nm becomes evident, but its connection with the 681 nm line is not clear. SHB was performable in the 681 nm line, whereby the hole was observable on warming the specimen up to 100 K (Fig. 4, b). After such kind of temperature cycling the width of the hole was restored at 5 K, yet the depth of the hole decreased remarkably.

To estimate the homogeneous widths of the holes, a narrow-line ($\delta \simeq 2$ MHz) CW ring laser was used. The dependence of the holewidths on the exposition doze for 649.5 and 681 nm line was measured (Fig. 5, a, b). An approximation to the "zero doze" gave the values 1.7 GHz and 4.0 GHz, respectively.

2. Discussion

First of all, we should note that very little is known about the origin of the defects which cause the spectral lines used for SHB. In [8], only a 681 nm line was observed in the luminescence spectrum of neutron-irradiated IaA-type crystals. The same can be said about extensive strong absorption background, although its appearance seems to be quite a regular phenomenon (for example in neutron-irradiated oxides ~ [4, 15]). One could possibly explain it by performing a comparison with the analogous phenomenon in glasses [16].

In the case of SHB in the 649.5 nm line we may propose that the burning mechanism could be light-induced defect site distortion which occurs during optical excitation of the defect. Such kind of HB mechanism exists in case of $Cm^{4+} : CeF_4$ crystal [17]. According to this model, 644.1 nm and 651.4 nm lines belong to the photoproduct which is created

in the process of HB in 649.5 nm line. Yet, the behaviour of the holes in this line during the thermocycling indicates that a reversible process (649.5 ← 644.1, 651.4 nm) is going on without any assistance by light as well. The barrier is not very high, the process starts at ~20 K. There is no evidence that the 655 nm line is connected with the above-discussed group of lines. To perform HB in the 655 nm line a pulse laser is needed, which indicates to a two-step or a two-photon HB process.

In spite of the fact that the temperature dependence of the holes was observed by using quite broad holes (Fig. 4, a, b), one can conclude that the broadening rate versus temperature is $\sim T^2$, which indicates to the existence of two-level systems in case of heavy-doze irradiated samples.

The measurements with a narrow-line ring laser gave homogeneous widths of 649.5 and 681 nm lines 0.7 and 2 GHz, respectively, which correspond to the lifetimes of about 215 and 80 ps. Such small values indicate either to radiationless channels in the excited states or to a strong modulation broadening mechanism.

The retardation of the SHB rate versus doze of the burning light (Fig. 5, a, b) can be explained in a natural way, if we take into account that the spectral lines used for HB are situated on the top of the strong continuous parasitic absorption background (optical density ~ 1.7). In this case SHB can be described by using the peculiarities of the process in the case of optically thick samples [18]. In our case the background does not take part in HB and the logarithmic slowdown of the hole depth versus light doze is the result.

To sum up, in virtue of the high Debye temperature (~1900 K) of diamond crystals, the zero-phonon lines of some defects exist even at room temperature. This allows in our case to observe spectral holes up to quite a high temperature (200 K), when the homogeneous width of the optical transititon becomes comparable with the inhomogeneous one.

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PÜSISPEKTRAALSÄLKAMINE NEUTRONVÄRVITUD TEEMANDIS

Neutronitega värvitud IaB-tüüpi loodusliku teemandi kristalli on uuritud spektroskoopiliselt ning agregaatdefektide neeldumisjoontes 649,5, 655 ja 681 nm on tehtud püsispektraalsälkamine. Teemantkristallide kõrge Debye' temperatuuri tõttu on heeliumi temperatuuril sissepõletatud spektraalsälgud jälgitavad objekti soojendamisel kuni 200 K.

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ВЫСОКОТЕМПЕРАТУРНОЕ ВЫЖИГАНИЕ СТАБИЛЬНЫХ СПЕКТРАЛЬНЫХ ПРОВАЛОВ В НЕЙТРОННО-ОКРАШЕННОМ АЛМАЗЕ

Проведено спектроскопическое исследование облученного нейтронами кристалла природного алмаза типа IaB. В линиях спектра поглощения 649,5 655 и 681 нм дефектных агрегатов проведено выжигание спектральных провалов. Благодаря высокой температуре Дебая в кристаллах алмаза выжженные при гелиевых температурах провалы наблюдаются и при повышении температуры до 200 K.