Photochromic effect in irradiated and annealed nearly IIa type synthetic diamond

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Abstract. We examined the effect of radiation damage and annealing on the optical properties of nitrogen-gettered nearly IIa type synthetic diamonds. It was found that the 2.156 eV centre, whose absorption is usually very weak, appears in these diamonds as one of the dominant absorption features. A new vacancy-related vibronic absorption system with zero-phonon line at 3.420 eV was observed. A pronounced photochromic effect was established for the 1.945, 2.085, 2.156, 3.420 and 4.325 eV absorption bands. Of all these bands only the 2.156 eV band remains in the absorption spectra after a proper photoexcitation. In contrast, for similarly treated type Ib diamonds we did not reveal any photoinduced changes in the 1.945 eV band absorption. Based on the results of optical bleaching and thermal recovery experiments, we conclude that the assignment of the 2.156 eV centre to the neutral charge state of the nitrogen–vacancy defect needs further verification.

1. Introduction

Most of the optical centres found so far in diamond are caused by nitrogen, which is the most abundant impurity in both natural and synthetic diamonds [1–3]. In the diamond lattice nitrogen may be present in different structural forms. The major ones are a single substitutional nitrogen atom (C-form), a pair of neighbouring substitutional nitrogen atoms (A-form) and four substitutional nitrogen atoms around a vacancy (B-form). Diamonds containing nitrogen impurity in the form of single substitutional atoms are termed as Ib type and those containing aggregated nitrogen forms are known as Ia type. Combination of the major nitrogen centres with the intrinsic point defects, i.e. vacancies and interstitials, gives rise to a diverse variety of optical centres. The most effective way to create intrinsic point defects in diamond crystal is irradiation with high-energy particles. Starting from the seminal works of Clark, Ditchburn and Dyer [4, 5] the effect of radiation damage on the optical properties of diamonds has been thoroughly studied in a prodigious number of works (for details, see the reviews [1–3]). At present the major radiation-induced phenomena in diamond are reasonably well understood. At the same time a great deal of uncertainty and inconsistency still remains in this field [6].

The 1.945 and 2.156 eV optical centres are known to be the major centres in irradiated and annealed type Ib diamonds. Furthermore, luminescence from both of these centres is frequently observed in as-grown CVD diamonds [7, 8]. It has been convincingly shown that the 1.945 eV centre is a vacancy trapped at a single substitutional nitrogen atom [9] and the

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charge state of the centre is singly negative $[N–V]^-$ [10]. The prevalence of the negative charge states is typical for defect centres in type Ib diamonds. It is accounted for by charge transfer from single substitutional nitrogen, which is a donor with an ionization energy of $\sim$1.7 eV [11].

The 2.156 eV centre is also comprised of a single nitrogen atom and a vacancy. Zaitsev *et al* [12] have proposed that a nitrogen interstitial on a $\langle 001 \rangle$ split site bound to a vacancy along the $\langle 001 \rangle$ axis is a defect responsible for the 2.156 eV system. Mita [13], subjecting type Ib diamonds to neutron irradiation and annealing, has observed that under high neutron dose the 1.945 eV absorption band decreases and simultaneously the 2.156 eV absorption band suddenly appears. The effect has been interpreted in terms of radiation-induced lowering of the Fermi level and a model for the 2.156 eV centre as the neutral charge state of the substitutional nitrogen–vacancy defect, $[N–V]^0$, has been proposed [13]. Recently, in the photoluminescence quenching experiments it has been found that under a certain additional illumination the decrease in emission from the 1.945 eV centre is accompanied by the increase of the 2.156 eV band luminescence intensity, and *vice versa* [14, 15]. The observed photochromic behaviour has been considered as further support for the assignment of the 2.156 eV centre to the neutral charge state of the nitrogen–vacancy defect.

Luminescence spectroscopy, which was applied in [14, 15], is generally a qualitative technique and it would be interesting to examine the photochromism of the nitrogen–vacancy centres using direct optical absorption measurements. However, a distinct feature of the 2.156 eV centre is very weak absorption strength, despite its strong luminescence. In [13] noticeable absorption in the 2.156 eV band was produced by heavy neutron irradiation of type Ib diamonds. But this method is restricted by a number of harmful effects, such as radioactivity and formation of multiply damaged regions in the diamond lattice. An alternative approach could be radiation damage of diamonds with low nitrogen content. For these diamonds one may expect that much lower irradiation dosages would be necessary to provide a corresponding lowering of the Fermi level. In high-pressure/high-temperature diamond synthesis, crystals with reduced nitrogen concentration can be readily obtained by addition of nitrogen-gettering elements, e.g. Ti, Zr, Al, to the growth system. Since pure diamonds correspond to IIa type, diamonds with low but still detectable nitrogen impurity we will refer to as nearly IIa type.

In the present work for the nitrogen-gettered nearly IIa type diamonds we found that after electron irradiation and subsequent annealing at 800 °C both the 1.945 and 2.156 eV systems appear as dominant absorption features. Besides, these diamonds also exhibited intense vibronic absorption bands with zero-phonon lines (ZPLs) at 2.085, 3.420 and 4.325 eV. The former is commonly observed in irradiated and annealed nitrogen-containing diamonds [6], but the detailed structure of this centre is still unknown. The 4.325 eV absorption system has been studied in [16]. It has been found that this band correlates in intensity with the 1.945 eV absorption band and has the same symmetry (A to E transition at a trigonal centre) and similar stress splitting parameters. Beside this unpublished work of de Sa [16] we did not find any other works concerned with the 4.325 eV absorption band. The 3.420 eV vibronic band, to the authors' knowledge, is observed for the first time.

For the irradiated and annealed nearly IIa type diamonds we revealed a pronounced photochromic effect. Upon a certain photoexcitation most of the vibronic bands can be completely removed from the absorption spectra and then restored by heat treatment. The results of optical bleaching and thermal recovery experiments are reported in the present paper. Using direct optical absorption measurements we examined the balance between the 1.945 and 2.156 eV bands and found that the $[N–V]^0$ model for the 2.156 eV centre needs further verification.
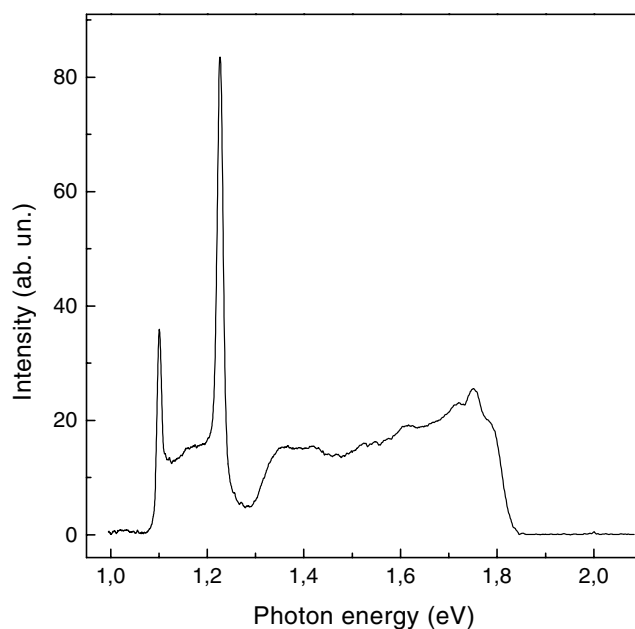
Figure 1. Spectrum of broadband near-infrared (NIR) light used in the photoinduction experiments. The light was selected from the mercury lamp by a combination of coloured glass and water filters. The spectrum was measured using a diffraction monochromator and spectrally independent detector.

2. Experimental details

Synthetic diamond crystals used in the present work were grown by the temperature gradient method on a high-pressure apparatus of a 'split-sphere' type (BARS) [17, 18]. An Ni–Fe alloy was used as the solvent/catalyst. For the most part we concentrated on nearly nitrogen-free diamonds, which were obtained by adding of 2 wt% of Ti to the growth system. Standard nitrogen-containing type Ib diamonds were employed for the parallel testing. The crystals were polished to form 1–1.5 mm thick plane-parallel plates.

The as-grown samples were irradiated by 2.5 MeV electrons with a dose of 1×10^{18} cm^{-2}. Temperature during the irradiation was kept to be not higher than 200 °C. The irradiation was performed using a commercial electron accelerator ELU-6 at Budker Institute of Nuclear Physics SB RAS, Novosibirsk. After electron irradiation the samples were annealed at 800 °C for 4 hours in a protective CO atmosphere.

Optical absorption measurements in the UV–visible–NIR range were carried out using a Shimadzu UV-3100 spectrophotometer with samples held at 80 K in a liquid nitrogen optical cryostat. Photoexcitation of samples was produced by a 250 W mercury lamp. The lamp was fitted to the spectrophotometer's sample chamber and the samples were illuminated directly inside the cryostat. The necessary excitation light from the mercury lamp was selected by interference and colour glass filters. The lines at 365 (365Hg or UV), 436 (436Hg or blue) and 546 (546Hg or green) nm as well as broadband near-infrared (NIR) light (the spectrum of this light is presented in figure 1) were used in the photoinduction experiments. In these experiments the samples were first annealed to 800 °C and then absorption spectra before and after illumination with a certain excitation light were measured. For the next excitation, prior to the illumination and absorption measurements, the samples were again annealed to 800 °C. We also examined the effect of the successive illumination of the samples with different excitation
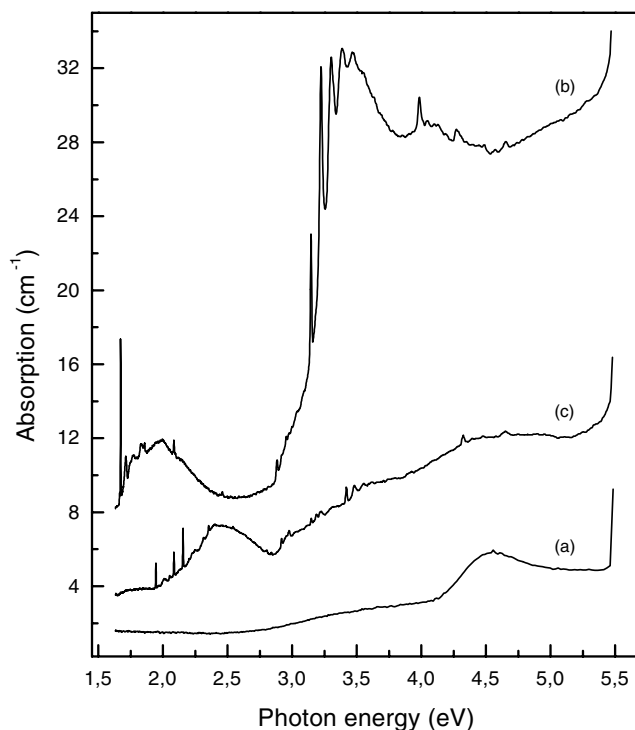
Figure 2. Absorption spectra recorded at 80 K for a nitrogen–gettered nearly IIa type diamond: (a) as-grown state, (b) after irradiation with 2.5 MeV electrons, (c) after subsequent annealing at 800 °C for 4 h. The spectra have been displaced vertically for clarity.

light. In this case, photoexcitations and absorption measurements were made in turn without an intermediate heating of the samples. The duration of each illumination was chosen to be long enough (20 minutes) to reach a quasi-stationary state (no further changes occurred in the absorption spectra on increasing the illumination duration). Thus, we eliminate the effect of the photoinduction kinetics and need not normalize the strength of photoinduced changes to the incident light intensity.

When the thermal stability of the photochromic effect was studied, the samples, after photoexcitation, were annealed at progressively increasing temperatures in the range of 100–800 °C. After heating to a certain temperature the sample was cooled and the absorption spectrum was measured, then the sample was heated to a higher temperature and the next point in the thermal recovery was obtained. The annealing was performed in an ordinary furnace in air or protective CO atmosphere.

During some preliminary experiments we found that the samples may be sensitive to the intense daylight illumination. Thus, throughout this study, the samples were annealed in the dark and all the intermediate operations, such as mounting the samples in the cryostat, were performed in darkened conditions. Besides, a special check was made on the influence of the sample illumination by the light from the spectrophotometer during the absorption spectra measurements. It was found that with the spectrophotometer slits used in the work the light intensity was too weak to produce any noticeable changes in the absorption spectra. Due to possible inhomogeneity of the optical centre distribution special precautions were made to measure absorption spectra from the same region of a sample. Using a 1 mm diameter aperture
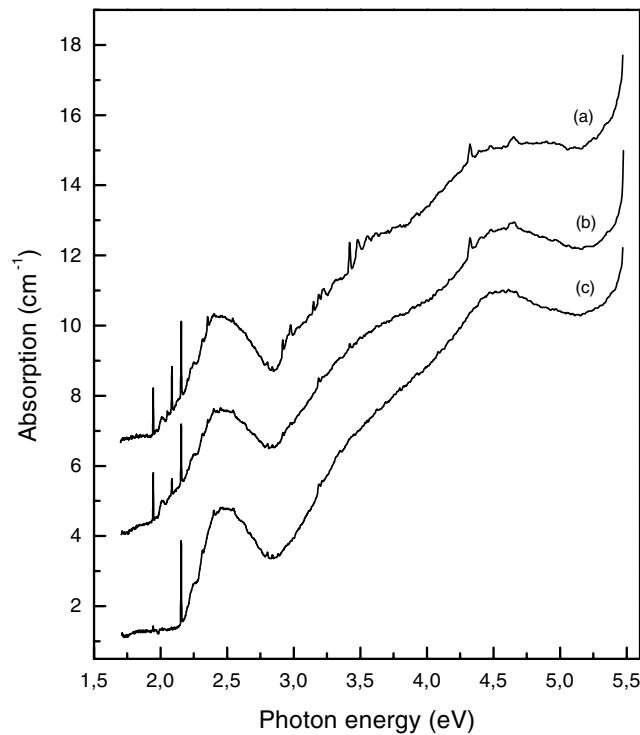
Figure 3. The effect of photoexcitation on the absorption spectrum of an irradiated and annealed nearly IIa type diamond. Starting from the initial state (spectrum (a)), the sample was successively illuminated with 365Hg line (spectrum (b)) and NIR light (spectrum (c)). The spectra have been displaced vertically for clarity.

absorption measurements were confined to {111} growth sectors.

In the present work we concentrate mainly on the changes occurring in the vibronic absorption bands produced by different optical centres. As a measure of the band intensity the absorption strength A integrated over the relevant zero-phonon line was used:

$$A = \int_{ZPL} \mathrm{d}E\, \mu(E) \tag{1}$$

where E is the photon energy measured in meV and $\mu(E)$ is the absorption coefficient measured in cm^{-1}.

3. Experimental results

Figure 2(a) shows a typical absorption spectrum measured for the as-grown nitrogen-gettered diamond samples. Weak continuously rising absorption in the visible–UV range and a band peaking at about 4.6 eV are caused by the residual impurity of single substitutional nitrogen. It has been shown previously [19] that the 4.6 eV band correlates in intensity with the infrared absorption band at 1130 cm^{-1}, which is related to the C-form nitrogen and commonly used for determining nitrogen concentration. Using expressions obtained by Chrenko *et al* [19] and Woods *et al* [20] we can estimate nitrogen concentrations in our nitrogen-gettered samples. For the sample whose spectra are presented in figure 2 we obtain a value of about 1 ppm and

this is a typical nitrogen concentration for all nearly IIa type diamonds used in the present work. It should be noted that despite a nickel-containing solvent/catalyst was used for the diamonds growth, none of the nitrogen-gettered samples showed any absorption features related to nickel impurity. So, if nickel is present in these samples, its concentration is lower than the limit of detection of the optical absorption technique.

Irradiation of the samples with 2.5 MeV electrons resulted in formation of both neutral (V^0) and negatively charged (V^-) vacancies, which give rise to the vibronic absorption bands with zero-phonon lines at 1.672 (GR1) and 3.150 (ND1) eV, respectively (figure 2(b)). Besides these dominant bands, some much weaker absorption features were also found after irradiation. These are a peak at 1.86 eV, a peak at 3.985 eV with an accompanying series of lines (so-called R11 centre) and a peak at 2.085 eV. The former two absorption systems are thought to be related to the self-interstitial [21]. Concentration of the vacancies produced by the irradiation can be estimated applying the relationships obtained by Davies *et al* [22] and Twitchen *et al* [23]. Again, for the spectrum shown in figure 2(b) we obtain 1.6 ppm for the neutral and 0.9 ppm for the negative vacancies. Note that the concentration of V^- is very close to the concentration of single substitutional nitrogen centres in the as-grown samples.

Annealing the irradiated samples at 800 °C for 4 h resulted in a substantial decrease of the vacancy-related absorption bands (figure 2(c)). In the same time the 2.085 eV peak with a correlated peak at 2.916 eV slightly increased in intensity and vibronic absorption bands with ZPLs at 1.945, 2.156, 3.420 and 4.325 eV appeared in the spectrum. Along with these major absorption systems, weak peaks at 2.051, 2.354, 2.804 and 2.840 eV were also found to appear on annealing. However their intensities are very low, actually just above the level of the instrumental noise, so that studying the photochromic effect we did not perform a detailed analysis for these minor absorption features. Of particular interest is the observed vibronic system with ZPL at 3.420 eV. The dominant phonon energies of this system lie at (60 ± 2) and (125 ± 5) meV. We did not find any references concerning this vibronic absorption band, so it seemingly is found for the first time. The possible origin of the 3.420 eV system will be discussed below.

In the photoinduction experiments we found that starting from the initial state, i.e. after annealing the samples to 800 °C, illumination of the samples with the 546Hg line and NIR light did not produce any noticeable changes in the vibronic bands absorption. However, starting from the same initial state, illumination with the 436Hg and 365Hg lines resulted in a considerable photochromic effect. Moreover, what is more surprising, if, after illumination with the blue or UV light, the sample was directly illuminated with the NIR light, the photoinduced changes became even more prominent. Figure 3 illustrates the changes of the absorption spectrum induced by the successive illumination of the sample with the 365Hg line (spectrum b) and the NIR light (spectrum c). It is clearly seen that as a result of this illumination procedure most of the vibronic systems found in the initial state completely disappeared in the absorption. The 1.945 eV band substantially decreased leaving only a weak peak at the ZPL and the 2.156 eV system slightly increased. No new sharp absorption features in the examined spectral range appeared as a result of the photoexcitation. The spectra presented in figure 3 also show that photoinduced changes occurred not only to the well resolved vibronic systems but also to some broad absorption bands and, possibly, the absorption continuum. An accurate analysis of these features is rather complicated. The only thing that can be defined more or less strictly is a broad absorption band with maximum at about 4.6 eV, which appears after the photoexcitation.

The results of the detailed analysis of the photoinduced changes occurring to the vibronic absorption bands are summarized in figure 4 (zero absorption strength means that intensity of a corresponding zero-phonon line is lower than the detection limit). It follows that all the
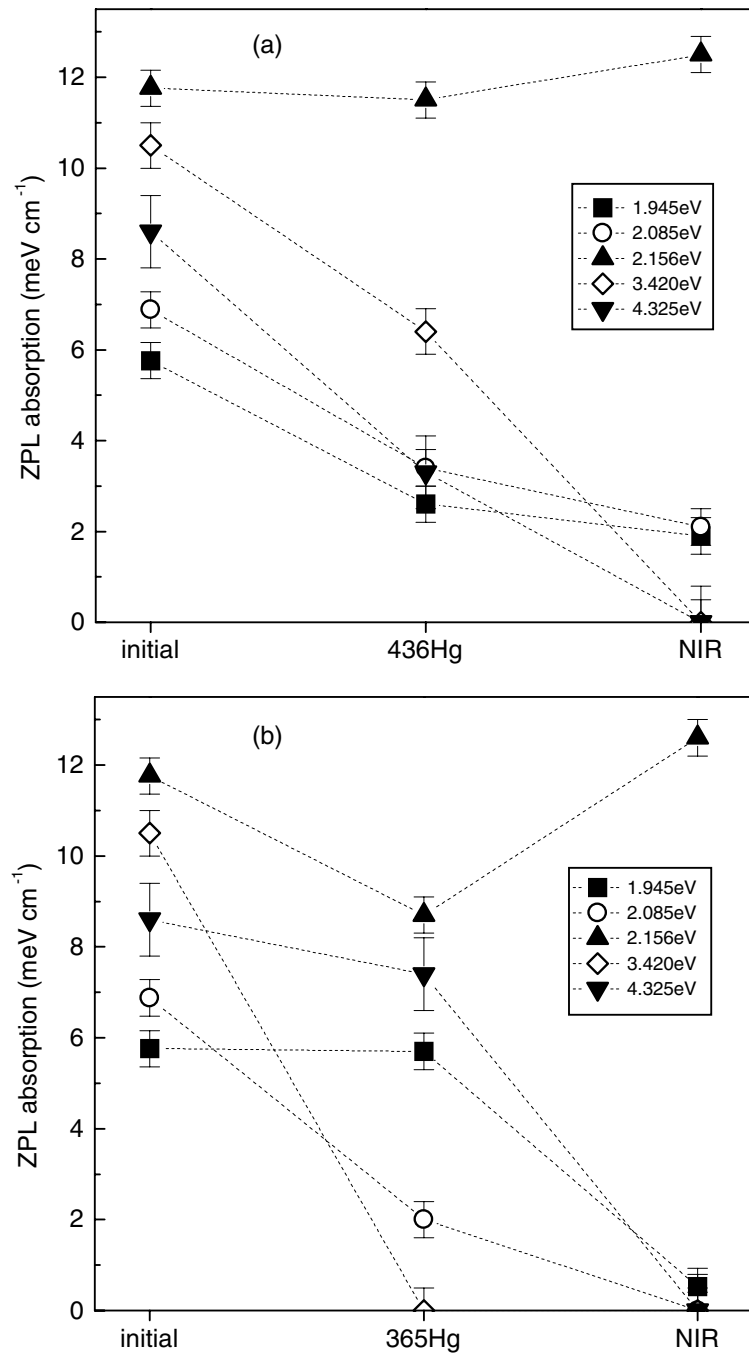
Figure 4. The effect of the photoexcitation on the absorption strength of the dominant vibronic absorption bands. The sample was successively illuminated with the 436Hg line and NIR light (a), and with the 365Hg line and NIR light (b).

absorption systems, which we take care of in the present work, are strongly photochromic. It should be stressed that starting from the same initial state, illumination of the samples with
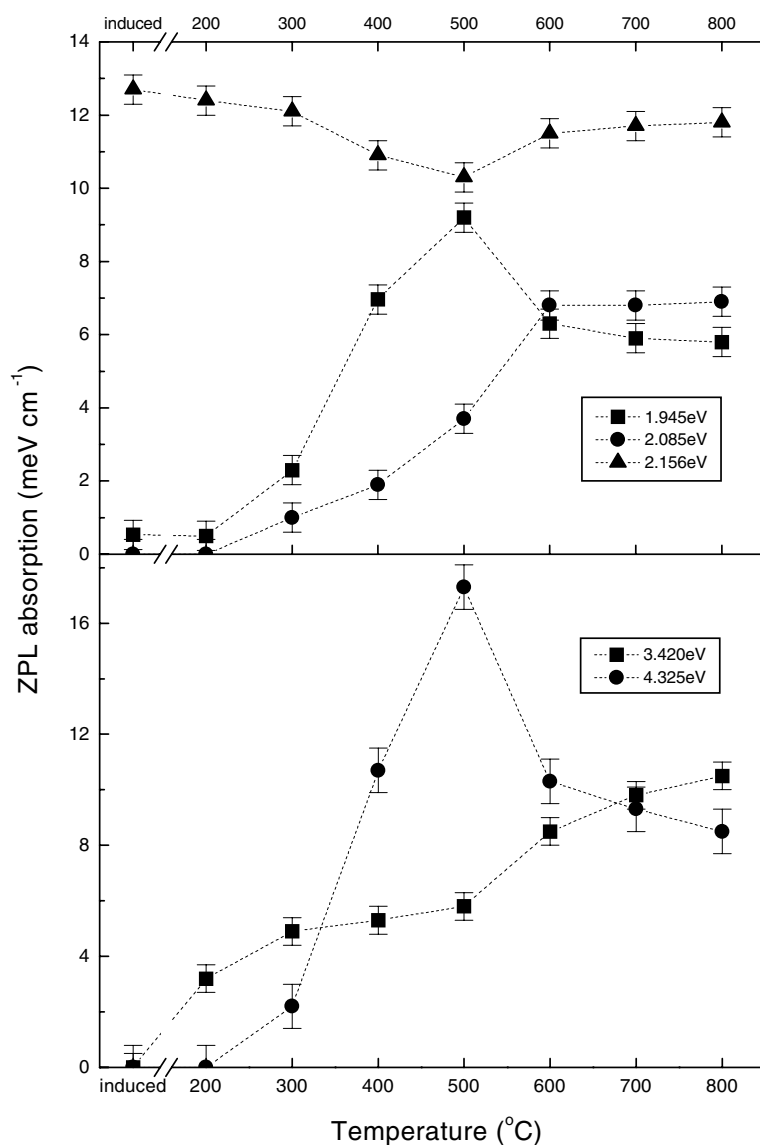
Figure 5. Thermal recovery of the photochromic absorption bands. The induced state was produced by successive illumination of a sample with the 365Hg line and NIR light.

the 436Hg and 365Hg lines has different influence on the absorption strength of the 1.945 and 2.156 eV zero-phonon lines. Illumination with the 436Hg line reduces the 1.945 eV absorption system and practically does not change the 2.156 eV system. Illumination with the 365Hg line results in a reverse effect. The 2.085 and 3.420 eV vibronic bands decrease after illumination with both the 436Hg and 365Hg lines, but the degree of the photoinduced changes is different for these systems. The 4.325 eV vibronic band upon the photoexcitation shows behaviour similar to that of the 1.945 eV band. We would like to note here once again that the data presented in figure 4 correspond to the quasi-stationary state in the sense that they do not change with increasing the illumination duration.

The photoinduced changes are stable upon heating the samples from 80 K to room temperature and start to decay at temperatures 200–300 °C. Heating of the samples to 800 °C completely restores the absorption spectra to the initial state, i.e. the state before the photoexcitation. Figure 5 shows the behaviour of the dominant absorption systems upon consecutive annealing of a sample photoexcited by the combined 365Hg and NIR illumination (see figure 3(c)). The 1.945 eV system starts to increase and the 4.325 eV system appears after heating the sample to 300 °C. At higher temperatures both the systems grow rapidly and show maximum absorption strength after heating to 500 °C. Heating to 600 °C leads to a step-wise decrease of the 1.945 and 4.325 eV systems and after heating to 700 °C they practically do not change. The 2.156 eV system demonstrates an annealing behaviour somewhat inverse to that of the 1.945 and 4.325 eV systems. Starting from 300 °C it gradually decreases and reaches minimum intensity after annealing to 500 °C. Annealing to 600 °C results in an increase of the 2.156 eV absorption band and, within the limit of error, it does not change at higher annealing temperatures. The 2.085 eV system appears after heating the sample to 300 °C and than grows continuously up to annealing to 600 °C, where it reaches an absorption magnitude corresponding to the initial state. The 3.420 eV system seems to have two stages in the thermal recovery. It appears after annealing to 200 °C. Then in the temperature range 300–500 °C it changes quite slightly and again increases at the annealing temperatures 600 °C and higher. A broad absorption band with maximum at about 4.6 eV, which was found to appear after the photoexcitation, starts to decrease at the annealing temperature of 300 °C and after heating to 400 °C it cannot be unequivocally identified in the absorption spectra.

All the experimental results presented in the above were well reproducible for multiple experimental cycles performed for the same sample and were similar for all nitrogen-gettered diamond samples used in the work.

The photochromic effect established for the nitrogen-gettered diamonds was also examined for nitrogen-containing type Ib diamond samples. The concentration of single-substitutional nitrogen in these diamonds was in the range 100–200 ppm. After electron irradiation and annealing at 800 °C for 4 h, their absorption spectra were completely dominated by the 1.945 eV vibronic band. Neither 2.085 nor 2.156 eV systems were found in the absorption. Absorption measurements for photon energies higher than 3 eV were prohibited by strong continuous absorption caused by single substitutional nitrogen. Photoexcitation procedures the same as for the nitrogen-gettered diamonds were applied. It was found that none of the photoexcitation produced any noticeable changes in the absorption spectra of the type Ib diamonds.

4. Discussion

Let us discuss first the effect of radiation damage and annealing on the optical properties of nitrogen-gettered nearly IIa type diamonds. These diamonds are characterized by very low but still noticeable concentration of single substitutional nitrogen, which according to our estimations is about 1 ppm. A moderate dosage (1×10^{18} cm^{-2}) of 2.5 MeV electrons results in formation of both neutral and negatively charged vacancies, with the total concentration of vacancies being even higher than that of the nitrogen. This implies that by the treatment the Fermi level is shifted well below from the energy level of the nitrogen donor. After annealing of the irradiated diamonds at 800 °C the appearance of the 2.156 and 2.085 eV absorption systems is observed. This finding is fully consistent with the results previously reported by Mita [13]. The only difference is that Mita applied heavy neutron irradiation to provide a corresponding lowering of the Fermi level in type Ib diamonds. The fact that both the 2.156 and 2.085 eV systems are usually difficult to detect in absorption for type Ib diamonds containing high amount of nitrogen impurity and appear if the Fermi level is sufficiently lowered indicates that

the charge state of the defect centres responsible for these systems is likely to be neutral. It is worth noting that the present study, besides supporting the results of Mita [13], also shows an effective way for creating the 2.156 eV centres in amounts sufficient for optical absorption spectroscopy. This would be helpful for further investigations of the specific features, e.g. strong deviation of the emission and absorption band shapes from the mirror image (compare figure 3(c) and, for example, figure 1(a) from [24]), inherent in the 2.156 eV centre.

Of considerable interest is the observed vibronic absorption band with ZPL at 3.420 eV. It is formed on annealing at temperatures where the vacancies are mobile. Thus, we may suppose that the centre responsible for this band contains at least one vacancy. The fact that this centre to the authors' knowledge has been found for the first time leads us to a further assumption that it is neither intrinsic nor nitrogen-related. As possible candidates for the impurity defect, which traps a vacancy, one may regard nickel and boron. Although we did not find any absorption bands related to the nickel impurity, nevertheless its presence in the as-grown nitrogen-gettered diamonds cannot completely be ruled out. Boron, which can easily be incorporated into the diamond lattice, is quite an abundant impurity in the graphite used in the high-pressure/high-temperature diamond synthesis. Actually, in some cases, providing nitrogen concentration is low, the absorption peaks due to uncompensated boron acceptors can be observed even if boron was not deliberately added to the growth system [25]. The IR absorption spectra measured for the diamonds used in this work did not reveal boron-related peaks. However, boron can be present in an optically inactive state being compensated by the nitrogen. Obviously, further investigations are necessary for the identification of the 3.420 eV vibronic band. The fact that the 3.420 eV band can be bleached by illumination and restored by heating indicates that the defect centre responsible for this band may exist in different charge states.

The photochromic effect observed in this study for the irradiated and annealed diamonds of nearly IIa type is of great concern and represents a challenging problem. In these diamonds the absorption strength of the 1.945, 2.085, 2.156, 3.420 and 4.325 eV bands is strongly affected by the photoexcitation. Except for the 2.156 eV band, all the other bands can be completely removed from the absorption spectra. In contrast, type Ib diamonds following the same irradiation and annealing do not exhibit any photochromic changes in the 1.945 eV absorption band, which completely dominates in this case. The absence of the photoinduced changes in the absorption of type Ib diamonds is apparently due to high concentration of nitrogen donors, which stabilize the position of the Fermi level. In nitrogen-gettered nearly IIa type diamonds nitrogen concentration is very low: actually, it is nearly the same or even lower than the concentration of vacancies created by the electron irradiation. Thus, the position of the Fermi level in these diamond crystals is not controlled by one dominant species but depends on the charge distribution over different electronic levels present in the forbidden band. Another factor that enables the observation of the photochromic effect in nearly IIa type diamonds is the presence of some specific centres acting as traps for the charge carriers. The constitutive role of the traps emerges from the following findings: (1) photoexcitation with photons whose energies are lower than the energies of zero-phonon transitions at the photochromic centres results in considerable photoinduced changes; (2) the photoinduced changes remain after turning off the illumination; (3) thermal recovery occurs upon heating the samples to relatively high temperatures. Since the 1.945 eV band corresponds to the negatively charged [N–V] centre, it is reasonable to suppose that its growth during the thermal recovery is associated with the depletion of some electronic traps. This band reaches maximum intensity after heating the samples to 500 °C. Assuming it is that temperature (T_m) when the Fermi level passes through the energy level of the relevant trap, we can roughly estimate the depth (E_t) of this trap using

an approximate relationship [26]:

$$E_t = 25kT_m. \tag{2}$$

For the temperature of 500 °C we obtain for the thermal activation energy a value of $\sim$1.7 eV. Note that this value is just the same as the ionization energy of single substitutional nitrogen donor. Furthermore, the broad absorption band with a maximum at 4.6 eV, which appears upon photoexcitation and vanishes on annealing, is rather similar to the nitrogen-related band peaking at the same energy. Thus, we may suggest that single substitutional nitrogen may be one of the traps involved in the recharging processes.

The results of the optical bleaching and thermal recovery experiments (see figures 4 and 5) clearly demonstrate that the photochromic effect revealed for nearly IIa type diamonds has quite complicated character. Illumination of the samples with both the blue and UV light induces considerable changes in the absorption spectra. But these changes become even more prominent if the blue or UV light illumination is followed by illumination with the NIR light. So, we may suppose that the photoinduced recharging processes proceed through a number of stages involving different trapping centres. On the thermal recovery most of the photochromic absorption bands show a noncontinuous behaviour, which is possibly due to a consecutive depletion of different electronic and hole traps. In attempts to gain an understanding of the observed photochromic effect we encounter three major difficulties. First, for all the centres whose photochromic behaviour is found in this work, the corresponding electronic levels have not been definitely located relative to the electronic band states of the host lattice. Second, the observed multistage character of the photo- and thermally induced recharging processes indicates that besides single substitutional nitrogen there must be present some other trapping centres, which so far are unknown. Third, optical transitions may proceed both from a defect level to the conduction band and from the valence band to a defect level, that complicates understanding of what actually happens upon the photoexcitation. In the present study we revealed only some general features of the photochromic changes in the irradiated and annealed nearly IIa type diamonds. It is obvious that this phenomenon urgently needs further detailed investigations with the application of other experimental techniques, e.g. EPR, thermally stimulated luminescence and electric current.

Finally, we would like to draw attention to some experimental findings, which appear to be of key importance.

Considering the experimental data obtained so far for the 2.156 eV optical centre it appears that the assignment of this centre to the neutral nitrogen–vacancy pair, $[N-V]^0$, is rather well justified. However the results we obtained studying the photochromic effect pose some questions for this model. As follows from the optical bleaching experiments (see figure 4) the 1.945 and 2.156 eV bands show weakly correlated behaviours under excitation with the blue and UV light. Illumination of samples with the 436Hg line results in a considerable decrease of the 1.945 eV band intensity, whereas the 2.156 eV band, within the limit of error, does not change. Illumination with the 365Hg line leads to a reverse effect: the 2.156 eV band decreases and 1.945 eV band remains the same. Using the data acquired from the optical bleaching and thermal recovery experiments we examined the balance between the 1.945 and 2.156 eV centres. Figure 6 shows a plot of absorption strength of the 1.945 eV ZPL versus absorption strength of the 2.156 eV ZPL, for multiple experimental cycles carried out for the same sample. From this figure one can see that in fact some general tendency towards an increase of the 2.156 eV band with decrease of the 1.945 eV does exist. But this trend is rather rough and moreover there are a number of experimental points which are out of the trend. Note that these jumped aside points were obtained from spectra recorded after illumination of a sample with the 365Hg line, that is no sample repositioning was involved and these points
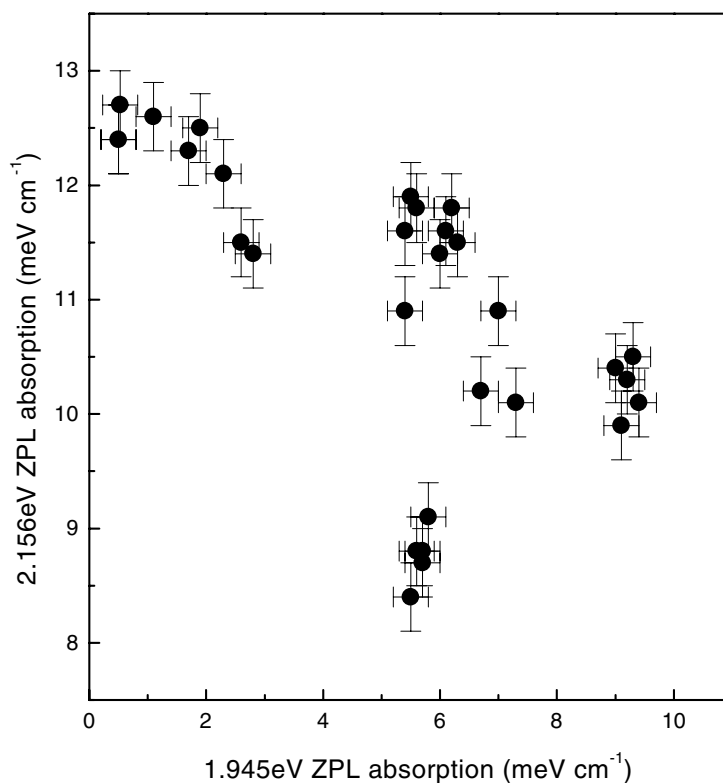
Figure 6. The absorption strength of the 1.945 eV ZPL versus the strength of absorption in the 2.156 eV ZPL. The data were obtained from multiple cycles of the photoinduction and thermal recovery experiments performed for the same diamond sample.

cannot be accounted for by the uncertainty in relocating a specific area on the sample surface. Thereby, the correlation between the 1.945 and 2.156 eV centres is not so straightforward as could be anticipated for different charge states of the same defect centre. But at the present stage we would refrain from concluding that the $[N–V]^0$ model for the 2.156 eV centre is incorrect. In fact, the situation may be more complicated if, for instance, the $[N–V]$ complex can exist in charge states other than neutral and negative. In any case further investigations are necessary to clarify the peculiar features found in this study for the 1.945 and 2.156 eV systems and to provide clear evidences for the assignment of the 2.156 eV centre to the neutral $[N–V]$ complex.

It was found that throughout all the experiments performed in this study the 1.945 and 4.325 eV absorption bands showed strikingly similar behaviours. In figure 7 we summarize the data obtained in the present work for the 1.945 and 4.325 eV zero-phonon lines. The correlation between these absorption bands is obvious, supporting previous results of de Sa [16]. The 4.325 eV vibronic system has a sharp zero-phonon line, which implies that neither ground nor excited states are in a band. Consequently, the ground state of the 4.325 eV centre should lie not higher than 1.2 eV from the valence band. The similarities between the 1.945 and 4.325 eV bands are so remarkable that the simplest suggestion could be that both the transitions occur at the same defect centre, i.e. $[N–V]^-$. In this case the first variant is that the same ground but different excited states are involved in the 1.945 and 4.325 eV transitions. However this
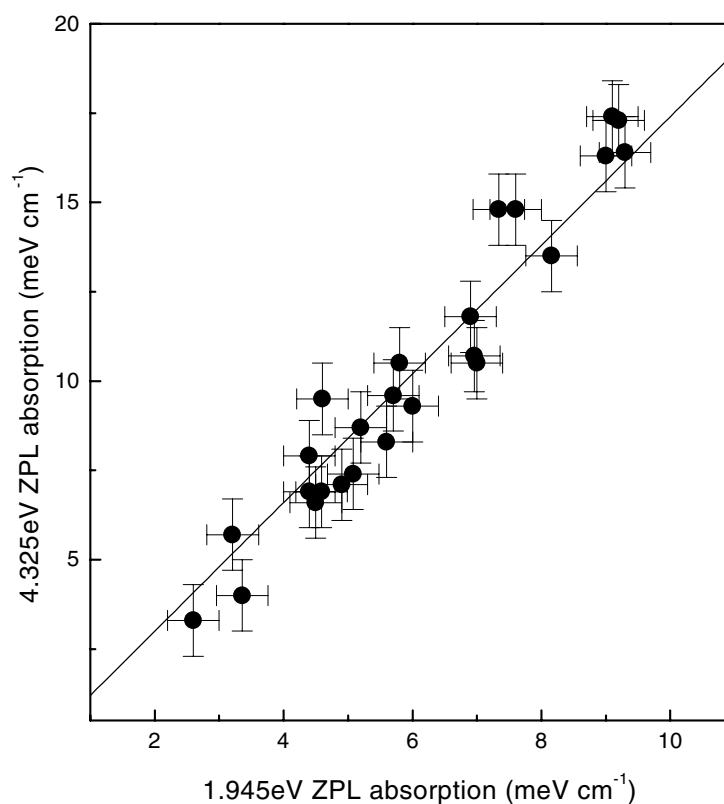
Figure 7. Experimental data for the strength of absorption in the 1.945 and 4.325 eV zero-phonon lines. The solid line shows the best fit to the data with the constraint that it passes through the origin to within the measurement error.

would imply that the $^3A_2$ ground state of the $[N–V]^-$ centre lies deep down in the forbidden band that appears to be unlikely. The second, more probable, variant comes from the result of theoretical work of Gross *et al* [27]. These authors using *ab initio* cluster methods have found that the $[N–V]^-$ centre has a filled a_1 level just above the valence band top and a transition from this level to the e level has been estimated to have an energy of 3–3.5 eV. This estimation is in fair agreement with the experimentally observed 4.325 eV transition. If however the 4.325 eV system corresponds to a distinct defect centre, it is most intriguing what it can be.

5. Summary and conclusions

For the nitrogen-gettered nearly IIa type diamonds we have found that after electron irradiation and subsequent annealing, along with the 1.945 eV band, the 2.085, 2.156, 3.420 and 4.325 eV vibronic bands appear as dominant absorption features. The 3.420 eV absorption system has been observed for the first time. It is suggested that either a nickel or boron impurity defect which captured a vacancy is the centre responsible for the 3.420 eV band. It has been established that all the vibronic bands found in the absorption are strongly photochromic. With an appropriate photoexcitation the 1.945, 2.085, 3.420 and 4.325 eV bands can be completely removed from the absorption spectra. Annealing the samples in the temperature range 200–800 °C annihilates the photoinduced changes. Defects acting as traps for the

charge carriers have been found to play a key role in the observed photochromic effect. It is demonstrated that single-substitutional nitrogen may be one of these traps. For nitrogen-containing type Ib diamonds following irradiation and annealing no photochromic changes have been observed in the absorption. The 1.945 eV band, which completely dominates in the absorption spectra of these diamonds, is stable upon the photoexcitation. The absence of the photochromic effect in type Ib diamonds is apparently due to rigid fixing of the Fermi level by single nitrogen donors. The balance between the 1.945 and 2.156 eV centres has been examined using direct optical absorption measurements. It has been found that the correlation between the 1.945 and 2.156 eV absorption bands is not stringent. Thus we may conclude that the assignment of the 2.156 eV centre to the neutral charge state of the [N–V] complex requires additional proof. The 1.945 and 4.325 eV vibronic absorption bands have been found to show strikingly similar behaviour during the both photoinduced recharging and thermal recovery processes. The observed correlation between these bands supports the results of an early unpublished work of de Sa [16]. A hypothesis that the 4.325 eV absorption band originates from a transition at the [N–V]$^-$ centre has been proposed.

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