The annealing of radiation damage in type Ia diamond

2009 J. Phys.: Condens. Matter 21 364209

(http://iopscience.iop.org/0953-8984/21/36/364209)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 364209 (8pp) doi:10.1088/0953-8984/21/36/364209

The annealing of radiation damage in type Ia diamond

Alan T Collins and Isaac Kiflawi

Physics Department, King's College London, Strand, London WC2R 2LS, UK

Received 5 April 2009, in final form 5 May 2009
Published 19 August 2009
Online at stacks.iop.org/JPhysCM/21/364209

Abstract
The kinetics of the recovery of radiation damage in type Ia diamond has been investigated using isothermal annealing at 600 °C. In diamonds having a reasonably homogeneous distribution of nitrogen the decay of the vacancy concentration with time can be approximately described by a single exponential. Previous investigations have identified 'fast' and 'slow' components in the annealing, and we show that the existence of more than one time constant is associated with inhomogeneous nitrogen concentrations. The measurements show further that, in order to obtain the oscillator strengths of nitrogen-vacancy centres, studies must be restricted to diamonds with moderately high nitrogen concentrations.

1. Introduction

In this investigation we address the issue of the 'fast' and 'slow' components in the annealing of the vacancy-related absorption reported by Davies *et al* (1992) for type Ia diamonds. We have also examined the validity of determining the oscillator strengths of nitrogen-vacancy centres from this type of measurement.

Irradiation of diamond at room temperature with electrons of energy 2–3 MeV produces vacancies and interstitials (Clark *et al* 1956). The vacancy can be present in two different charge states (Davies 1977)—neutral (V^0) or negative (V^-). V^0 gives rise to the 'GR' optical absorption; this comprises the GR1 vibronic band with a zero-phonon line (ZPL) at 1.673 eV, and higher excited states, GR2–GR8, at energies from 2.88 to 3.04 eV. V^- produces the ND1 absorption band with a ZPL at 3.150 eV. The $\langle 100 \rangle$ split-interstitial, believed to be in the neutral charge state, has its most prominent absorption in a peak at 1.859 eV. This is a localized vibrational mode (Smith *et al* 2004), associated with the much weaker ZPL at 1.685 eV.

The ratio of $[V^-]$ to $[V^0]$ depends principally on the concentration of nitrogen in the diamond and the form in which it is present (Davies 1977). (The square brackets here denote concentrations.) Single substitutional nitrogen behaves as an electrical donor, with ionization energy of 1.7 eV (Farrer and Vermeulen 1972). When this is the dominant impurity the diamonds are classified as type Ib, and for nitrogen concentrations in excess of a few tens of parts per million (ppm), the vacancies in an irradiated specimen are present predominantly as V^- (Davies 1977). In the majority of natural diamonds the nitrogen has aggregated to form A centres (pairs of nearest-neighbour substitutional nitrogen atoms (Davies 1976)) and B centres (four substitutional nitrogen atoms symmetrically surrounding a vacancy Loubser and van Wyk (1981)). When most of the nitrogen is aggregated, the diamonds are classified as type Ia, and the subdivisions IaA and IaB refer to specimens which contain nitrogen principally in the A form or the B form, respectively. The majority of natural diamonds contain both A aggregates and B aggregates, and are classified as type IaA/B. The A centre appears to have donor-like properties, with an ionization energy of approximately 4 eV (Denham *et al* 1977), but typically only about 25% of the vacancies are in the negative charge state in type Ia diamonds.

Some rare natural diamonds, classified as type IIb, have substitutional boron as the major impurity, at a typical concentration of 0.3 ppm. The boron behaves as an acceptor, with an ionization energy of 0.37 eV (Collins and Williams 1971). In irradiated type IIb diamonds $[V^-]$ is very small compared to $[V^0]$ (Davies 1977).

Boron, and the three forms of nitrogen described above, give rise to characteristic absorption in the infrared spectral region. When none of the characteristic absorptions is detectable the diamond is classified as type IIa. Again, in irradiated type IIa diamond, $[V^-]$ is small compared with $[V^0]$ (Davies 1977).

Assuming uniformity, the absolute concentration of V^- can be measured using electron paramagnetic resonance (Twitchen *et al* 1992), and therefore the strength of the ND1 absorption can be calibrated to determine $[V^-]$ using optical spectroscopy. In practice the area (or 'integrated absorption') of the ZPL is used from a plot of absorption coefficient in cm^{-1} versus photon energy in meV. For any defect, i, the area of the

ZPL may be written as

$$A_i = f_i[i], \tag{1}$$

where f_i is the oscillator strength for the defect and $[i]$ is the concentration (Davies *et al* 1992). From an analysis of the annealing of vacancies in type Ia diamonds Davies *et al* concluded that

$$f_{\mathrm{ND1}}/f_{\mathrm{GR1}} = 4.0 \pm 0.2. \tag{2}$$

One of the assumptions in deriving this value is that all the vacancies are captured by nitrogen during the annealing.

The ratio $f_{\mathrm{ND1}}/f_{\mathrm{GR1}}$ can, in principle, also be determined directly by changing the charge state of the vacancy. Dyer and du Preez (1965) showed that, by illuminating the diamond with intense light having a wavelength lying within the ND1 absorption band, A_{ND1} decreased and A_{GR1} increased. Following such a charge transfer the equilibrium ratio of $[\mathrm{V}^-]$ to $[\mathrm{V}^0]$ could be restored by heating the specimen for 4 h at 500 °C. The data obtained by Dyer and du Preez were measured at very low resolution, but it is possible to determine from their results that $f_{\mathrm{ND1}}/f_{\mathrm{GR1}}$ lies between 5.5 and 10 (Davies *et al* 1992). A recent high-resolution study (Iakoubovskii *et al* 2003) has determined that $f_{\mathrm{ND1}}/f_{\mathrm{GR1}} = 8$, whereas unpublished results from De Weerdt (2007) indicate that the ratio is 2.0 ± 0.3. The reasons for these inconsistencies in the ratio $f_{\mathrm{ND1}}/f_{\mathrm{GR1}}$ are not known at present. (It is, of course, important that the intensity of illumination to which the diamond is exposed during the measurement of the absorption spectrum is much less than that required to promote the charge-transfer process $[\mathrm{V}^-] \rightarrow [\mathrm{V}^0]$.)

When an irradiated type Ia diamond is annealed at 800 °C for 2 h, all, or almost all, of the GR1 and ND1 absorptions are destroyed. In a type IaA diamond the dominant absorption in the visible region is then the H3 vibronic band, with a ZPL at 2.463 eV, and in a type IaB diamond the H4 vibronic band with a ZPL at 2.499 eV predominates (Davies 1972, Clark and Davey 1984). In mixed-type IaA/B diamonds, both H3 and H4 are formed. The concentrations of the H3 and H4 centres are proportional to the areas of the corresponding ZPLs; in addition, the concentrations of the A and B forms of nitrogen, $[N_{\mathrm{A}}]$ and $[N_{\mathrm{B}}]$, respectively, can be determined from infrared absorption measurements in the defect-induced one-phonon region (Davies 1972, Clark and Davey 1984). Using diamonds covering a wide range of nitrogen concentrations, Davies (1972) and Clark and Davey (1984) have shown that [H3]/[H4] is proportional to $[N_{\mathrm{A}}]/[N_{\mathrm{B}}]$. The interpretation here is that at 800 °C the vacancies are mobile and they wander through the crystal until they are trapped at one of the forms of nitrogen. (Vacancies first become mobile at lower temperatures, certainly below 550 °C, but very much longer annealing times are required to destroy all the vacancy-related absorption.)

In type Ib diamonds, containing at least a few tens of ppm of nitrogen, the dominant optical centre produced after irradiation and annealing is the negative nitrogen-vacancy centre $(\mathrm{N-V})^-$ with a zero-phonon line at 1.945 eV (Davies and Hamer 1976). Many natural diamonds classified as 'type Ib' may contain similar concentrations of single nitrogen and A aggregates, and Collins (1980) noted that, in such specimens, after irradiation and annealing, the $(\mathrm{N-V})^-$ absorption was very much stronger than the H3 absorption. Assuming that the oscillator strengths of the two centres were similar (this assumption has subsequently been justified (Davies 1999)) Collins estimated that the ratio of trapping cross sections for single nitrogen and the A aggregate is ∼20.

The trapping cross sections for the A and B aggregates are also different; for type IaA/B diamonds the ratio of the areas of the H3 and H4 zero-phonon lines may be written quantitatively (Davies 1972, Clark and Davey 1984) as

$$A_{\mathrm{H3}}/A_{\mathrm{H4}} = 4 \times [N_{\mathrm{A}}]/[N_{\mathrm{B}}]. \tag{3}$$

This may also be expressed as

$$A_{\mathrm{H3}}/A_{\mathrm{H4}} = 2 \times [A]/[B], \tag{4}$$

where $[A]$ and $[B]$ are the concentrations of A and B aggregates, respectively. The different trapping cross sections for the various forms of nitrogen have been attributed to the presence of energy barriers (Mainwood 1994); having reached a trapping centre of a particular type, the vacancy has to overcome an energy barrier before being finally trapped to form a new defect. The energy barriers are different for the different forms of nitrogen (Mainwood 1994) and this leads to the differences in trapping cross sections.

At a constant temperature, when the annealing of vacancies occurs by a single, first-order process, the number of vacancies $V(t)$ at time t is related to the number $V(0)$ at the start of the anneal by

$$V(t) = V(0)\exp(-t/\tau), \tag{5}$$

where τ is a thermally activated decay time (Davies *et al* 1992). For vacancies diffusing in a simple cubic lattice, the probability P of reaching a trapping site is

$$P = C\nu \exp(-E_{\mathrm{a}}/k_{\mathrm{B}}T), \tag{6}$$

where C is the concentration of traps, ν is the attempt-to-escape frequency, E_{a} is the activation energy for vacancy diffusion, k_{B} is Boltzmann's constant and T is the temperature (Collins 1998). Although derived for a simple cubic lattice, the principles underlying equation (6) will also apply to the diffusion of vacancies in a diamond lattice.

Having reached the trapping centre, the vacancy can either climb the potential barrier, or diffuse away again. The overall probability P' of a vacancy-related defect being formed is therefore

$$P' = g(E_{\mathrm{B}})C\nu \exp(-E_{\mathrm{a}}/k_{\mathrm{B}}T), \tag{7}$$

where $g(E_{\mathrm{B}})$ is a function involving the barrier energy E_{B}. P' is effectively $1/\tau$ in equation (5), and we see that, for isothermal annealing of homogeneous diamonds with different concentrations of a single type of trapping centre:

$$C\tau = \text{constant}. \tag{8}$$

As expected from equation (8), during isochronal annealing irradiated type IIa diamonds must be heated to a higher temperature than irradiated type Ia diamonds in order to completely eliminate the GR1 absorption. However, the vacancies *can be* destroyed, and the annealing proceeds principally by first-order kinetics (Davies *et al* 1992), showing that type IIa diamonds contain trapping centres other than nitrogen. It is probable that the vacancies disappear at dislocations (Davies *et al* 1992).

In a typical experiment, annealing an irradiated low-nitrogen single-crystal diamond, produced by chemical vapour deposition, at 900 °C for 1 h, reduced the GR1 absorption from 9.4 to 0.7 meV cm^{-1} (Charles 2009). Substituting this information into equations (5) and (6), with $E_a = 2.3$ eV and $\nu = 10^{13}$ Hz (Davies *et al* 1992), yields the concentration of traps as $C = 7 \times 10^{-7}$ (i.e. 0.7 ppm). That calculated value is comparable with the measured change in the concentration of vacancies (∼0.4 ppm, using the oscillator strength from Davies (1999) of $f_{\mathrm{GR1}} = 1.2 \pm 0.3 \times 10^{-16}$ meV cm^{-1}, and dividing by 1.763×10^{17} to convert to ppm). The similarity of these two values gives confidence in the validity of this approach.

Finally, in this section, we note that, if an irradiated type IIa diamond is annealed at ∼400 °C, there is significant reduction (typically 15–20%) in the intensity of the GR1 band and all of the absorption associated with the ⟨100⟩ split-interstitial is destroyed (Allers *et al* 1998). In type Ia diamonds a similar reduction in the intensity of the GR1 band occurs on annealing at 400 °C, but no H3 or H4 absorption is produced (Kiflawi *et al* 2007), indicating that the vacancy is not mobile at this temperature. The fact that all the interstitial-related absorption is destroyed, but only ∼20% of the vacancy absorption, suggests that, during the irradiation, some interstitials are lost by alternative processes and that the rest form vacancy–interstitial pairs. At ∼400 °C these interstitials are mobile and annihilate with the nearby vacancies (Kiflawi *et al* 2007).

In previous studies of the annealing of vacancies in type Ia diamond at 600 °C the decay of the GR1 ZPL exhibited both fast and slow components (Davies *et al* 1992, Lawson *et al* 1992). Those authors ruled out recombination of vacancies and interstitials to account for the fast process, because the fast decay of GR1 absorption was correlated with a fast growth of H3 absorption. In the present investigation we have pre-annealed electron-irradiated diamonds at 400 °C in order to destroy the ⟨100⟩ split-interstitials. The annealing behaviour of the GR1 and ND1 centres has then been studied in detail, together with the formation of H3 and H4 centres.

2. Experimental details

The specimens chosen for this investigation were selected from a group of natural diamonds that had been used previously to study the creation of vacancies by irradiation damage (Kiflawi *et al* 2007). To facilitate the optical studies, each diamond had been polished to provide two parallel ‘windows’ on opposite sides of the crystal, with the rest of the stone retaining the original rough surfaces.

The nitrogen content of the diamonds, and the forms in which it was present, were determined by measuring the infrared absorption spectra at room temperature using a Nicolet Avatar 360 Fourier transform spectrometer with a beam condenser, and decomposing the absorption in the one-phonon region into the various components, using the proper conversion factors (Boyd *et al* 1994, 1995). To reduce the effects of possible inhomogeneity in nitrogen concentration, we chose samples where the ‘window’ area is less than 1 mm^2 and a thickness typically ⩽1 mm. The typical dimensions of the diamonds were 1.5–3 mm. Vacancies had been created by irradiating the diamonds at room temperature with 2×10^{18} cm^{-2} electrons of energy 3 MeV. (One specimen (N9-26) was irradiated at 2 MeV.) Absorption spectra in the ultraviolet, visible and near-infrared spectral regions were measured at 77 K using a Perkin-Elmer Lambda 800 double-beam grating spectrometer. In this instrument the sample is positioned after the monochromator, which scans from long wavelengths to short wavelengths. This arrangement minimizes the possibility of charge-transfer processes of the type described in section 1.

All the samples (except N9-26) were initially annealed at 400 °C to eliminate the ⟨100⟩ split-interstitials; this was monitored by the disappearance of the absorption peak at 1.859 eV associated with the interstitial (Kiflawi *et al* 2007).

To investigate the decay rate of vacancies and the speed of formation of H3 and H4, two type IaA and three type IaB diamonds, all with different nitrogen concentrations, were isothermally annealed at 600 °C for times up to 157 h. In an additional study, the relationship between the nitrogen concentration and the concentration of H3 centres formed after annealing was studied using seven type IaA diamonds (including the two that had been isothermally annealed at 600 °C). All these specimens were annealed at 900 °C for 4 h, after which the vacancies were completely annealed out. The nitrogen dependence of the formation of H4 centres was also checked using three type IaB specimens.

3. Results and discussion

3.1. The annealing of vacancies

As expected, annealing at 600 °C reduced the concentration of the neutral vacancies and caused the formation of H3 and H4 centres. Three variations in the decay curves for GR1 have been observed. For some diamonds, the decay differs little from that of a single exponential (figure 1(a)); for other specimens (figure 1(b)) the data are fitted much better using the two-exponential function

$$[\mathrm{V}^0] = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \qquad (9)$$

where a_1 and a_2 are constants determining the relative proportions of the ‘fast’ and ‘slow’ decays. The data for diamond B2 (figure 1(c)) could be fitted to equation (9) with $\tau_2 \gg \tau_1$ or to the expression

$$[\mathrm{V}^0] = a_1 \exp(-t/\tau_1) + \text{constant}. \qquad (10)$$

Equations (9) and (10) are, of course, equivalent when $\tau_2 \to \infty$, and there is little to choose between these two functions when fitting the annealing data for this diamond.

Although the behaviour in figure 1(a) is close to that of a single exponential, the fit is not entirely satisfactory because

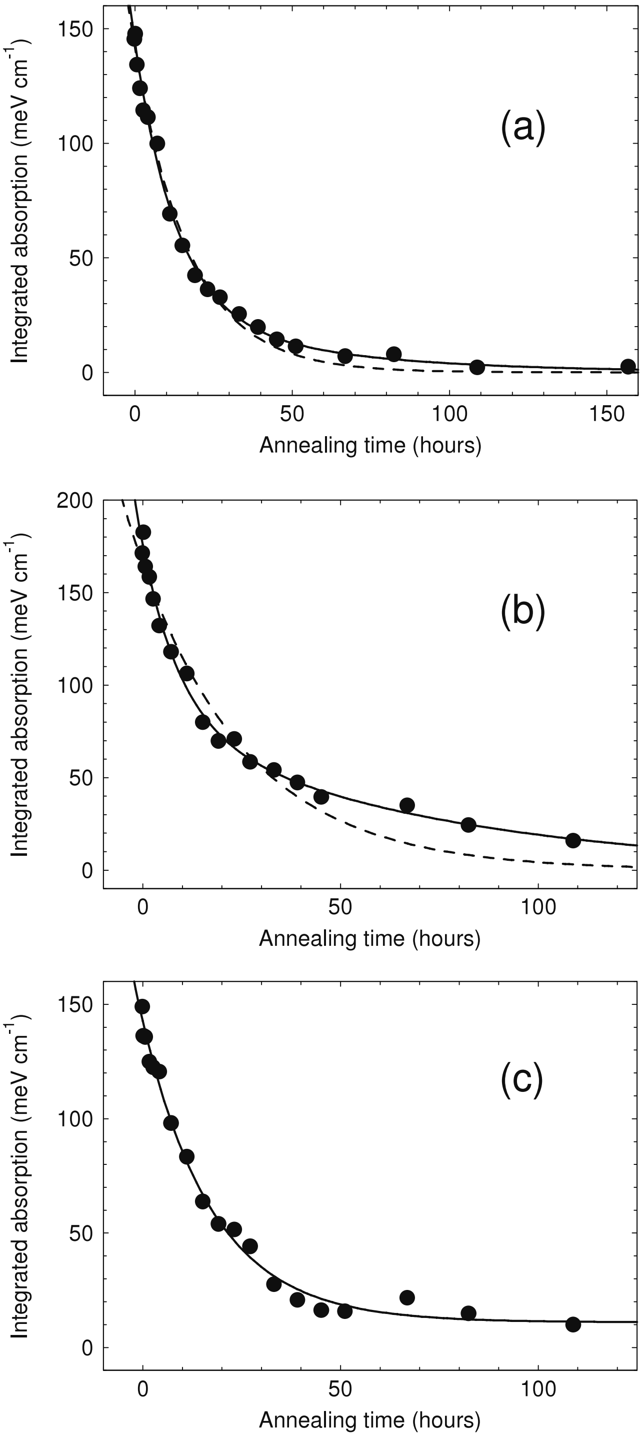

Figure 1. Annealing data for the GR1 zero-phonon line in three different diamonds, A18 (a), B3 (b) and B2 (c), heated at 600 °C. In (a) and (b) the best fit to a single exponential (equation (5)) is shown by a dashed line and the best fit to two exponentials (equation (9)) is shown by a continuous line. In (c) the data are fitted to a single exponential plus a constant (equation (10)).

some GR1 absorption remains long after the single exponential decay has become negligible. Figure 2 shows the information for figure 1(a) plotted using a logarithmic scale, and it is clear that the data at long annealing times require a two-exponential fit.

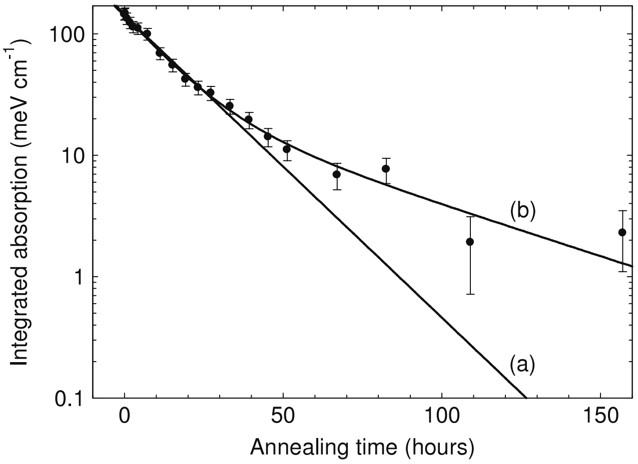

Figure 2. Annealing data for diamond A18 used to obtain figure 1(a), plotted on a logarithmic scale. (a) and (b) show the fits to a single exponential and to two exponentials, respectively.

Table 1 shows the parameters determined, using the Origin graphics program, from two-exponential fits to the isothermal annealing measurements carried out on five diamonds. Some of the uncertainties in table 1 are large, and this is a result of fitting experimental data which has a certain amount of ‘noise’. From repeated measurements on the same specimen we estimate that the average uncertainty in measuring the area (typically 150 meV cm^{-1}) of the GR1 zero-phonon line before annealing is approximately ±5%. In addition, all the area measurements have an uncertainty, which we estimate as (0.5–1.0 meV cm^{-1}), associated with determining the ‘background’ curve which must be subtracted before the area of the ZPL is evaluated. Although both of these uncertainties are relatively small, they can generate large errors in the parameters calculated from a two-exponential fit.

For only two specimens (A5 and A18) is the decay dominated by the fast exponential with reasonably small uncertainties in the parameters a_1 and τ_1. The time constant τ_1 is more than twice as large for A18, and the nitrogen concentration is almost $3\frac{1}{2}$ times lower, than for specimen A5. From equation (8), $C\tau$ = constant, we expect τ to be larger in diamonds with a lower nitrogen concentration, as observed, although numerical agreement with the equation is poor. We also note that, although the two diamonds have been treated identically, for the best-fitting curves, the proportion a_2/a_1 of the ‘slow decay’ is 0.05 for A5 and 0.24 for A18. It is well known that the nitrogen concentration in natural diamonds is inhomogeneous (Lang 1979) and this fact, taken with the observations reported above, suggests that the existence of more than one time constant in the isothermal decay is a result of an inhomogeneous nitrogen concentration. This proposal is supported by observations on diamond B2.

Examination of diamond B2 under an optical microscope, part way through the annealing sequence, clearly showed that the sample was inhomogeneous. One region was still green, indicating that very little annealing of the GR1 centre had occurred, while the remainder of the diamond was yellow because of the presence of H4 centres. Infrared absorption

Table 1. Parameters a_1, τ_1, a_2 and τ_2 determined from two-exponential fits to the isothermal annealing measurements for two type IaA diamonds (A5 and A18) and three type IaB diamonds (B2, B3 and B5). $[N_A]$ and $[N_B]$ are the concentrations of nitrogen in the A aggregate and B aggregate forms, respectively.

Sample	$[N_A]$:$[N_B]$ (ppm)	a_1 (meV cm^{-1})	τ_1 (h)	a_2 (meV cm^{-1})	τ_2 (h)
A5	995:0	149 ± 4	5.6 ± 0.4	7.3 ± 4.0	88 ± 78
A18	288:26	117 ± 26	13 ± 2.5	27 ± 26	51 ± 36
B2	12:452	131 ± 62	17.7 ± 6.7	~ 11	~ 6000
B3	0:811	95 ± 21	9.5 ± 2.4	80 ± 13	70 ± 40
B5	0:924	85 ± 17	5.7 ± 1.0	63 ± 17	21 ± 4

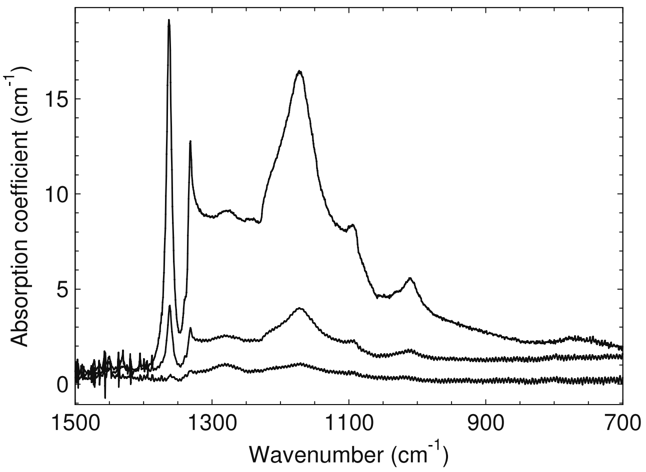

Figure 3. Infrared spectra for the type IaB diamond B2. The top spectrum was recorded with the full area of the sample illuminated with the infrared beam. The other two spectra were recorded for small regions within that area, using an infrared microscope. The bottom spectrum was obtained from the section of the diamond in which the GR1 zero-phonon line annealed relatively slowly.

Table 2. Nitrogen concentrations $[N_A]$ and $[N_B]$ in the A aggregate and B aggregate forms, respectively, determined for five samples using an infrared beam to illuminate the whole area of the sample, and using an infrared microscope to examine different small locations, *a* to *e*, within those areas.

Sample:	A5	A18	B2	B3	B5
$[N_A]$:$[N_B]$ through the whole area	995:0	288:25	14:452	0:811	0:924
Various locations					
a	995:0	310:0	14:400	10:448	0:943
b	995:0	288:25	14:450	15:296	0:920
c	970:0	288:25	12:380	9:800	0:895
d	970:0	270:20	9:73	0:800	0:924
e	933:0		9:50		

spectra were therefore obtained from several locations on this specimen, using an infrared microscope in which the beam was focused to an area 100 μm square on the diamond surface, and the nitrogen concentration was found to be much lower in the green region (figure 3). Following this observation, microscopic measurements were made on all the specimens and the results are summarized in table 2.

We see that diamonds A5, A18 and B5 appear reasonably homogeneous, and for diamond A18 the decay curve had a shape close to that of a single exponential (figure 1(a)). Specimen B3 is somewhat inhomogeneous, and a fitting equation with two time constants is essential to fit the decay curve (figure 1(b)).

Because the diamonds had only two polished surfaces it was only possible to detect the lateral inhomogeneity using infrared spectroscopy, but the nitrogen concentration may well be inhomogeneous as a function of depth (i.e. perpendicular to the polished surface) in these diamonds. As a simple model we can consider a diamond which has two 'layers'—one with a high nitrogen concentration and the other with a lower nitrogen concentration. The decay curve will then simply be the sum of two exponentials. Although a given diamond is unlikely to contain regions with just two different populations of nitrogen, an adequate fit to the decay curve can nevertheless be obtained with two exponentials. Where a type Ia diamond also has a region of near-type IIa material, the decay curve can be fitted to a single exponential plus a constant (as for diamond B2), where the 'constant' is actually a very slowly decaying exponential.

We have noted above that three diamonds appeared to be reasonably homogeneous. For these specimens 80% or more of the initial decay can be fitted by a single exponential and table 3 shows the $C\tau$ products. We find that values are approximately the same for samples A5 and A18. However, the result for the type IaB diamond B5 is surprising. As discussed in section 3.2, $g(E_B)$ in equation (7) is a factor of approximately 2 lower for trapping at the B aggregates, compared with trapping at the A aggregates. The $C\tau$ product for the type IaB diamond would therefore be expected to be a factor of 2 higher than that observed for the type IaA diamonds, whereas, within the calculated uncertainties, the value is comparable.

3.2. The dependence of H3 and H4 formation on the nitrogen concentration

A diamond that has been irradiated and annealed to 400 °C will contain both negative and neutral vacancies. These will both contribute to the final concentration of vacancy–nitrogen centres created after annealing. In order to compare our results with those of Davies *et al* (1992) we will calculate a 'vacancy absorption' $A_{\mathrm{GR1}} + \frac{1}{4}A_{\mathrm{ND1}}$.

In figure 4 we plot for seven fully annealed type IaA diamonds (circles) the ratio of the 'H3 area' to the vacancy absorption, versus nitrogen concentration; here the H3 area is the area of the H3 ZPL at the end of the annealing and the vacancy absorption is determined before annealing at 600 °C.

Table 3. $C\tau$ products for three diamonds for which the isothermal annealing curves were dominated by a single exponential decay.

Diamond	Nitrogen concentration (ppm)	Concentration of nitrogen trapping centres, C (ppm)	Time constant τ (h) for a single exponential decay	$C\tau$ (ppm h)
A5	965 ± 20	482 ± 10	6.3 ± 0.3	3040 ± 160
A18	290 ± 20	145 ± 10	17.4 ± 0.7	2520 ± 200
B5	920 ± 20	230 ± 5	11.0 ± 0.5	2530 ± 130

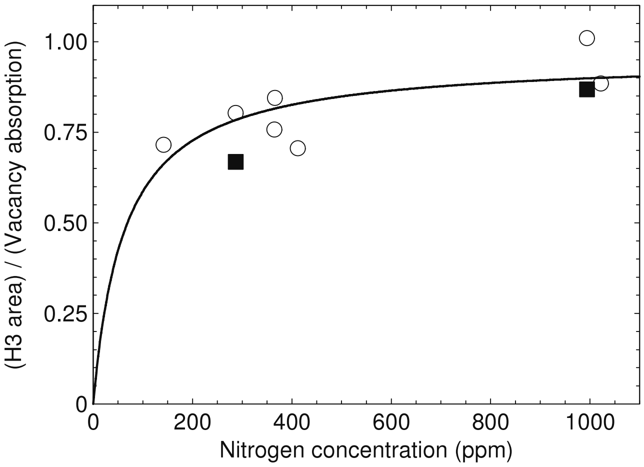

Figure 4. Ratio of 'H3 area' to 'vacancy absorption' (see text for definitions of these terms) as a function of the nitrogen concentration in seven type IaA diamonds (circles). The uncertainty in the ratio for each datum point is ∼8%. For two diamonds the squares show this same ratio obtained from a plot of annealing data, like that shown in figure 5. For those points the uncertainties are ∼4%. The curve shows the best fit of equation (11) to the data denoted by circles.

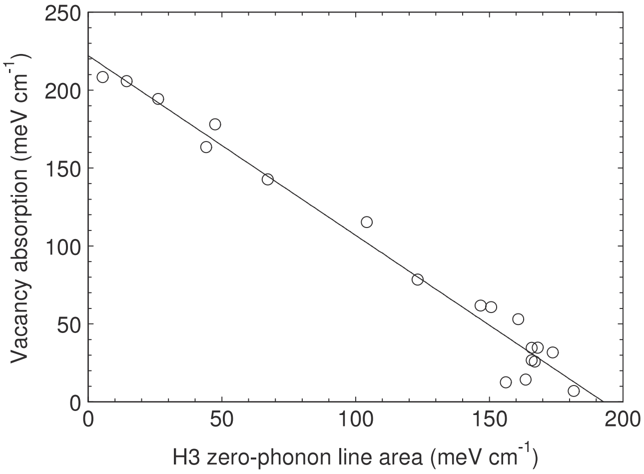

Figure 5. 'Vacancy absorption' (see the text for the definition of this term) plotted as a function of the area of the H3 zero-phonon line, determined from the isothermal annealing curve at 600 °C. The straight line is a least-squares fit to the data.

If all the vacancies were trapped by the A aggregates the ratios would all be the same within experimental error. In fact, there appears to be a general increase as $[N]$ increases. We have confirmed that this is the case by fitting a straight line to the points shown by circles to yield a gradient of $(25\pm8)\times10^{-5}$. A weighted least-squares fit to all the data points in figure 4 gives a straight line with a gradient of $(26 \pm 6) \times 10^{-5}$. These fits strongly suggest that there is a nitrogen dependence, and this view is reinforced by measurements on the type IaB diamonds reported below. We attribute this dependence to the presence of trapping centres other than nitrogen.

If all the diamonds contain the same concentration of alternative vacancy traps, the H3 to vacancy ratio R will have the form

$$R = \frac{a \times [N_A]}{([N_A] + b)}, \qquad (11)$$

where a and b are constants. The curve through the points in figure 4 is the best fit of this function to the data. Unfortunately there is a lack of data near the origin.

It is also possible to derive a value for the ratio used in figure 4 from isothermal annealing data by plotting the vacancy absorption versus the H3 area at each stage of the annealing. We have carried out this procedure for the two reasonably homogeneous type IaA diamonds, A5 and A18, and figure 5 shows the plot for the former. The reciprocal of the gradient of the straight line through the data gives the required ratio. The values obtained were 0.868 ± 0.034 for A5 and 0.667 ± 0.025 for A18, and are represented by squares in figure 4. Both points are lower than the ratio calculated after the same diamonds were annealed at 900 °C, but these differences (which are both less than 1.5 standard deviations) are attributed to experimental uncertainty.

Data similar to those in figure 4, with a fit to equation (11), are plotted in figure 6 for three type IaB specimens. For diamonds B2 and B5 the ratios were obtained from the isothermal annealing data, using a procedure like that used to obtain figure 5. The datum point for the diamond nearest the origin is for a type IaB diamond (N9-26) that had been annealed at 800 °C in a previous investigation without a 400 °C pre-anneal. The initial GR1 absorption was therefore reduced by 25% to allow for the typical reduction in the area of the GR1 ZPL that occurs on annealing at 400 °C (Kiflawi *et al* 2007). In addition, the ND1 absorption was not measured for that diamond. However, for the other two diamonds in figure 6, the areas of the ND1 and GR1 ZPLs were similar after the initial anneal at 400 °C. We have assumed that that would also have been the case for N9-26, and that allows us to estimate the 'vacancy absorption' destroyed.

Despite the gross assumption underlying equation (11), and the limited number of diamonds available for study, figures 4 and 6 clearly indicate that the proportion of vacancies trapped by nitrogen decreases as the nitrogen concentration decreases. This behaviour can be understood if vacancies may also be trapped at alternative sites. The behaviour in figure 6

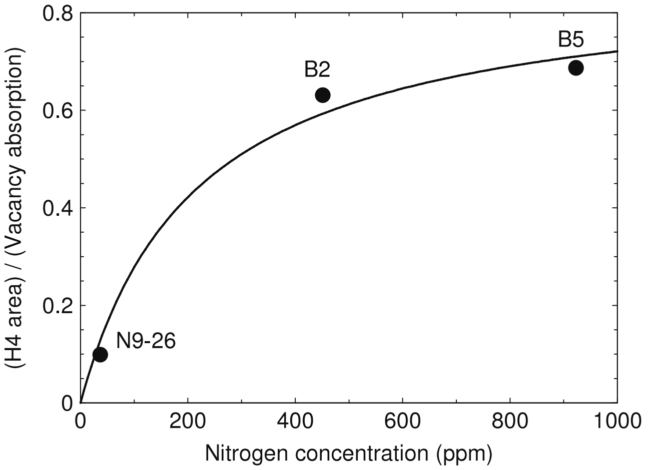

Figure 6. Ratio of 'H4 area' to 'vacancy absorption' as a function of the nitrogen concentration in three type IaB diamonds. The uncertainties in the ratios are ~4% for B2 and B5, and ~25% for N9-26. The curve shows the best fit of equation (11) to the data.

Table 4. Comparison of the ratios f_{H3}/f_{GR1} and f_{H4}/f_{GR1} obtained by Davies *et al* (1992) with those determined in the present investigation.

Ratio	Davies *et al* (1992)	This work
f_{H3}/f_{GR1}	0.82 ± 0.03	0.92 ± 0.06
f_{H4}/f_{GR1}	0.87 ± 0.01	0.88 ± 0.14

is consistent with the findings by Davies *et al* (1992). They obtained $f_{H4}/f_{GR1} = 0.87 \pm 0.01$ for three diamonds with nitrogen concentrations between 900 and 1100 ppm. However, for three additional diamonds, with $[N_B]$ between 75 and 450 ppm, the intensity of the H4 ZPL was up to 2.2 times smaller, relative to the initial damage, than that for the type IaB diamonds with higher nitrogen concentrations.

Davies *et al* did not observe any dependence of f_{H3}/f_{GR1} on nitrogen concentration, but their specimens contained only a narrow range of nitrogen concentrations (200–350 ppm) compared with 150–1000 ppm used in the present investigation. The data in figure 4 indicate that A_{H3}/(vacancy absorption), and hence f_{H3}/f_{GR1}, does depend on $[N_A]$ and suggest that the value obtained by Davies *et al* will be an underestimate (because of the low nitrogen concentrations used).

The limits as $[N_A] \to \infty$ in figure 4, and $[N_B] \to \infty$ in figure 6, give the ratios f_{H3}/f_{GR1} and f_{H4}/f_{GR1}, respectively. As shown in table 4, the value for f_{H3}/f_{GR1} obtained in the present investigation is somewhat larger than that obtained by Davies *et al*, as expected, whereas the two different values for f_{H4}/f_{GR1} are comparable.

Because of the assumptions made in plotting figures 4 and 6, and the small number of specimens available (particularly for figure 6), the values in column 3 of table 4 need to be treated with caution. It is pleasing that the cluster of points in figure 4 with nitrogen concentrations around 300 ppm have a f_{H3}/f_{GR1} ratio similar to that obtained by Davies *et al* for diamonds with nitrogen concentrations between 200 and 350 ppm. However, the value for f_{H4}/f_{GR1} obtained by Davies *et al* was for three type IaB diamonds with nitrogen concentrations in the range 900–1100 ppm; the value obtained in the present investigation from an isothermal annealing of a type IaB diamond with $[N_B] = 924$ ppm was significantly lower at 0.69 ± 0.03. The apparent agreement in table 4 between the ratio obtained by Davies *et al*, and that obtained from the extrapolation of figure 6, is therefore fortuitous.

Despite some disagreement between the estimates of the ratio of oscillator strengths for type IaB diamond between this work, and that of Davies *et al*, there is no doubt that, for the same initial concentration of vacancies (after pre-annealing at 400 °C), the concentration of H3 centres produced in type IaA diamond, and the concentration of H4 centres produced in type IaB diamond, both increase as the nitrogen concentration increases. This means that the most reliable values for the ratio of oscillator strengths will be obtained at high nitrogen concentrations.

4. Conclusions

We have shown that, in reasonably homogeneous type Ia diamonds, the decay of the GR1 absorption during isothermal annealing can be approximately fitted by a single exponential. However, in all cases a better fit to the data is obtained using two exponentials, particularly when the distribution of the nitrogen is inhomogeneous. It is likely that the 'fast' and 'slow' components for the vacancy annealing, observed by Davies *et al* (1992), have their origin in sample inhomogeneity.

The assumption made by Davies *et al* that all the vacancies are trapped by the nitrogen appears to be approximately true only for fairly high nitrogen concentrations (~1000 ppm). Consequently the value they obtained for f_{H3}/f_{GR1} is probably an underestimate. The actual values of f_{H3} and f_{H4}, rather than the ratios of those quantities to f_{GR1}, must await a definitive determination of f_{ND1}/f_{GR1}.

References

Allers L, Collins A T and Hiscock J 1998 *Diamond Relat. Mater.* **7** 228–32
Boyd S R, Kiflawi I and Woods G S 1994 *Phil. Mag.* B **69** 1149–53
Boyd S R, Kiflawi I and Woods G S 1995 *Phil. Mag.* B **72** 351–61
Charles D R 2009 *PhD Thesis* King's College London
Clark C D and Davey S T 1984 *J. Phys. C: Solid State Phys.* **17** L399–403
Clark C D, Ditchburn R W and Dyer H B 1956 *Proc. R. Soc.* A **234** 363–81
Collins A T 1980 *J. Phys. C: Solid State Phys.* **13** 2641–50
Collins A T 1998 *Diamond Relat. Mater.* **7** 1257–8
Collins A T and Williams A W S 1971 *J. Phys. C: Solid State Phys.* **4** 1789–800
Davies G 1972 *J. Phys. C: Solid State Phys.* **5** 2534–42
Davies G 1976 *J. Phys. C: Solid State Phys.* **9** L537–42
Davies G 1977 *Nature* **269** 498–500
Davies G 1999 *Physica* B **273/274** 15–23
Davies G and Hamer M F 1976 *Proc. R. Soc.* A **348** 285–98
Davies G, Lawson S C, Collins A T, Mainwood A and Sharp S J 1992 *Phys. Rev.* B **20** 13157–70
De Weerdt F 2007 *PhD Thesis* University of London
Denham P, Lightowlers E C and Dean P J 1977 *Phys. Rev.* **161** 762–8

Dyer H B and du Preez L 1965 *J. Chem. Phys.* **42** 1898–906

Farrer R G and Vermeulen L A 1972 *J. Phys. C: Solid State Phys.* **5** 2762–8

Iakoubovskii K, Kiflawi I, Johnston K, Collins A T, Davies G and Stesmans A 2003 *Physica* B **340–342** 67–75

Kiflawi I, Collins A T, Iakoubovskii K and Fisher D 2007 *J. Phys.: Condens. Matter* **19** 046216

Lang A R 1979 *The Properties of Diamond* ed J E Field (London: Academic) pp 425–69

Lawson S, Davies G, Collins A T and Mainwood A 1992 *J. Phys.: Condens. Matter* **4** L125–31

Loubser J H N and van Wyk J A 1981 *Diamond Conf. (Reading)* unpublished abstracts

Mainwood A 1994 *Phys. Rev.* B **49** 7934–41

Smith H E, Davies G, Newton M E and Kanda H 2004 *Phys. Rev.* B **69** 045203

Twitchen D J, Hunt D C, Smart V, Newton M E and Baker J M 1992 *Diamond Relat. Mater.* **8** 1572–5