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# Properties of optically active vacancy clusters in type IIa diamond

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## Abstract

In this paper we report on the positron lifetime results obtained for brown and colourless natural diamond. Optical effects of the observed vacancy defects in brown, high pressure, high temperature (HPHT) treated colourless and naturally colourless type IIa diamond samples were studied by combining the positron measurement with monochromatic illumination. Brown diamond was found to contain optically active vacancy clusters (40–60 missing atoms) strongly correlated with the optical absorption spectra. The optical activity of these vacancy clusters is manifested by a photo-excitation induced change of charge from neutral to negative. The clusters gradually disappear during the HPHT treatments, and the samples treated at 2500 °C resemble colourless samples optically and show similar positron lifetimes. The results show that the brown colour originates from the vacancy clusters and that their removal by the HPHT treatment causes the loss of coloration.

## 1. Introduction

Brown colour is common in natural diamond and also diamond synthesized by chemical vapour deposition (CVD). In both cases, it is well known that the brown colour can be removed by high pressure high temperature (HPHT) annealing [1–4], but the origin of the colour and the microscopic mechanisms behind its removal have remained unclear. For both kinds of diamond, the absorption coefficient in the visible region of the spectrum shows a monotonic increase towards shorter wavelengths with no specific threshold for the onset of this effect. This suggests that the defects responsible for the colour introduce a continuum of states within the bandgap and it is therefore unlikely that they are simple impurity-related point defects.

In the case of brown type IIa natural diamond, the brown colour is thought to be related to defects created during plastic deformation whilst in the earth, and hence traditionally dislocations have been considered as the most probable cause of the brown coloration. However, transmission electron microscopy of brown natural type IIa diamond has indicated that the dislocation densities are of the order of  $10^9 \text{ cm}^{-2}$ , not affected by the HPHT treatment [5]. Furthermore, the theory suggests that this density is not high enough for dislocations to be responsible for the observed optical absorption [6].

Positron annihilation spectroscopy is an efficient tool for studying crystallographic defects containing open volume, namely vacancies. Positrons can get trapped to negative and neutral vacancies, leading to an increase in the positron lifetime and a narrowing of the Doppler broadened positron–electron annihilation energy distribution due to the locally reduced electron density. Positrons can be used to probe the vacancy types, charge states and often also the vacancy concentrations. Positron annihilation experiments can be combined with monochromatic illumination [7–9] in order to observe vacancies in optically excited charge states, similar to optical deep level transient spectroscopy or electronic paramagnetic resonance combined with illumination.

Both natural and synthetic diamond has been studied with positron annihilation spectroscopy to some extent during the past decade [10–13]. Some of the basic positron parameters have been determined, such as the positron lifetime in the defect free crystal lattice ( $\tau_B = 100\text{--}110 \text{ ps}$ ) and the lifetime of a positron trapped at a monovacancy ( $\tau_B = 140\text{--}150 \text{ ps}$ ), based on experiments in electron-irradiated samples. Clusters of vacancies with positron lifetime values in the range 300–450 ps have also been observed in diamond specimens [14]. Typically the presence of these vacancy clusters has correlated with the occurrence of brown colour, suggesting that there could be a relation between the two, while conclusive evidence

was obtained only recently by combining optical illumination during positron experiments with optical absorption data on brown, HPHT-treated and colourless type IIa diamond [15].

In this work, we compare dark brown diamond to a HPHT-treated colourless sample cut from the same specimen, and show that large vacancy clusters (tens of missing atoms) present in the brown material become more attractive to positrons when illuminated at low temperature with wavelengths in the visible range. The illumination induced changes in the positron data correlate with optical absorption features. Then we show by using the temperature dependence of the positron data with and without illumination that the large vacancy clusters are optically excited to a negative charge state, while the other defects observed in the diamond samples are insensitive to illumination. Finally we examine the effects of consecutive HPHT treatments at different temperatures and study the details of the gradually disappearing brown coloration.

## 2. Method

### 2.1. Experimental details

All the natural diamond samples studied in this work are of type IIa, i.e., their nitrogen concentration is below the infrared or ultraviolet absorption detection limit ( $\sim 10^{18} \text{ cm}^{-3}$ ). In the first three sections of the paper, a dark brown type IIa diamond sample is studied. The sample was cut into 4 pieces: two pieces were kept as is and the other two were made colourless by HPHT treatment. In addition, a naturally colourless type IIa diamond sample was measured as a reference. In the last section a natural type IIa 28.8 carat brown diamond sample was used in order to study the loss of coloration in more detail. This large sample was annealed at temperatures 1860, 2080, 2300 and 2500 °C and pairs of  $\sim 0.2$  ct pieces were cut for optical and positron measurements.

Positron lifetime spectroscopy can be used to study defects with open volume. The method is based on the detection of the radiation emitted during the annihilation of positrons with the electrons in the sample material [16, 17]. Prior to annihilation the positrons rapidly lose their kinetic energy in a matter of a few picoseconds. After thermalization, positrons are in diffusive state in the interstitial space of the lattice, repelled by the positive ion cores. During the thermal diffusion positrons can get trapped at negative and neutral vacancies, causing an increase in the positron lifetime due to the locally reduced electron density.

The positron lifetime in the sample can be measured using a  $\beta^+$ -active isotope, such as  $^{22}\text{Na}$  used in this work. In practice the lifetime is measured as the time difference between the 1.27 MeV photon emitted almost simultaneously (the time difference is in the femtosecond range) with the positron and one of the two photons emitted in the annihilation of the positron. The experimental positron lifetime spectrum is of the form

$$-\frac{dn(t)}{dt} = \sum_i^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right), \quad (1)$$

where  $k$  different defect types contribute to the spectrum, each with a lifetime component  $\tau_i$  (inverse of the decay constant,  $\tau_i = \lambda_i^{-1}$ ) and the intensity  $I_i$  gives the fraction of positrons annihilating with the lifetime in question. The lifetime components correspond to slopes observed in the annihilation spectra when plotted on a semi-logarithmic scale. The experimental spectrum is decomposed (using a numerical fitting algorithm) into 1–3 discrete components corresponding to annihilations in a delocalized state in the lattice and/or localized state(s) at open volumes. The positron lifetime given by the component increases proportionally to the size of the open volume in question (see section 2.3). The decomposition of the lifetime spectra is unambiguous when the lifetime values differ sufficiently, i.e.  $\tau_2/\tau_1 > 1.5$ . The increase of the average lifetime  $\tau_{\text{ave}} = \sum_i I_i \tau_i$  above the lifetime in bulk material is a direct indication of open volume defects (vacancies) being present, even if the decomposition represents only a best fit to the spectrum without any physical meaning. This is due the fact that the average positron lifetime coincides with the centre of the mass of the annihilation spectrum, giving a high statistical accuracy of less than 1 ps.

The positron measurements were performed in a cryostat cooled by a closed-cycle He cryocooler capable of achieving temperatures between 10 and 330 K. The cryostat was equipped with the possibility to shine monochromatic light on the samples in order to examine the possible photo-excitation of the defects [18]. The positron measurements were performed in darkness and under monochromatic illumination with energies of 0.7–3.1 eV with photon fluxes  $10^{16}$ ,  $10^{15}$  and  $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$  between energies 0.7–1.2, 1.2–2.0 and 2.0–3.1 eV, respectively.

The annihilation spectra were collected with a conventional fast–fast spectrometer with Gaussian time resolution of 250 ps (full width at half maximum). The samples were sandwiched with a 20  $\mu\text{C}$  positron source. The source material was carrier free  $^{22}\text{NaCl}$  solution deposited onto a thin 1.5  $\mu\text{m}$  Al-foil. Roughly  $2 \times 10^6$  annihilation events were collected for each measurement point. The experimental lifetime spectrum given by equation (1) was analysed as a sum of exponential decay components convoluted with a Gaussian resolution function. Annihilations in the source material (Al-foil, NaCl) and as positronium were subtracted (200 ps 0.75%, 400 ps 2.9%, 1500 ps: 0.15–0.30%) from the spectra prior to the detailed analyses.

### 2.2. Data analysis

Positron annihilation techniques are based on the fact that thermalized positrons can get trapped at open volume defects. The transition rate  $\kappa$  to the defect (called the positron trapping rate) is proportional to the defect concentration  $c_D$ . The trapping rate is therefore  $\kappa_D = \mu_D c_D$ , where the proportionality constant  $\mu_D$  is called the positron trapping coefficient and depends on the type of the defect ( $\mu_D \approx 10^{15} \text{ cm}^3 \text{ s}^{-1}$  for neutral monovacancies [19, 20]). In the simple case of only one open volume defect being present the trapping rate is easily estimated, as the average lifetime is then

given by

$$\tau_{\text{ave}} = \left( \frac{\lambda_B}{\lambda_B + \kappa_D} \right) \tau_B + \left( \frac{\kappa_D}{\lambda_B + \kappa_D} \right) \tau_D, \quad (2)$$

where  $\tau_B = \lambda_B^{-1}$  is the positron lifetime in the lattice and  $\tau_D$  the positron lifetime at the defect. Changes in  $\tau_{\text{ave}}$  can be observed when  $\kappa_D \approx 0.01\text{--}100\lambda_B$ , resulting in a concentration detection limit of about  $10^{15} \text{ cm}^{-3}$  for monovacancies, while about  $10^{19} \text{ cm}^{-3}$  monovacancies are needed to saturate the signal. The situation in the latter case is called saturation trapping, as then the defect concentration is high enough for all positrons to get trapped prior to annihilation in the lattice. In the case of more than one kind of open volume defect trapping positrons, the trapping rate can be evaluated only in some special cases. However, even then the relative behaviour can be considered in the analysis.

An important feature of positron annihilation spectroscopy is that positron trapping to defects is sensitive to changes in the environment such as temperature and light. The trapping coefficient of a neutral vacancy is independent of temperature, whereas in the case of a negative vacancy it varies as  $T^{-1/2}$  due to the enhanced transition rate from a free state to a bound state in a Coulomb potential [21]. When measuring the positron lifetime as a function of temperature this behaviour is easily observed. Furthermore, in some cases the charge state of a defect can be manipulated by photo-excitation: this can then be observed as a change in the trapping of positrons to that particular defect [22]—at low temperatures the difference between the trapping coefficients of a neutral and negative vacancy can be more than one order of magnitude.

In the case of saturation trapping, the determination of the actual defect concentration is difficult—only a lower bound estimate can be given. In the two-defect model the trapping is in saturation when  $\kappa_{1,2} \gg \lambda_B - \lambda_{D1,2}$ , where  $\lambda_{D1,2}$  are the decay constants of defects 1 and 2. In this case the experimental lifetime values correspond to the decay constants of the defects,  $1/\tau_{1,2\text{exp}} = \lambda_{D1,2}$  and the ratio of trapping rates corresponds to the ratio of experimental intensities [23]:

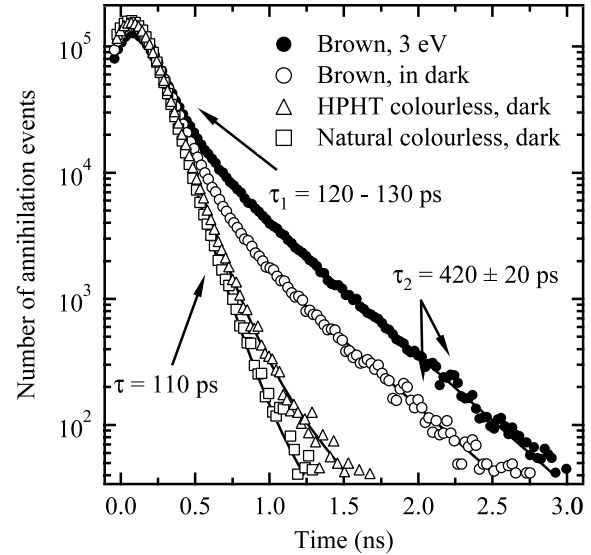
$$\frac{I_{1,\text{exp}}}{I_{2,\text{exp}}} = \frac{\kappa_1}{\kappa_2}. \quad (3)$$

### 2.3. Theoretical calculations

Positron lifetimes in vacancy defects can be theoretically estimated [24, 25]. The positron annihilation rates were calculated using the conventional scheme with the local density approximation for electron–positron correlation effects and the atomic superposition method in the numerical calculations. The positron annihilation rate is defined by

$$\lambda = \frac{1}{\tau} = \pi r_0^2 c \int d\mathbf{r} |\Psi_+(\mathbf{r})|^2 n(\mathbf{r}) \gamma[n(\mathbf{r})], \quad (4)$$

where  $r_0$  is the classical radius of electron,  $c$  the speed of light,  $n(\mathbf{r})$  electron density and  $\gamma[n]$  enhancement factor of the electron–positron correlation. The positron lifetime is indicative of the size of the vacancy defect, as the overlap between the electron and positron wavefunctions decreases



**Figure 1.** Experimental positron lifetime spectra for colourless HPHT-treated and naturally colourless diamonds in the dark and for brown diamond in the dark and with 3.0 eV photon illumination energy.

when the open volume in the defect increases. In our calculations we used the Boronski–Nieminen enhancement factor [26, 27]. It takes into account the lack of complete positron screening due to the lack of conduction electrons in wide bandgap semiconductors, and takes the form

$$\gamma[n(r)] = \pi r_0^2 c n [1 + 1.23r_s + 0.8295r_s^{3/2} - 1.26r_s^2 + 0.3286r_s^{5/2} + \frac{1}{6}(1 - 1/\epsilon_\infty r_s^3)], \quad (5)$$

where  $r_s = (\frac{3n}{4\pi})^{1/3}$ ,  $n$  is the electron density and  $\epsilon_\infty$  is the dielectric constant for infinite frequency. For diamond  $\epsilon_\infty = 5.7$  [28].

## 3. Positron lifetimes in natural diamond: experiment and theory

### 3.1. Experiment

Positron lifetime spectra measured at 20 K for the brown samples, the colourless HPHT-treated and naturally colourless samples are shown in figure 1, and the results of the fitting procedure are summarized in table 1. It is evident from the spectra that brown diamond shows a much higher average positron lifetime  $\tau_{\text{ave}}$  than colourless diamond, with  $\tau_{\text{ave}}$  further increasing when the brown samples are illuminated with 3.0 eV light. The average positron lifetimes for the samples are 119 ps for natural colourless diamond, 122 ps for the HPHT-treated colourless diamond and 165 ps for the brown untreated diamond in the dark and 227 ps with illumination of 3.0 eV. All the values are above the defect free bulk lifetime  $\tau_B$  of 100–110 ps as reported in [29], implying that there are open volume defects in all the samples, possibly such as monovacancy type defects with lifetimes of 140–150 ps [13]. The lifetime spectra can be decomposed into two lifetime components, with the smaller lifetime component being  $\tau_1 = 110\text{--}130$  ps as shown in the figure and the larger component being  $\tau_2 = 340 \pm 10$  ps

**Table 1.** Positron lifetime results at 20 K in the dark (unless otherwise stated). The uncertainties are 1 ps for  $\tau_1$ , 0.2–0.3% for  $I_2$ , and 10–20 ps for  $\tau_2$ .

Sample	$\tau_{ave}$ (ps)	$\tau_1$ (ps)	$\tau_2$ (ps)	$I_2$ (%)
Brown	164	125	405	12.2
HPHT colourless	122	118	340	2.5
Natural colourless	119	115	350	1.5
Brown, 3.0 eV illumination	227	132	421	33.2

**Table 2.** Theoretical positron lifetimes for small open volume defects.

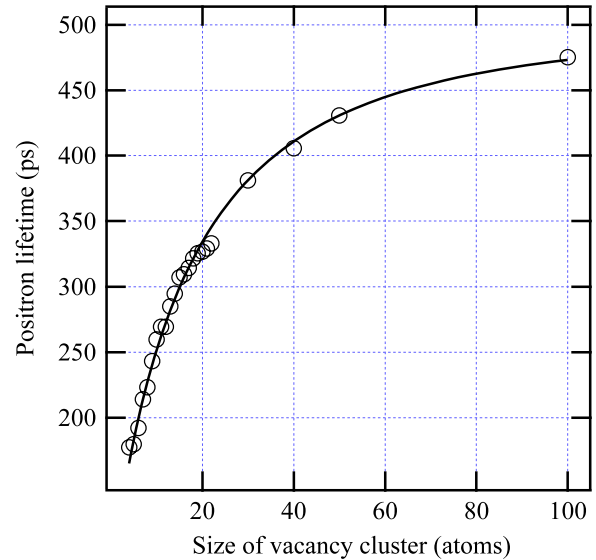
Defect type	Positron lifetime (ps)
Defect free lattice	90
Ideal monovacancy	96
Monovacancy with 5% relaxation	116
Glide dislocation	96
Shuffle dislocation	129

in the HPHT-treated sample and  $\tau_2 = 405 \pm 10$  ps in the brown sample when measured in the dark. A lifetime of about 400 ps corresponds to a very large vacancy cluster with several tens of atoms missing as previously observed in type IIa diamond samples [11]. This lifetime component is slightly longer,  $\tau_2 = 420 \pm 20$  ps, when the brown sample is illuminated with 3.0 eV photons. The difference of  $\tau_{ave}$  between the brown and the colourless samples is mostly due the much larger annihilation intensity of the defect responsible for the longer lifetime. It is also seen in the brown samples that the increase in the average lifetime when illuminated with 3.0 eV is due to increase of intensity of the second lifetime component. This behaviour indicates that the defects corresponding to the long lifetime component become more attractive traps for positrons, suggesting that the charge state of the defect becomes more negative.

### 3.2. Theoretical calculations

In order to estimate the sizes of the open volume defects observed in diamond, we calculated theoretically the positron lifetimes for dislocations, vacancies and for vacancy clusters up to 100 missing atoms. For the defect free bulk the calculated lifetime is  $\tau_B^{calc} = 90$  ps, slightly smaller than the reported experimental value for defect free lattice. This  $\sim 10$  ps underestimation is expected to be seen in all the calculated lifetimes. In the case of small open volume defects, the positron lifetimes are calculated in a monovacancy (without relaxation and with 5% outwards relaxation) and for glide and shuffle dislocations. The results are summarized in the table 2.

The positron lifetime in a monovacancy without relaxation is only 6 ps longer compared to the defect free lattice, and much less than the reported 45 ps experimental difference between the bulk lattice and the monovacancy. However by relaxing the atoms surrounding the vacancy by 5% outwards results already in a 26 ps difference, and relaxing by 10% gives a difference longer than 45 ps. It should be noted that the effect of positron repelling the atoms surrounding a vacancy can be substantial, as seen for example for the C vacancy in SiC or the vacancy in Si [30, 31].

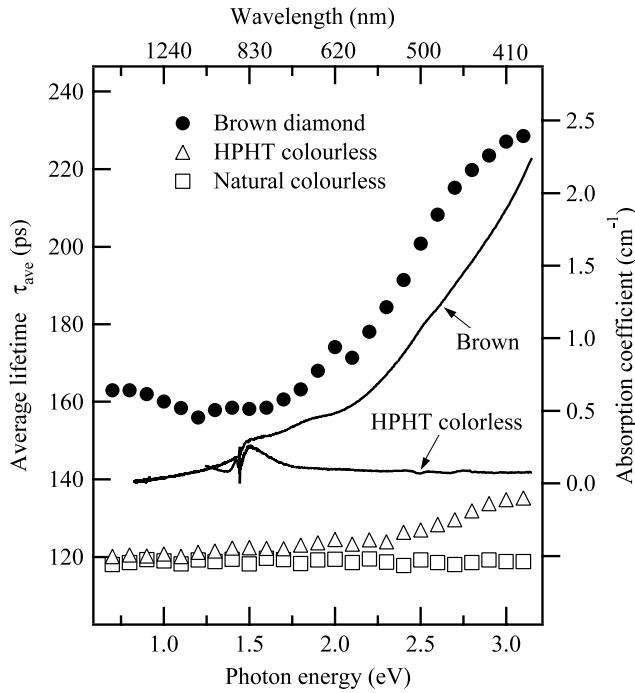


**Figure 2.** Theoretical positron lifetimes in vacancy clusters versus the size of the cluster.

The relaxed dislocation structures were obtained from [32]. The outward relaxation caused by positrons has not been taken into account, but it is not expected to affect the calculated lifetimes as positrons are able to move freely in one dimension along the dislocation. Interestingly, the positron lifetime in the glide dislocation is 6 ps longer compared to bulk, while the difference is 39 ps for the shuffle dislocation, close to the experimental value for the monovacancy. Hence all these defects with small open volume can contribute to the observed shorter lifetime component of  $\tau_1 = 115$ –132 ps.

Positron lifetimes have also been calculated for very large vacancy clusters. The results are shown in figure 2. The smaller vacancy clusters were created as in [33]. For larger clusters the atoms were removed spherically according to their distance from the origin of the cluster and the relaxation omitted, as for large open volumes the relaxation effects are negligible. It can be seen from the figure that the positron lifetimes saturate at values close to 500 ps. It can also be seen that the sensitivity of the positron lifetime to the size of vacancy cluster (number of missing atoms) is significantly reduced when there are tens of atoms missing. However, when the positron lifetime is 400 ps the number of missing atoms can still be analysed to a precision of around 10 atoms. For the positron lifetime in the range 400–440 ps the number of missing atoms is in the order of 40–60 atoms.

It is worth noting that for the positron lifetime to be very long the cluster must have three dimensional open volume, i.e. the smallest dimension of the cluster limits the positron lifetime. It is possible that the large vacancy cluster seen with positrons has many more atoms missing, but with the smallest dimension roughly corresponding to the diameter of the spherical cluster. However, theoretical calculations support the assumption that the vacancy clusters are roughly spherical, based on the calculated formation energies of the clusters [34]. Hence it can be concluded that the  $\tau_2 = 420 \pm 20$  ps lifetime corresponds to a roughly spherical vacancy cluster consisting of 40–60 missing atoms.

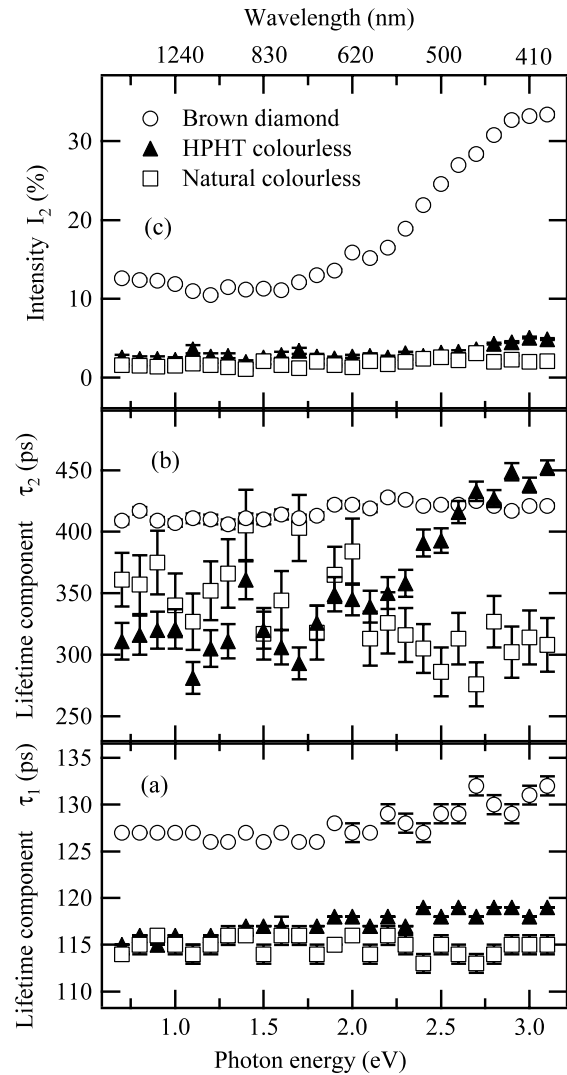


**Figure 3.** Average positron lifetimes (left) and absorption coefficient (right) for brown diamond, colourless HPHT-treated diamond and natural colourless diamond samples under illumination with monochromatic sub-bandgap ( $E = 0.7\text{--}3.1$  eV) light. The photon flux was kept constant during each measurement, but at high photon energies only a somewhat lower flux was obtained due to limitations in the intensity of the light source (halogen lamp), hence the ‘jumps’ in some of the data at photon energies of 1.2 and 2.0 eV. Photon fluxes between  $10^{14}$  and  $10^{16}$   $\text{cm}^{-2} \text{s}^{-1}$  were used.

#### 4. Optical effects on positron lifetimes

Figure 3 shows the average positron lifetime in the brown, colourless HPHT-treated and naturally colourless diamond samples measured at 20 K as a function of illumination photon energy in the range 0.7–3.0 eV (wavelengths 1800–400 nm). The absorption spectra of the samples are also shown for comparison. The average lifetime in the naturally colourless sample stays constant over the whole photon energy range, implying that there are no defects trapping positrons that would be sensitive to illumination. In the HPHT-treated colourless diamonds the average lifetime starts to increase monotonically after 2.0 eV with the average lifetime increasing from 120 to 135 ps, indicating that there are defects sensitive to illumination. In the brown samples the average lifetime is much higher than in the colourless samples as shown in section 3.1 even without illumination. When the samples are illuminated, the average lifetime slightly decreases between energies 1.0 and 1.9 eV before starting to increase rapidly after 2.0 eV. The featureless monotonic increase of the average lifetime correlates qualitatively with the absorption coefficient.

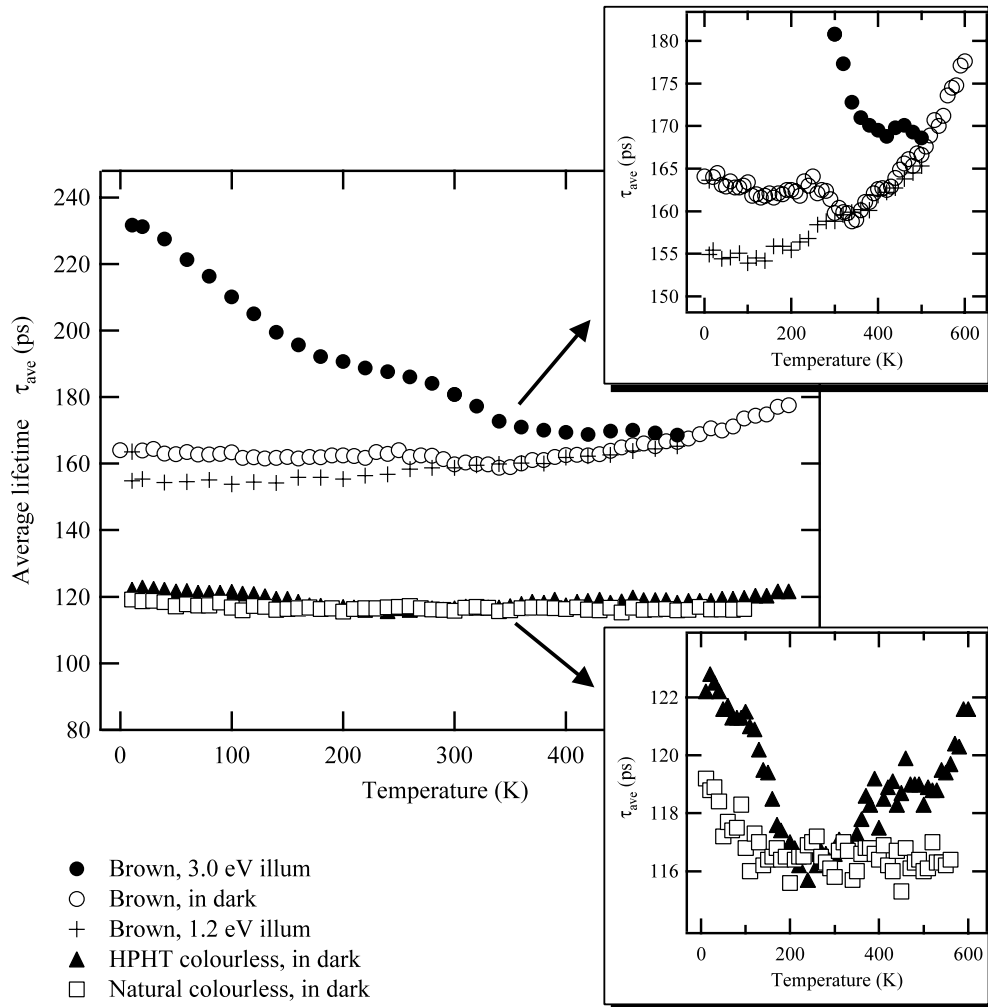
The shorter and longer lifetime components ( $\tau_1$  and  $\tau_2$ ) and the intensity of the longer component ( $I_2$ ,  $I_1 + I_2 = 1$ ) of the three diamond samples have been plotted in figure 4 panels (a)–(c) in order to understand the behaviour of the average lifetime. From the intensities it is seen that the drastic



**Figure 4.** Lifetime components and corresponding intensity of the diamond samples discussed in figure 3. Panels (a), (b) and (c) show the shorter lifetime component, the longer lifetime component and the intensity corresponding to the longer lifetime component, respectively. Error bars size of the symbol (top, bottom).

increase in the average lifetime is due to the increased fraction of annihilations in the large vacancy clusters regardless of the illumination energy. The average lifetime replicates all the spectral features of the intensity in the brown samples as seen from the discontinuities due to changes of the photon flux at 1.2 and 2.0 eV. The discontinuities indicate that the photo-excitation effect is not at saturation with a photon flux of  $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$  at 2.0 eV.

In all the samples, the shorter lifetime component  $\tau_1$  is nearly constant in the whole energy range, increasing slightly towards higher photon energies. This means that the trapping to vacancy type defects is in saturation at low temperatures and that  $\tau_1$  represents annihilations in small vacancy defects and annihilations from the free state in the lattice are not observed. When positron trapping at defects is not in saturation, the shortest lifetime observed in the spectra is given by  $\tau_1 = (\lambda_B + \kappa_{\text{tot}})^{-1}$  [23], and should decrease strongly from values close



**Figure 5.** Average lifetimes in brown diamond as a function of temperature with 1.2 and 3.0 eV and without illumination. The brown diamond shows a very large temperature effect especially with 3.0 eV illumination.

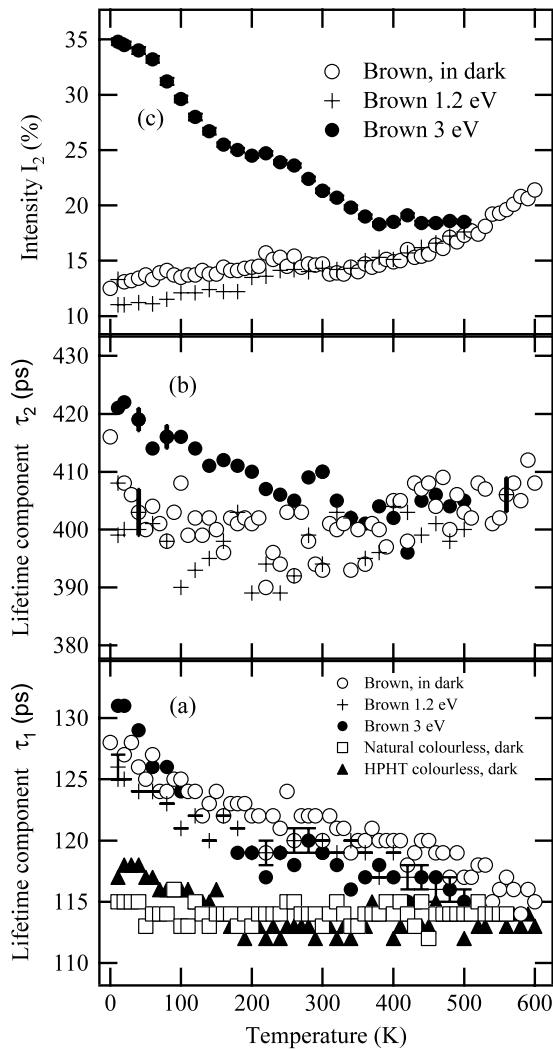
to the bulk lifetime  $\tau_B$  when trapping at defects is enhanced. This clearly is not the case in the data in figure 4. As the positron trapping coefficient to a vacancy cluster is roughly proportional to the number of vacancies in the cluster [35], the total monovacancy concentration (either as monovacancies or bound to vacancy clusters) can be estimated based on the saturation, giving a lower-limit estimate of  $10^{19} \text{ cm}^{-3}$ .

In principle, there are two possible explanations for the increase of intensity of the longer lifetime component  $\tau_2$  in the brown samples: (i) the vacancy clusters corresponding to the long component become more attractive to the positrons or (ii) the defects corresponding to the shorter component become less attractive, leading to an increased fraction of annihilations in the vacancy clusters. It turns out that the first option is the correct one, as examined in detail in section 5 when measuring the positron lifetime as a function of temperature. There is, however, an effect observable already in figure 4 that suggests this. The effect is best seen in the colourless HPHT-treated sample: in addition to  $I_2$  increasing, the longer component's lifetime also increases drastically with the photon energy in darkness, the longer lifetime component is  $\tau_2 \approx 340 \text{ ps}$ . It decreases to  $\tau_2 \approx 310 \text{ ps}$  when illuminated with  $\sim 1 \text{ eV}$

photons, and increases all the way up to  $\tau_2 \approx 440 \text{ ps}$ , similar to the brown sample, when illuminated with photons of energy above 2.5 eV. This implies that the longer lifetime component is a combination of an optically active vacancy cluster producing a lifetime component of  $\tau_2 = 420 \pm 20 \text{ ps}$  and another defect with a shorter (but significantly longer than  $\tau_1$ ) positron lifetime. It should be noted that the average lifetime in the natural colourless sample does not show any optical activity when illuminated. Even though a 400 ps component can be fitted, the lack of optical activity suggests that this component is caused by positrons annihilating in the NaCl of the positron source.

## 5. Temperature dependence of positron lifetimes

Positron lifetimes were measured as a function of measurement temperature (10–600 K) in the brown, colourless HPHT-treated and natural colourless samples in order to obtain information about the charge states of the vacancy defects. The average lifetimes in the samples are shown in figure 5, and the lifetime components  $\tau_1$  and  $\tau_2$  and the corresponding intensity are shown in figure 6 in the panels (a), (b) and (c), respectively.



**Figure 6.** Lifetime components and intensity of the diamonds discussed in figure 5 with panels (a), (b) and (c) show the shorter lifetime component, the longer lifetime component and the intensity corresponding to the longer lifetime component. Error bars in panels (a) and (c) are smaller than the markers, in panel (b) a few representative error bars are shown. A clear  $T^{-1/2}$  behaviour is seen for the vacancy cluster with 3.0 eV illumination.

The average positron lifetime measured in darkness in the brown diamond is fairly constant at 10–300 K, decreases slightly between 300 and 400 K, and increases significantly above 400 K. When illuminated with 3.0 eV photons, it is clear that the average positron lifetime decreases with increasing temperature in the range 10–400 K, indicating that the defects responsible for the elevated average lifetime are negatively charged. Interestingly, when measured under 1.2 eV illumination, all the structure in the average positron lifetime below 400 K is lost. The temperature dependence of the average positron lifetime in the colourless samples, both HPHT-treated and natural, is significantly weaker. A small decrease of the average positron lifetime with increasing temperature is observable at temperatures below 200 K in both colourless samples, and an increase at high temperatures similar to (but much weaker than) than in the brown sample is observed in the colourless HPHT-treated sample.

The shorter lifetime component  $\tau_1$  in the brown samples both in darkness and under illumination is the same, indicating that the illumination does not affect the (at least) two kinds of small vacancy defects competing in positron trapping and influencing  $\tau_1$ . It was shown already in the previous section that positron trapping is in saturation. In addition, the temperature behaviour of this component shows that the larger of these two kinds of small vacancy defects is in the negative charge state, attracting positrons more efficiently at lower temperatures. The larger of these defects could be a complex involving a monovacancy or a shuffle dislocation (see the calculated lifetimes in table 2), while the smaller defect could be a glide dislocation. Unfortunately a more precise analysis of the types or concentrations of the defects contributing to the shorter lifetime component is not possible based only on the present experiments.

When the brown diamonds are illuminated with photon energy 3.0 eV the annihilation intensity in the large lifetime cluster increases drastically as discussed in section 4. With the increase of the measurement temperature, the average lifetime shows  $T^{-1/2}$ -behaviour in the temperature range 10–300 K, unlike in the dark. This behaviour can be attributed to the long lifetime component based on the intensity  $I_2$  which shows the  $T^{-1/2}$  features in the temperatures 10–300 K. Further proof of this is seen from the behaviour of the  $\tau_2$  which also decreases (even if slightly) with increasing temperature, showing that it is the largest clusters that become negatively charged. No such effects are seen when the samples are not illuminated. This implies that the vacancy clusters change their charge state from neutral to negative and are therefore responsible for the illumination effect visible to positrons. Looking closely at the temperature dependence of the average positron lifetime and  $I_2$  in the range 10–300 K, a step-like feature can be observed around 200 K: the decrease first slows down and then accelerates. This could be due to the thermal recombination of electrons from the clusters back to the valence band level [18]. When the brown samples are illuminated with with photon energy 1.2 eV the resulting average lifetime at low temperatures is about 10 ps lower compared to the situation without illumination, but this effect disappears when the sample temperature is increased to 300 K. This difference is explained by the intensity behaviour of the longer component which is slightly lower at low temperatures. Also the longer lifetime component  $\tau_2$  is slightly lower than in darkness, suggesting that at least a part of the larger clusters can become less attractive (i.e., positively charged) at this illumination photon energy. The increase of positron trapping to the vacancy clusters at high temperatures, seen as the increase of the average lifetime and  $I_2$  in the brown samples, is probably due to the self-shielding effect, studied in detail in [36].

The colourless samples show nearly constant average positron lifetime through the whole temperature range. In the natural colourless sample the average lifetime decreases some 2 ps when the temperature increases from 10 to 300 K. The HPHT-treated sample shows slightly larger decrease of 6 ps. This behaviour of the colourless samples can be understood by looking at the shorter lifetime component  $\tau_1$  in the figure 6.



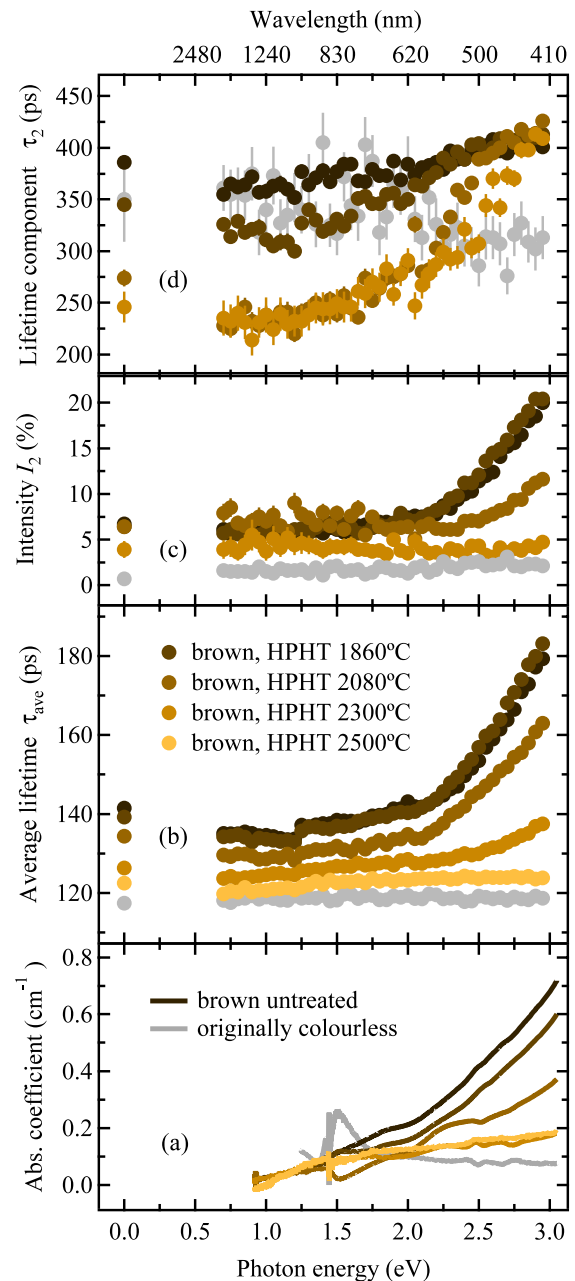
The values of the components are similar for both, the positron lifetime is above the defect free bulk value, implying that there are open volume defects present. Also the  $T^{-1/2}$ -behaviour typical of negative charged small vacancies is present in  $\tau_1$  of both colourless samples, even though the effect is fairly small. The longer lifetime components (not shown) are fairly constant, the only effect seen is the slight increase of  $I_2$  in high temperatures in the colourless HPHT-treated samples, as is also seen in the average positron lifetime.

It can be concluded that the brown colour of diamond can be attributed to the photo-excitation of electrons into the vacancy clusters. In order to obtain more detailed information about the correlation of optical absorption and the concentration of vacancy clusters a brown diamond sample has been annealed at different temperatures. The results of the optical absorption and positron lifetime are presented in section 6.

### 6. HPHT: removal of vacancy clusters and loss of brown coloration

A more detailed picture of the effects of the HPHT process can be obtained by performing optical absorption and positron annihilation experiments after different treatments. To this end, data were acquired on samples cut off from an originally brown 28.8 carat (5.8 g) diamond after HPHT treatments of 1 h at gradually increasing temperatures from 1860 to 2500 °C. The effect of the HPHT treatment is negligible at 1860 °C, while a gradual decrease and eventual disappearance of the broadband absorption and the features in the average positron lifetime can be observed at HPHT treatment temperatures of 2080–2500 °C (figures 7(a) and (b)). The HPHT treatment performed on the originally browner natural sample in the previous sections was shorter than the total time of the treatments performed on the present brown sample, observable both in the absorption coefficient and the positron lifetime, hence the differences in figures 3 and 7. These results very clearly support the important correlation, shown in the previous sections, between the absorption associated with the brown colour and the positron annihilation signal related to vacancy clusters.

Detailed analysis of the longer lifetime component of the annihilation spectra is shown in figures 7(c) and (d). The behaviour of the lifetime components is qualitatively similar to in the samples in section 4. The shorter lifetime component, not shown in the figure, is the same in all the originally brown samples:  $\tau_1 = 120\text{--}125$  ps throughout the illumination range, indicating that trapping does not affect the shorter lifetime component and hence all positrons annihilate as trapped at defects (saturation trapping). Interestingly, in the originally brown samples, the second lifetime component is  $\tau_2 = 250\text{--}420$  (correlated with the colour: the deeper the brown colour, the longer the lifetime), decreases by 20–50 ps when illuminated with photons of energy less than 1.0 eV, and then gradually increases to  $\tau_2 = 420 \pm 20$  ps (the same in all samples) with increasing photon energy. It should be noted that the changes in  $\tau_2$  with illumination are the most dramatic in the samples HPHT-treated at highest temperatures, while in



**Figure 7.** Positron lifetime results for various untreated and HPHT-treated diamond samples under illumination with similar energies and fluxes as in figure 4. Panel (a) shows the absorption coefficient measured in the same samples. Panels (b), (c) and (d) show the average positron lifetime, the longer lifetime component separated from the annihilation spectra and its intensity as a function of photon energy (illumination wavelength). The data points shown at photon energy 0.0 eV were measured in darkness.

(This figure is in colour only in the electronic version)

the originally colourless sample neither the intensity nor the lifetime of the longer component depends on the illumination.

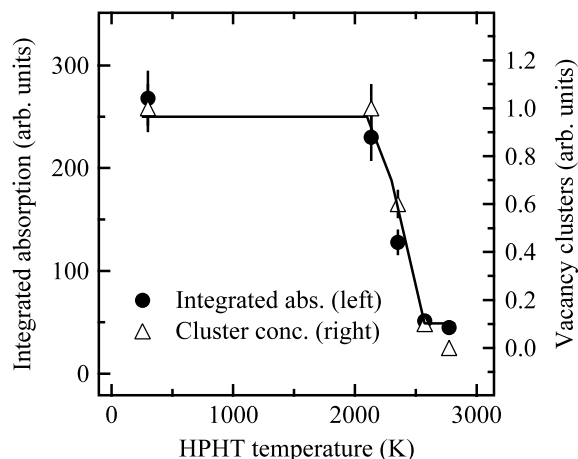
The data in figure 7(d) show that two kinds of clusters compete in positron trapping: larger vacancy clusters producing a lifetime of  $\tau_2 \geq 420 \pm 20$  ps (40–60 missing atoms) and smaller vacancy clusters producing a lifetime of  $\tau_2 \leq 230 \pm 15$  ps (6–10 missing atoms). There is

a correlation between the strength of the optical absorption responsible for the brown colour of the samples and the relative concentrations of the vacancy clusters of the two different sizes: the stronger the absorption of the sample, the more there are larger vacancy clusters compared to smaller vacancy clusters. Interestingly, these smaller vacancy clusters are more resistant to HPHT treatment, as they anneal out slower than the larger vacancy clusters. This is opposite to the expected behaviour where the stability of vacancy clusters is typically predicted to increase with size [37, 38]. Also experiments show that thermal annealings at extreme conditions in other strongly bonded semiconductors such as GaN or SiC typically lead to the removal of small vacancies and/or increase in vacancy cluster size [39, 40]. From the figure it is seen that these smaller clusters are present already in the untreated brown diamond, suggesting that they are not created in the HPHT treatment by partial dissociation of the larger clusters. Unfortunately, based on the present experiments, a more detailed discussion about the origin of this  $\sim 230$  ps lifetime component is not possible. It should be noted that the thermal formation of new (mono)vacancies at the annealing temperatures is not important. An upper limit for the thermally formed monovacancies can be estimated by assuming that the only impurities are the N donors and taking the theoretically predicted vacancy formation energy for the doubly negatively charged vacancy as  $(13.1 - 2 \times [E_F - E_{VBM}])$  eV [41], where  $E_F - E_{VBM}$  is the distance of the Fermi level from the valence band edge. This results in thermally generated vacancy concentration of  $\sim 10^{16} \text{ cm}^{-3}$  at the highest annealing temperature of  $2500^\circ\text{C}$ , several orders of magnitude less than already present in the samples.

Figure 8 shows the behaviour of the broadband absorption for isochronal annealing along with the relative concentrations of the large vacancy cluster defects. The latter are estimated using a two-defect model presented in section 2.2, with a sufficiently high concentration of monovacancy-size defects to cause saturation trapping. In addition, as the shorter lifetime component  $\tau_1$  is not affected by the HPHT treatments, it is reasonable to assume that the concentration (and hence trapping rate) of the monovacancy-size defects do not change in these treatments. Integrated absorption in the ultraviolet region has been used to avoid instrumental artefacts and corrections have been made to account for reflection losses and additional absorption from other known defects not related to the brown colour. The absorption data have been modelled assuming first order kinetics and a vibration frequency equal to the Raman frequency of diamond ( $4 \times 10^{13}$  Hz). The best fit is shown by the line. This gives an activation energy for the removal of the brown colour of around 8 eV. If the breakdown of the vacancy clusters is related to the similar process of graphitization in diamond, then we would expect activation energies around 7.5–11 eV as these correspond to the graphitization activation energies on 110 and 111 surfaces [42].

## 7. Summary

Positron lifetime results show that vacancy clusters with  $420 \pm 20$  ps positron lifetime and 40–60 atoms missing are



**Figure 8.** Absorption data integrated in the ultraviolet region and the relative concentrations of the larger vacancy clusters as a function of isochronal annealing temperature. The solid line shows the best fit of the annealing activation energy to the absorption data.

responsible for the brown colour in type IIa natural diamonds. Evidence of this is twofold: (i) intensity of the positrons annihilating in the vacancy clusters increases when the samples are illuminated, in correlation with the optical absorption spectrum, and (ii) the vacancy clusters disappear during HPHT treatment in good correlation with loss of the brown coloration. When the positron lifetime was measured as a function of photon energy and temperature, it was found that the vacancy cluster is in neutral charge state when in the dark and in negative charge state when illuminated with optical wavelength photons. This indicates that photo-excitation of electrons to the vacancy clusters takes place, absorbing the photons. When diamond is HPHT-treated the large vacancy clusters dissociate and the brown coloration is lost.

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