Sub-threshold excitation of luminescence of defects in diamond

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Abstract
Optically active defects in diamond can be excited by photons with an energy less than that of the zero-phonon transition. We show that this process is thermally activated. For diamonds in which one type of defect is dominant, the activation energy is equal to the energy difference between the zero-phonon line and the photons used for excitation.

1. Introduction

The work reported here has been carried out in an effort to understand the mechanism by which optical centres in diamond can be excited with photons having a lower energy than that of the zero-phonon line (ZPL). We refer to this process as 'sub-threshold excitation'. Previous work has shown that luminescence can be observed from the 3H, H3, H4 and TR12 centres with sub-threshold excitation (Iakoubovskii *et al* 2001, Vlasov *et al* 2001). Each of these optical centres has a sharp ZPL with a vibronic absorption band to higher energies, and a vibronic luminescence band to lower energies.

A possible explanation for the observed phenomenon has been given by Iakoubovskii *et al* (2001), who suggested that the photons ionize the negatively charged counterpart of the centre, which then converts into an excited neutral centre. In that model, the subsequent de-excitation of the neutral centre gives rise to the observed photoluminescence. Vlasov *et al* (2001), on the other hand, argued that the process is thermally activated, although their result showed a deviation from Arrhenius behaviour at low temperatures (Vlasov *et al* 2001).

In our more extensive investigations on the H3, H4, $(N–V)^-$ and 3H centres we confirm that the thermally activated mechanism is the correct interpretation. For these defects the electronic ground and excited states are non-degenerate and can couple to the lattice by linear electron–phonon coupling. The strength of the electron–phonon coupling is characterized by the Huang–Rhys factor S. For a given centre, the zero-phonon transition probability $P_{ZPL}(T)$ at temperature T is determined by the Huang–Rhys factor and the one-phonon density of states, and, in all cases, increases at lower temperatures (Davies 1974, 1981).
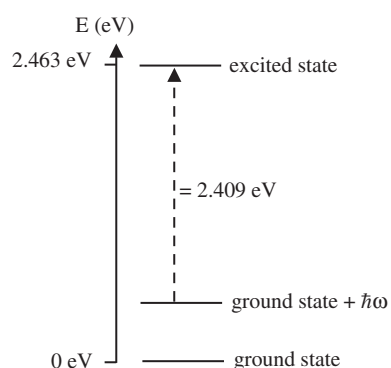
Figure 1. Schematic representation of the model for the sub-threshold excitation. Excitation is from a state which lies at energy $\hbar\omega$, equal to the energy difference between the zero-phonon line transition and the energy of the Ar$^+$ laser photons (2.409 eV).

A schematic representation of the proposed sub-threshold excitation process is given in figure 1. The excitation occurs from thermally populated levels in the phonon density of states associated with the ground state. If E is the difference between the zero-phonon energy and the energy of the exciting light (2.409 eV in this case), the excitation requires the absorption of one or more phonons having a total energy of $\hbar\omega = E$.

If we assume a Boltzmann distribution for the population of the phonon states, then the probability of absorbing one phonon of energy E will be given approximately by

$$C_1 g(E) \exp[-E/(k_B T)],$$

where $g(E)$ is the phonon density of states and k_B is the Boltzmann constant. Similarly, the probability of absorbing two phonons, with energies E_1 and E_2, and with $E_1 + E_2 = E$, is

$$C_2 g(E_1) \exp[-E_1/(k_B T)] g(E_2) \exp[-E_2/(k_B T)] = C_2 g(E_1) g(E_2) \exp[-E/(k_B T)].$$

The constants C_1 and C_2 describe the relative probabilities of the one- and two-phonon processes. Transitions involving the absorption of three or more phonons are also possible. Once the centre has been excited, then, provided there are no non-radiative recombination paths, we expect the intensity of the luminescence, following relaxation to the ground state, to be given by

$$I(E, T) \propto G(E) \exp[-E/(k_B T)] P_{ZPL}(T). \tag{1}$$

Here $G(E)$ represents the appropriate combination of multiphonon processes, and will be discussed further in section 3.3.

There are two ways in which this model can be verified. Using a fixed-wavelength laser to excite the luminescence, and varying the temperature, should give a variation in the intensity of the luminescence proportional to $\exp[-E/(k_B T)] P_{ZPL}(T)$. Alternatively, using a tunable laser, with the specimen at constant temperature, measuring the integrated intensity of the ZPL at different excitation wavelengths should map out the multiphonon function $G(E)$ multiplied by $\exp[-E/(k_B T)]$.

2. Experimental details

Measurements have been made on 11 different diamonds, initially selected using absorption and/or luminescence spectroscopy. Important characteristics of these specimens are summarized in table 1.

Table 1. Details of diamonds used in this investigation.

Sample name	Defect creation	Defect studied via sub-threshold excitation
0337	Irradiation and annealing Conditions: unknown	H3
W1a	Naturally occurring	H3
HRD1	Naturally occurring	H3
2b	HPHT annealing of a brown type Ia diamond Conditions: 1900 °C, 7 GPa, 20 h	H3
R1 (two measurements)	Naturally occurring	3H
H4-1 (three measurements)	Irradiation and annealing Conditions: 2 MeV e$^-$ + 800 °C (2 h)	H4
S1	Irradiation and annealing Conditions: 8 MeV e$^-$ + 800 °C (2 h)	H3 and H4
N2a	Irradiation and annealing Conditions: 8 MeV e$^-$ + 800 °C (2 h)	H3 and H4
S10	Irradiation and annealing Conditions: 4 MeV + 800 °C (2 h)	H3 and H4
Edu1	Naturally occurring	3H and H4
Type Ib sample	Irradiation and annealing Conditions: 2 MeV e$^-$ + 800 °C (2 h)	(N–V)$^-$

2.1. Specimen details

Five samples with relatively strong H3 absorption were studied. One (sample 0337) was an irradiated and annealed specimen for which the details of the irradiation and heat treatment are unknown. Another (sample 2b) was a brown type Ia diamond that had been colour enhanced using annealing for 20 h at high temperature (1900 °C) and high pressure (7 GPa). Samples W1a and HRD1 are brown type Ia samples with naturally occurring H3 defects.

Three type Ia samples (S1, N2a, S10), with different concentrations of nitrogen in the A and B aggregate forms, were irradiated and annealed at 800 °C for 2 h, producing H3 and H4 centres. Samples S1 and N2a had been irradiated with 8 MeV electrons, and sample S10 with 4 MeV electrons.

Diamond R1 was a type Ia specimen with naturally occurring 3H centres present. Diamond Edu1 exhibited naturally occurring luminescence from the 3H and H4 centres, and diamond H4-1 was a type IaB specimen that had been irradiated with 2 MeV electrons and annealed at 800 °C for 2 h to produce H4 centres. Because only one specimen of each of these three examples of diamond was available, measurements were taken at more than one location on each diamond's surface.

Nitrogen–vacancy centres, (N–V)$^-$, were produced by 2 MeV electron irradiation and annealing for 2 h at 800 °C in a low-nitrogen diamond grown by high-pressure, high-temperature synthesis.

2.2. Photoluminescence as a function of temperature

Photoluminescence measurements as a function of temperature were carried out with a Renishaw 2000 micro-Raman system equipped with a HeCd laser (325 nm, 3.814 eV laser line) and an Ar$^+$ laser (514.5 nm, 2.409 eV laser line). The samples were cooled in an Oxford Instruments MicrostatN cryostat, and the temperature was controlled by an ITC601 controller.

Good thermal contact was ensured by glueing the samples to the cryostat with silver DAG. The samples were located as close as possible to the thermocouple. Before recording a PL spectrum at different temperatures, the cryostat was allowed to thermally stabilize for at least 2 min. Sample inhomogeneity is a major problem when working with natural diamond samples. Slight deviations from the original position of the sample due to thermal dilatation of the cryostat can give erroneous results. This problem was circumvented by repositioning the sample in the X and Y directions with respect to the origin of a thin (1 μm) laser-inscribed reference cross on the diamond's surface. After the measurement, the position of the sample was checked to ensure that no drift of the sample position had happened during the measurement. Spectra were recorded at different temperatures, held to ±0.5 K, normally at intervals of not more than 20 K.

2.3. Photoluminescence as a function of exciting energy

The intensity of the zero-phonon line of the N–V defect as a function of excitation energy was measured using an XY Dilor Raman spectrometer equipped with a cooled and intensified 512-diode array multichannel detector. The resolution of the spectrograph was approximately 1.3 nm at the wavelength of the zero-phonon transition (637 nm).

The photoluminescence from the diamond sample was excited with a tunable Coherent CR-599 dye laser. Laser lines between 639.4 and 688.5 nm were produced by pumping a continuously circulating solution of DCM (4-dicyanomethylene-2-methyl-6-p-diethylaminostyryl-4-H-pyran) dye with up to 5.5 W of 532 nm radiation from a frequency doubled Nd–YAG Coherent Verdi 5 laser. At each wavelength the intensity of the output from the dye laser was measured and used to correct the luminescence intensity afterwards.

The diamond sample was placed on a cold stage at a temperature of 150 K in a constant flow of dry nitrogen, held at a pressure slightly above atmospheric to eliminate water vapour and keep the sample surface free of ice. Indium was used to mount the sample and this was then bonded to the cooling element, ensuring good thermal contact. The indium was also moulded to mask the diamond, and select a reasonably homogeneous region.

The temperature chosen (150 K) was sufficiently low that there was only a small amount of thermal broadening of the ZPL of the $(N–V)^-$ centre, but also sufficiently high that the luminescence intensity did not decrease too rapidly with increasing energy separation between the ZPL and the laser line (see equation (1)). The temperature was stabilized for 20 min before measurements were taken; the temperature stability was estimated to be better than ±1 K.

3. Results and discussion

All the results presented involve measuring the integrated area of the zero-phonon line. For each defect, the ZPL was least-squares fitted with a Lorentzian curve and a suitable quadratic background was subtracted.

3.1. Measurement of the transition probability

The integrated areas of the H3, H4 and 3H zero-phonon lines were measured as a function of temperature from 77 to 240 K, using excitation at 325 nm. Data for the H3 and H4 ZPLs, together with the calculated curve for the H3 transition probability, are shown in figure 2.

The calculated curve is given by equation (3.29) from Davies (1981):

$$I_0 = \prod_{i=1}^{N} \exp[-S_i \coth(\hbar\omega_i/2kT)] J_0[S_i \mathrm{cosech}(\hbar\omega_i/2k_B T)] \tag{2}$$
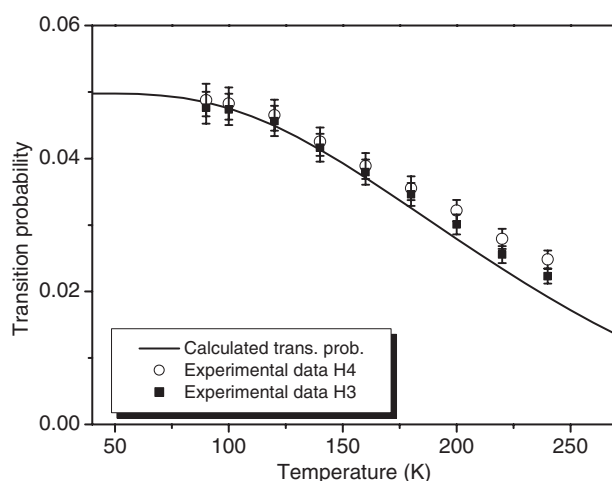
Figure 2. Intensities of the H3 and H4 zero-phonon lines, recorded in luminescence, using excitation at 325 nm. The solid line is the calculated transition probability of the H3 centre as a function of temperature. The amplitudes of the H3 and H4 ZPLs have been rescaled to the amplitude of the calculated curve at 77 K.

where S_i is the Huang–Rhys factor S/N when the electron–phonon interaction is spread over N modes and J_0 is a Bessel coefficient. Two modes were taken into account, one at 41 meV and one at 152 meV, together with a Huang–Rhys factor of $S = 3$ (Davies 1981, Zaitsev 2001).

A curve was also calculated for the H4 ZPL, using two modes at 40 and 154 meV, with $S = 3$ (Davies 1981, Zaitsev 2001). Not surprisingly, because of the similarity of the parameters used, this curve was almost indistinguishable from that for the H3 centre. In both cases the experimental data in figure 2 diverge somewhat from the calculated curves at higher temperature.

Data in figure 2 for the H3 ZPL were obtained from a type IaA diamond in which [H3] ≫ [H4] and data for the H4 ZPL were obtained from a type IaB diamond in which [H4] ≫ [H3]. Here the quantities in square brackets indicate the concentrations of the corresponding defect. However, very similar data were obtained from type IaA/B diamonds containing similar concentrations of H3 and H4 centres.

The transition probability for luminescence from the 3H centre was calculated with a single mode in the one-phonon spectrum at 67 meV and a Huang–Rhys factor $S \sim 0.8$ (Zaitsev 2001). However, as shown in figure 3, the experimental data from sample R1 do not follow the calculated curve well, indicating the presence of non-radiative decay channels. For that reason the experimentally measured transition probabilities were used to correct the sub-threshold data for the 3H centre.

3.2. Sub-threshold excitation as a function of temperature

Figure 4 shows the logarithm of the integrated area of the H3 zero-phonon line, plotted against the reciprocal of temperature, using excitation at 514.5 nm. Similar data were obtained from all the diamonds in which the H3 centre was the dominant defect. The lower plot shows the data without correction for the transition probability. A line to guide the eye has been drawn through the points at low temperature, and the data points at high temperature clearly diverge from this line. When the data points are corrected for the transition probability, as in the upper
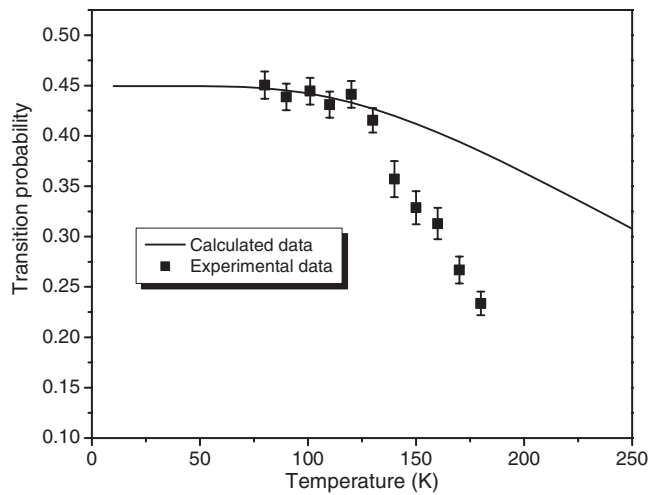
Figure 3. The experimentally measured and calculated transition probabilities of the 3H centre as a function of temperature.
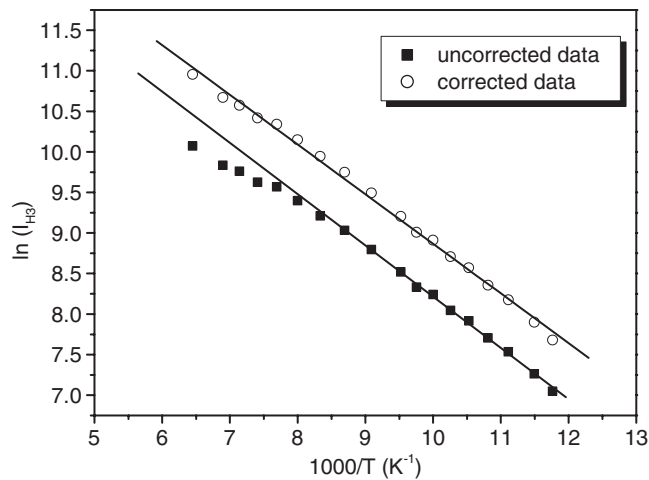

Figure 4. Arrhenius plots of the integrated intensity of the H3 zero-phonon line, using sub-threshold excitation at 514.5 nm. Data in the lower plot are uncorrected for the change in transition probability with temperature; the line through the low-temperature points is a guide to the eye. Data in the upper plot are corrected; the line is the best fit to the data.

plot, all the points lie on a straight line, as expected from equation (1), and the gradient of this line, $-E/k_B$, gives an energy equal, within the experimental uncertainties, to the energy separation between the zero-phonon transition and the energy of the laser.

Similar data were obtained from the diamond in which the H4 centre was the dominant defect, and for diamond R1 in which the 3H centre was the major defect giving rise to luminescence in the vicinity of 2.46 eV. Figure 5 demonstrates that the Arrhenius plot for the 3H centre is an excellent straight line, once the raw data have been corrected for the experimentally measured transition probability.

In each case the activation energies for the H3, H4 and 3H defects, summarized in table 2, are close to those expected.
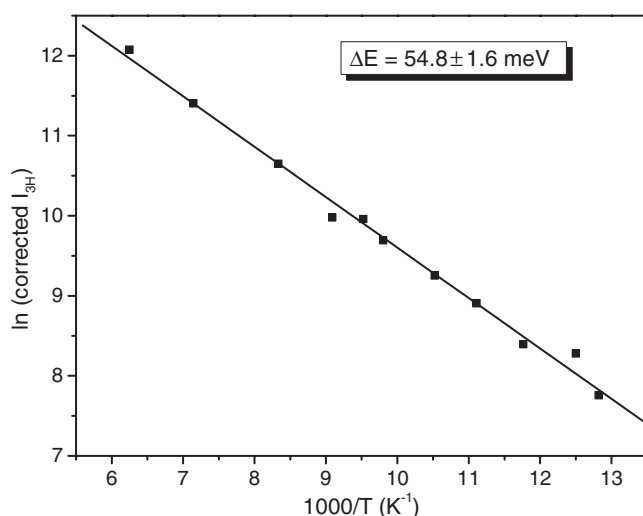
Figure 5. Arrhenius plot of the integrated intensity of the 3H zero-phonon line, using sub-threshold excitation at 514.5 nm. The data have been corrected for the experimentally measured temperature dependence of the transition probability.

Table 2. Activation energies for sub-threshold-excited photoluminescence, compared with the differences between the exciting energy and that of the corresponding zero-phonon line. All values for the activation energies are averages of the results for all the samples.

ZPL position (eV)	Number of samples	Energy difference between ZPL and excitation (meV)	Activation energy (meV)
2.463 (H3)	5	53.9	55.8 ± 4.6
2.499 (H4)	3[a]	89.9	83.5 ± 1.1
2.462 (3H)	2[b]	52.9	55.0 ± 4.5

[a] Three measurements at different locations on the same sample.
[b] Two measurements at different locations on the same sample.

3.2.1. Diamonds containing more than one type of defect. In diamonds exhibiting H3 and H4 luminescence with a comparable intensity (when excited at 325 nm) the integrated intensities of the sub-threshold-excited ZPLs deviate from Arrhenius behaviour at higher temperatures. Figure 6(a) shows data for the H3 centre in a diamond containing predominantly H3 centres and a diamond containing similar concentrations of H3 and H4 centres. Figure 6(b) shows a similar comparison for the H4 centre. For the diamond containing predominantly H4 centres the Arrhenius plot is linear up to at least 240 K, whereas, when H4 and H3 centres are present together, the data are not strictly exponential. Furthermore the gradient at lower temperatures is smaller than the gradient observed for diamonds containing only H4 centres. For specimens containing mainly H3 centres (figure 6(a)) the plot is linear up to at least 240 K (although the high-temperature data are not shown here) whereas, for a diamond containing both H3 and H4 centres, the data deviate from a linear plot at high temperatures. This deviation is opposite in sign for the two defects; at high temperatures the H4 intensity always increases, while the H3 intensity always decreases, relative to the linear extrapolations of the low-temperature data. Interestingly, the Arrhenius plot of the *ratio* of the H3 and H4 integrated intensities is a good straight line, giving an activation energy which is close to the energy difference between the zero-phonon lines (figure 7 and table 3).
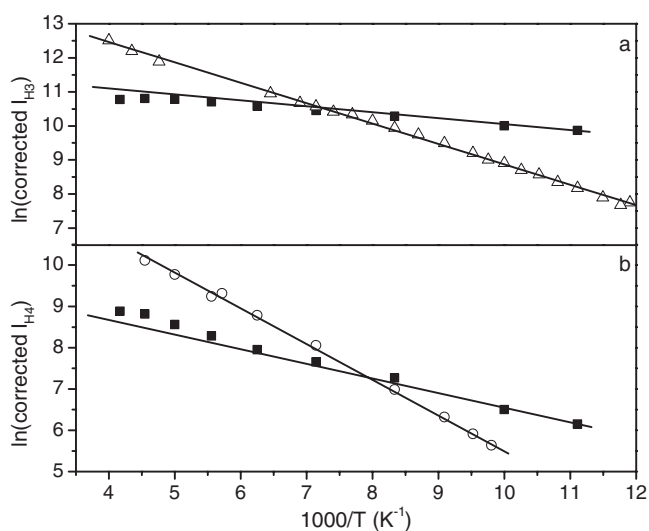
Figure 6. Arrhenius plots, using sub-threshold excitation at 514.5 nm, for the integrated intensity of (a) the H3 zero-phonon line, for a diamond containing predominantly H3 centres (triangles) and a diamond containing similar concentrations of H3 and H4 centres (squares); (b) the H4 zero-phonon line, for a diamond containing predominantly H4 centres (circles) and a diamond containing similar concentrations of H3 and H4 centres (squares). The lines in (a) and (b) for the data from the diamond containing both H3 and H4 defects are linear extrapolations of the low-temperature behaviour. In all cases the data have been corrected for the change in transition probability with temperature.
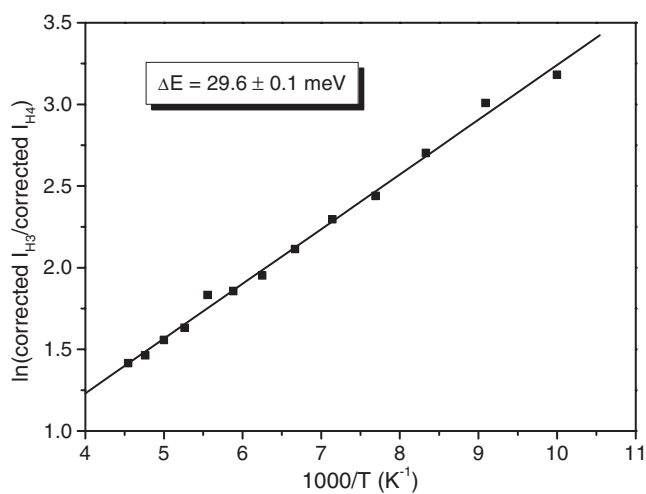

Figure 7. Arrhenius plot of the ratio of the integrated intensities of the H3 and H4 zero-phonon lines, using sub-threshold excitation at 514.5 nm, for a diamond containing both defects. The data are corrected for the changes in the transition probabilities with temperature.

However, when H4 and 3H centres are present together, there is no deviation from Arrhenius behaviour of either the H4 luminescence or the 3H luminescence. Figure 8 shows plots for these two defects, present in the same diamond, and both sets of data lie on good straight lines. The results are summarized in table 3 which shows that the activation energies
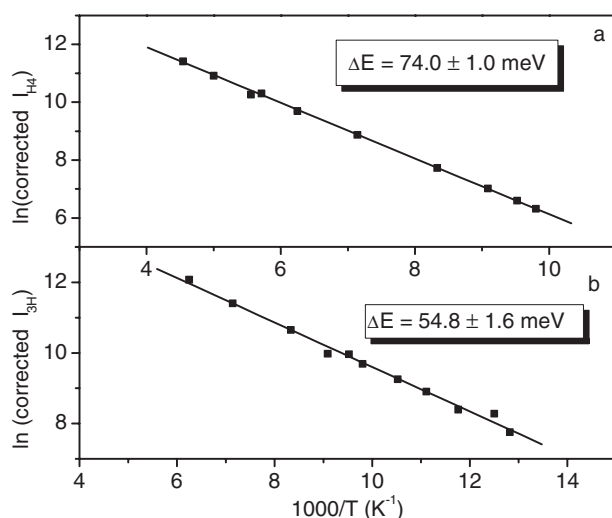
Figure 8. Arrhenius plots of (a) the H4 ZPL, (b) the 3H ZPL, corrected for the changes in the transition probabilities with temperature, for a diamond containing both defects.

Table 3. Results of the analysis on samples with more than one sub-threshold-excited defect. Three samples containing both H4 and H3 centres were measured; in each case the activation energies were ill-defined and only the average activation energy derived from the ratio plots is given. Only one sample containing both H4 and 3H defects has been analysed.

Defect combination	Activation energy (meV)	Activation energy (meV) from ratio plots
H4 + H3	Not well-defined	31.0 ± 1.7
H4 + 3H	H4: 87.1 ± 0.5	—
	3H: 54.8 ± 1.6	

agree with the spectroscopic difference in energy between the laser line and the corresponding ZPL.

A number of possible mechanisms have been considered to account for the behaviour observed when H3 and H4 centres are present in the same diamond. We consider first whether H4 PL can be reabsorbed and generate additional H3 luminescence with a temperature dependence that would lead to the behaviour shown in figure 6. In a diamond containing similar concentrations of H3 and H4 centres, the relative intensities of the H4 and H3 emissions produced by sub-threshold excitation will be $I_{H4}/I_{H3} \sim 0.01$ at 90 K and ~ 0.1 at 180 K. (We assume here—see equation (1)—that $g_1(E)$ at 514.5 nm and $P_{ZPL}(T)$ are similar for the two centres.) Only a small fraction of the H4 photons, in the energy range where the H4 luminescence band overlaps with the H3 absorption band, can potentially excite H3 luminescence. Furthermore, because of the confocal geometry used, only those H4 photons absorbed within the small volume of the diamond sampled by the microscope have any significance. Following absorption of H4 photons, it is only those H3 centres which emit in a direction that can be collected by the numerical aperture of the microscope which will be detected. It is clear that the intensity of such a signal will be completely negligible compared with that from the H3 centres excited by sub-threshold illumination at 514.5 nm. H3 absorption competing with the H4 absorption is not a possible explanation for the following reasons: (i) different relative concentrations of H3 and H4 defects cause deviations from Arrhenius
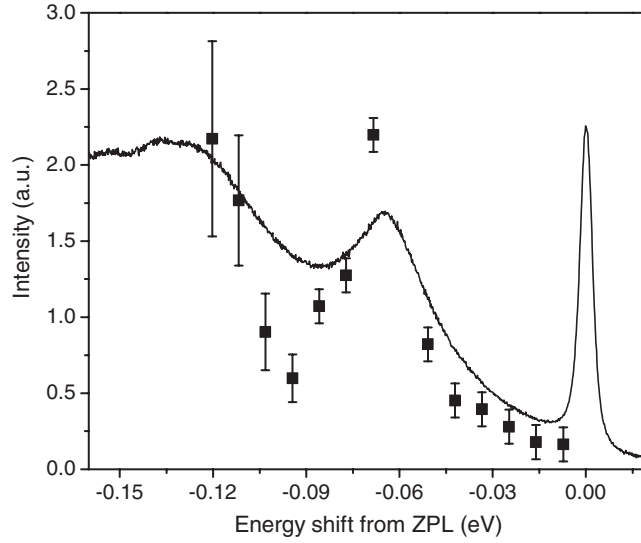
Figure 9. The intensity of the 637 nm zero-phonon line observed in photoluminescence, divided by $\exp[-E/(k_B T)]$ (data points), following sub-threshold excitation, compared with the photoluminescence spectrum measured at 150 K, divided by ν^3. The horizontal axis shows the energy from the position of the ZPL. The diamond was held at a temperature of 150 K. The error bars for the lowest-energy data points increase significantly since the intensity of the $(N–V)^-$ signal decreases rapidly as the energy between the ZPL and the laser line increases.

behaviour in the same sense; (ii) in some specimens the absorption coefficients are very small; (iii) there is no deviation from Arrhenius behaviour for diamonds containing both the 3H and H4 defects. A possible explanation for the behaviour shown in figure 6 is that there is a thermally activated energy exchange between the H4 and H3 centres, and the data in figure 7 are consistent with such a proposal.

3.3. Sub-threshold excitation as a function of energy

Equation (1) shows that, at constant temperature, following sub-threshold excitation, the intensity of the ZPL in photoluminescence should be proportional to $G(E)$ multiplied by $\exp[-\Delta E/(k_B T)]$. $G(E)$ here is the multiphonon transition probability for the absorption of ground-state phonons. This can be derived from the photoluminescence vibronic band which is produced by the coupling between the electronic transition and ground-state phonons.

If the one-phonon density of states $I_1(\nu)$ is known (where ν is the frequency), the second $I_2(\nu)$, third $I_3(\nu)$, ... phonon replicas can be calculated by convolution of the one-phonon spectrum with itself, then with $I_2(\nu)$, ... as in equation (3):

$$I_n(\nu) = \int_0^{\omega_m} I_1(x) I_{n-1}(\nu - x)\, \mathrm{d}x. \tag{3}$$

Here ω_m is the cut-off frequency of the one-phonon spectrum (165 meV).

The square of the integrated intensity of the I_n curve is proportional to

$$|I_n|^2 \sim S^n \frac{\mathrm{e}^{-S}}{n!}, \tag{4}$$

where S is the Huang–Rhys factor and n is the index of the nth-phonon replica (Davies 1981). The sum of all the phonon replicas, with the appropriate amplitudes from equation (4), is

equivalent to $G(E)$. To obtain the shape of the photoluminescence vibronic band, this function is multiplied by ν^3 (Davies 1981).

It follows that $G(E)$ may be obtained from a PL spectrum, plotted as photons per unit energy interval, by dividing every point in the PL spectrum by ν^3.

Figure 9 shows the intensity of the $(N–V)^-$ ZPL at 637 nm, divided by $\exp[-E/(k_B T)]$, plotted against E at $T = 150$ K, where E is the energy separation between the ZPL and the laser line. The experimental points are compared with the photoluminescence vibronic band, measured at 150 K, divided by ν^3, and it can be seen that a tolerable agreement has been obtained. Unfortunately the sensitivity of this technique drops off rapidly with increasing ΔE.

The PL spectrum used to calculate $G(E)$ was not corrected for the response function of the spectroscopic equipment. Nevertheless, over the small energy range covered, the shape of $G(E)$ has been determined with sufficient accuracy for comparing with the data obtained using sub-threshold excitation.

4. Summary

Diamonds containing predominantly H3 or H4 centres, illuminated with a laser having an energy slightly less than that of the zero-phonon transition, exhibit luminescence due to sub-threshold excitation. Both types of centre show the same behaviour with temperature; the excitation process is thermally activated with an activation energy equal to the energy difference between the laser photons and the energy of the corresponding zero-phonon transition. The same phenomenon is also observed for diamonds containing 3H centres. This conclusion contrasts with that of Iakoubovskii *et al* (2001) who found that the intensity of the zero-phonon line for sub-threshold-excited H3 luminescence was almost temperature independent. However, they made measurements only at 120 and 300 K, and did not correct the intensity of the luminescence for the large change in transition probability.

In diamonds that contain similar concentrations of H3 and H4 centres the sub-threshold excitation of both defects shows a deviation from Arrhenius behaviour. However, an Arrhenius plot of the ratio of the H3 and H4 integrated intensities yields an activation energy which is close to the energy difference between the zero-phonon lines. This may indicate that there is a thermally activated energy transfer between the H3 and H4 centres.

The $(N–V)^-$ centre also exhibits sub-threshold excitation, and varying the excitation energy with the diamond at a fixed temperature maps out the phonon distribution derived from the PL spectrum—in further confirmation of the proposed model.

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