LETTER TO THE EDITOR

Migration energy of the neutral vacancy in diamond

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Abstract. When irradiated nitrogen-rich natural diamond is heated isothermally, the vacancies are destroyed at two rates. In both processes vacancies migrate to and are trapped at the nitrogen. The faster process coincides with a sharpening of the optical transitions of the vacancy. Both processes have the same activation energy of $E_m = 2.3 \pm 0.2$ eV. By annealing nitrogen-free diamond, E_m is shown to be the migration energy of the neutral charge state of the vacancy.

In this letter we examine the thermal annealing of the vacancy in diamond. We show that in common nitrogen-rich natural diamonds the vacancy anneals through two distinguishable processes. Both have the same activation energy of 2.3 ± 0.2 eV, which is shown to be the migration energy of the neutral charge state of the vacancy.

Radiation damage of diamond produces an optical absorption and luminescence band, known as the 'GR1' band, with its zero-phonon line at 1.673 eV. This band is unambiguously associated with the neutral charge state V^0 of the vacancy (see Lowther and Stoneham (1978) and references therein). Nitrogen is an impurity found in almost all diamonds. Irradiation of the relatively rare 'nitrogen-free' diamonds, refered to as 'type IIa' diamonds, produces vacancies predominantly in the neutral charge state (Davies 1977). In a small proportion of natural diamonds, and in most diamonds synthesized at high pressure, the nitrogen is present as isolated substitutional nitrogen atoms. These nitrogen atoms are deep donors with an ionization energy of 1.9 eV (Farrer 1969). They convert V^0 to a negative charge state which we will denote by V^- (Davies 1977); however, we have no experimental data on the precise charge on the vacancy. V^- is recognizable by its optical absorption band with a zero-phonon line at 3.15 eV. In most natural diamond (referred to as 'type Ia' diamond) the impurity nitrogen is aggregated into a pair of nearest-neighbour substitutional atoms known as the 'A' aggregate or a larger ('B') aggregate. The concentrations of nitrogen in the A and B aggregates can be measured from their vibrational absorption bands (Woods *et al* 1990), and total nitrogen concentrations of the order of 10^{20} cm^{-3} are typical. In electron-irradiated type Ia diamonds the V^0 and V^- absorption bands are always observed to be of comparable strengths (Davies 1974). The precise relative strengths of the bands depend on the conditions of the measurement since photochromic processes occur (Dyer and du Preez 1965).

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When the relatively pure type IIa diamond is annealed, the concentration of V^0 centres is reduced. It is not known whether the mechanism of their destruction is by migration of V^0 or by the motion of a mobile species to V^0. (The results presented here will establish that the V^0 centres migrate to a trapping point.) In contrast, it is well-established that in type Ia diamond the vacancies migrate to and are trapped at A or B nitrogen aggregates. A vacancy trapped at an A aggregate produces absorption in the 'H3' band with its zero-phonon line at 2.463 eV; trapped at a B aggregate it gives absorption at 2.498 eV in the 'H4' band (Davies 1972, Clark and Davey 1984). The 'H2' defect (Mita *et al* 1990) is not created at the relatively low annealing temperatures used in this work.

For this study, two sets of natural diamonds were selected. One set had between 3.5–6.2×10^{19} cm^{-3} nitrogen in the A form, and between 0.03–1.8×10^{19} cm^{-3} nitrogen in the B form, as measured from the optical absorption generated in the one-lattice phonon region (Woods *et al* 1990). From earlier work (Davies 1972, Woods *et al* 1990) we expect the absorptions in the H4 and H3 zero-phonon lines to be in the ratio

$$H4/H3 = 0.25 N_B/N_A \tag{1}$$

where N_B and N_A are the concentrations of nitrogen atoms in the B and A aggregates. In our sample with the highest ratio of the concentrations of B and A nitrogen, $N_B/N_A = 0.29$, the ratio of absorption in the H4 and H3 zero-phonon lines is predicted from equation (1) to be $H4/H3 = 7 \times 10^{-2}$, in agreement with observation after annealing this sample. The H4 and H3 bands have almost identical properties, including their radiative lifetimes (Collins *et al* 1983, Crossfield *et al* 1974), implying that in all the samples of this set the A aggregates dominated over the B aggregates for capturing vacancies. The second set of samples was chosen to contain negligible nitrogen (in practice less than $\approx 10^{17}$ cm^{-3}). All the diamonds were about 1.5 mm thick. They were irradiated at room temperature with nominal doses of 5×10^{17} cm^{-2} 2-MeV electrons. The samples were annealed at temperatures of 600, 650, 700 or 750 °C in a quartz tube evacuated to 10^{-5} Torr to prevent graphitization. The upper limit on the temperature was fixed by the need to keep the heating time of the tube substantially less than the anneal times, and the lower limit by the need for an acceptably quick result. Absorption spectra were recorded with the samples at 77 K in the full white light of a tungsten lamp. Order sorting for the dispersive monochromator was by filters placed after the sample. In all cases we have measured the strength of absorption by integrating the absorption coefficient $\mu(E)$ at photon energy E over the relevant zero-phonon line, measured at 77 K.

In the type Ia diamonds, first-order reaction kinetics are expected, since the concentration of nitrogen trapping centres is over two orders of magnitude greater than the vacancy concentration. However, we have observed that in all our type Ia samples the decay of the GR1 (V^0) line is not given by a single exponential (figure 1(*a*)). The measured absorption $A(V^0)$ can be accurately parameterized by the sum of two exponentials

$$A(V^0) = A_0[a_1 \exp(-t/\tau_1) + (1 - a_1) \exp(-t/\tau_2)] \tag{2}$$

where A_0 is the initial strength of the GR1 line, τ_1 and τ_2 are the two exponential decay times, and a_1 is the fraction which decays with time constant τ_1. The growth
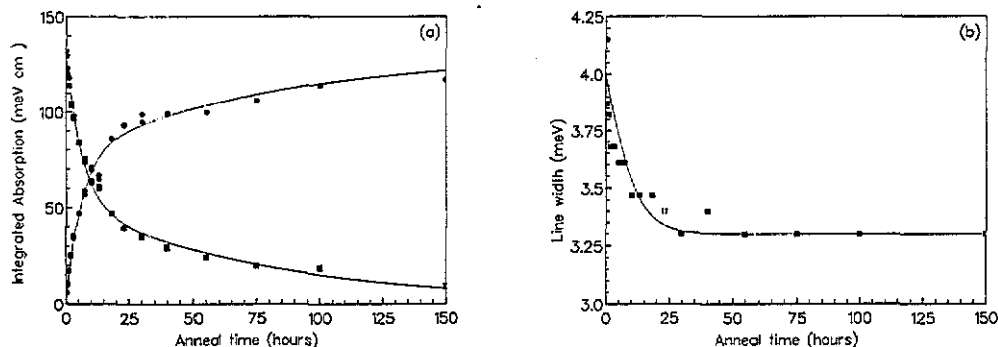
Figure 1. Data taken during the annealing at 600 °C of a type Ia diamond. (*a*) Experimental points show the decrease in GR1 intensity (■) and the growth of H3 intensity (●). The lines are calculated using equations (2) and (3) with $a_1 = 0.595$, $\tau_1 = 5.92$ hours, $\tau_2 = 77$ hours, $A_0 = 131$ meV cm^{-1}, $A_\infty = 130$ meV cm^{-1}. (*b*) Experimental points show the decrease in full width at half height of the GR1 line. The line is calculated from equation (4) with $w_1 = 2.4$ meV, $w_2 = 1.65$ meV and with the other parameters determined from the fit in (*a*).

of the 2.463 eV H3 zero-phonon line in the same samples is closely described by 'inverting' equation (2) into a saturating exponential

$$A(H3) = A_\infty[1 - a_1 \exp(-t/\tau_1) - (1 - a_1)\exp(-t/\tau_2)]. \tag{3}$$

The only adjustable parameter used in the fit to the H3 data of figure 1(*a*) is A_∞, the strength of the H3 line after infinite annealing; we have used the decay times τ_1 and τ_2, and the fractionation, a_1, derived from the decay of V^0. Note that both decay processes contribute equivalently to the growth of the H3 centres.

Two distinct stages are also observed in the variation of the full width at half height of the GR1 line during the anneal. In all our samples the line sharpened during the faster anneal process, as shown in figure 1(*b*) for the same sample used in figure 1(*a*). We recall that the widths of zero-phonon lines are caused by the spread of perturbations of the optical centres in their different local environments in the samples (Stoneham 1969). The data suggest that those vacancies which anneal quickly are in more highly perturbed environments than those which anneal slowly. We take the simplest representation of this idea and assume that there are only two different types of environment for the vacancies. We assume that the zero-phonon lineshapes are given by Lorentzian functions, so that the intensity at photon frequency ν is $I(\nu) \propto 1/(w^2 + \nu^2)$, where the full width at half height is $2w$. After an anneal time t the the zero-phonon lineshape is then given by

$$I(\nu) = \frac{r_1}{w_1^2 + \nu^2}\exp(-t/\tau_1) + \frac{r_2}{w_2^2 + \nu^2}\exp(-t/\tau_2) \tag{4}$$

where $2w_1$ and $2w_2$ are the widths of the zero-phonon lines in the two environments, and the ratio

$$\frac{r_1}{r_2} = \frac{w_1 a_1}{w_2(1 - a_1)}$$

is determined by the fraction a_1 of the GR1 absorption which decays with time constant τ_1. The width at long anneal times fixes $2w_2 = 3.3$ meV. The line through

the data on figure 1(b) is the full width at half height calculated numerically for the lineshape equation (4) using $2w_1$ (= 4.8 meV) as the only adjustable parameter. The measured widths are adequately fitted by this simple model.

Our data show that the vacancies can be regarded as being in two distinctly different types of environment. We examine next the origin of the difference. Some of the vacancies may have self-interstitials, C_i, trapped nearby, analogous to the non-reorientable fraction of the divacancies in silicon (Watkins 1975). The perturbations of V^0 in these closely spaced V^0, C_i pairs could produce additional linewidth. Fast recombination of the closely spaced V^0, C_i pairs plus the slower trapping of V^0 by longer-range migration to the nitrogen would lead to a two-exponential decay. However, this mechanism can be ruled out by the observed growth of H3 during both parts of the annealing—both decay processes necessarily involve motion of the vacancy to the nitrogen.

It appears that we must attempt to describe the data solely in terms of vacancies and nitrogen. The nitrogen impurity is a major source of strain in diamonds (Kaiser and Bond 1959). The additional linewidth at the start of the anneal could be thought to be caused by the fast-annealing V^0 centres being in regions of particularly high nitrogen content. This possibility can be excluded since the H3 centres formed first would be in regions of high nitrogen and would give a broad zero-phonon line. The line would then sharpen progressively as the annealing proceeded and H3 centres were formed in the regions of lower nitrogen. This variation of the width of the H3 line during the annealing has not been observed in any of our samples. A second possibility, which is consistent with all our data, is that a fast-annealing V^0 is created close to one nitrogen aggregate. These highly perturbed vacancies are likely to be rapidly captured at the nearby nitrogen, sharpening the GR1 zero-phonon line at a rate characterized by the fast decay time.
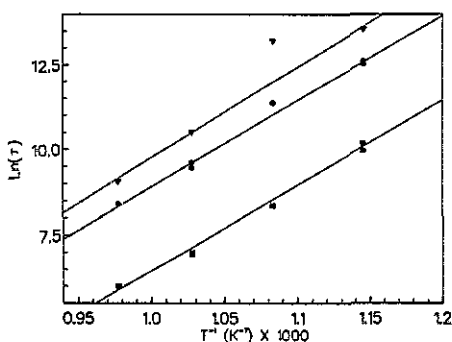

Figure 2. Arrhenius plots of the measured fast and slow exponential decay rates (measured in seconds) for type Ia samples (■, ●), and for type IIa samples (▼).

We can confirm that in both decay processes the vacancy moves with the same energetics by noting that both the fast and the slow exponential decay times obey an Arrhenius temperature activation

$$\tau = \tau_0 \exp(E_m / kT) \tag{5}$$

with the *same* activation energy (figure 2) of

$$E_m = 2.3 \pm 0.2 \text{ eV}. \tag{6}$$

The values of τ_0 used for the lines on figure 2 for the fast and slow decay rates are

$$\tau_0^1 = 4.6 \times 10^{-9}\text{s} \qquad \tau_0^2 = 5.5 \times 10^{-8}\text{s}. \qquad (7)$$

The uncertainty in E_m corresponds to uncertainties in τ_0 by a factor of 12 larger or smaller.

Since the GR1 line is destroyed by motion of the vacancy, the activation energy is the migration energy of the vacancy. However, it is not necessarily the migration energy of V^0, since as we have noted, both V^0 and V^- are present in irradiated type Ia diamonds. After the first few annealing stages the ratio of the absorptions produced by V^0 and by V^- is invariant in all our type Ia diamonds. The width of the 3.150 eV (V^-) line also sharpens during the anneal, exactly as for the 1.673 eV (V^0) line. This does not imply that V^0 and V^- anneal with the same activation energies—only one charge state may be involved in the migration as long as the same equilibrium is re-established between the concentrations of V^0 and V^- before the measurement.

In an attempt to identify which species, V^0 or V^-, is migrating in the type Ia diamonds, we have annealed four relatively pure type IIa diamonds in which only the V^0 absorption can be detected. Palmer (1961) annealed one type IIa diamond at successively higher temperatures of 500, 600 and 700 °C and derived two activation energies for the destruction of the GR1 band, 1.62 and 2.35 eV. We have examined four type IIa diamonds. In each sample there was a fast initial decay (figure 3) which possibly represents Palmer's low energy process. Because we do not know the fate of the vacancies in these diamonds we cannot in this case exclude the recombination of closely spaced V^0, C_i pairs during the fast decay phase. After the initial decrease the decay was then accurately exponential with a decay time whose temperature dependence is shown in figure 2.
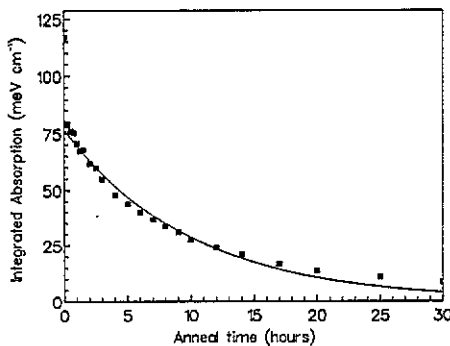

Figure 3. Experimental points show the decrease in GR1 intensity during the annealing at 700 °C of a type IIa diamond. The line shows a fit to the slow decay component, using $A_0 = 76.8$ meV cm^{-1} and $\tau = 10.16$ hours.

By using type IIa diamond the charge state of the migrating vacancy is fixed as neutral, but the dominant trapping points are unknown. Dislocations, which are particularly prevelant in type IIa diamonds, are possible traps. (The observation of first-order kinetics rules out pairing of V^0 centres to form di-vacancies.) The decay time is determined by the jump rate but also by the density of traps which is likely to differ between the different diamonds. Of the four datum points for the type IIa

samples, three lie on a straight line on the Arrhenius plot (figure 2) and give an activation energy of

$$E_m^0 = 2.4 \pm 0.1 \text{ eV} \tag{8}$$

essentially in agreement with E_m (equation (6)) for type Ia diamonds. We know that in type Ia diamond the vacancy anneals by migrating (to the nitrogen). Since $E_m^0 \approx E_m$, the annealing of vacancies with this activation energy in type IIa diamond is also due to their motion to a trapping point and not by movement of another defect to V^0.

In our type IIa diamonds there was no evidence for the V^- band at 3.15 eV, and so this activation energy is assigned to the migration energy of V^0.

We have demonstrated that in the most common diamond, type Ia diamond, the thermal annealing of vacancies is activated by an energy of $E_m = 2.3 \pm 0.2$ eV. In these diamonds, V^0 and V^- co-exist, and both centres are observed to be destroyed at the same rates and with the same behaviour of their zero-phonon linewidths. The annealing may be expected to be governed by the charge state with the lower activation energy. In type IIa diamonds the neutral charge state predominates. In three out of four type IIa diamonds we have observed the same activation energy as in type Ia diamonds. Consequently we assign the migration energy of 2.3 eV to V^0. This value is close to the activation energy of 2.35 eV derived from annealing one type IIa diamond by Palmer (1961). Bernholc *et al* (1988) calculated an energy of 1.9 ± 0.1 eV for the movement of a carbon atom from a site neighbouring a vacancy to the saddle point between the two atomic sites; this value included an allowance for relaxation at the saddle point but did not include the Jahn–Teller relaxation, E_{JT}, of the vacancy (Bernholc 1992). Their energy should be increased by E_{JT} to obtain the migration energy. From the luminescence bandshape, $E_{JT} = 200 \pm 50$ meV (Davies 1982), giving a calculated migration energy of 2.1 ± 0.15 eV, in close agreement with our measurement. Since we assign vacancy migration in type Ia diamond to the motion of V^0, V^- must move at a slower speed, at a given temperature, suggesting that its migration energy is probably larger.

Finally we draw attention to three problems brought to light by this work. First, in all our type Ia diamonds the fraction of vacancies which anneal by the fast process is close to 50% of the total number of vacancies. If these vacancies are within a few atomic spacings of nitrogen aggregates, as is implied by our arguments, then there must exist a mechanism for the preferential creation of vacancies near nitrogen. Secondly, the pre-exponential factors τ_0 in equation (7) are larger than expected for vacancies trapped at nitrogen aggregates. We have identified the slow capture process in type Ia diamonds with those vacancies which are initially not correlated in position with the nitrogen. For a random walk to trapping points present at 300 ppm we expect V^0 to make $\approx 10^6/300$ atomic jumps, i.e., there must be about 3300 successful attempts by a neighbouring atom to enter the V^0 site. Vacancy-related centres in diamond are characterized by a vibrational quantum of 40 meV (10^{13} Hz). Consequently we expect $\tau_0^2 \approx 3.3 \times 10^{-10}$ s, two orders of magnitude smaller than the observed value of equation (7) and outside our estimated uncertainty in that value. The third intriguing aspect of the annealing process is the surprisingly low capture radius for vacancies at B aggregates compared to that at A aggregates (equation (1)).

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