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Cathodoluminescence studies of isotope shifts associated with localised vibrational modes in synthetic diamond

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Abstract. Sharp structure between 2.60 and 2.64 eV observed in the cathodoluminescence spectra of synthetic diamond, following radiation damage and annealing at 300 °C, has been identified as a series of local-mode phonon replicas of the zero-phonon line at 2.807 eV. By examining the isotope shifts of these replicas in diamonds grown using ^{13}C (and containing natural nitrogen) compared with diamonds synthesised from natural carbon and doped with ^{15}N , we conclude that the optical centre contains one nitrogen atom in association with the interstitial produced by the radiation damage. The local-mode structure is very similar to that observed for the system with a zero-phonon line at 3.188 eV, which has also been shown to be a single nitrogen plus interstitial centre. Coupling of the 2.807 eV electronic transition to lattice modes is, however, much weaker than for the 3.188 eV transition. In diamonds which have not been thermally annealed the intensities of these vibronic bands, initially zero, are observed to increase with increasing time under the influence of the electron beam—a phenomenon observed previously for the 2.156 eV optical centre. The absence of localised vibrational modes, the response of the zero-phonon line to random strain and the greatly increased luminescence intensity following annealing at 800 °C lead us to propose that the 2.156 eV centre involves single nitrogen with one or more vacancies.

1. Introduction

In this paper we show, for the first time, that the sharp lines between 2.60 and 2.64 eV in the cathodoluminescence spectra of irradiated and annealed synthetic diamond are local-mode phonon replicas of the zero-phonon transition at 2.807 eV. From studies of this structure in diamonds grown from ^{13}C , containing natural nitrogen, and diamonds grown from natural carbon and doped with a mixture of ^{14}N and ^{15}N , we show that the optical centre contains a single nitrogen atom.

Recent developments in the synthesis of diamond by Sumitomo and De Beers enable large diamonds to be grown on an economic basis by the temperature-gradient method (see, e.g., Shigley *et al* 1986, 1987). This has led to renewed interest in the study of point defects in diamond, and to a better understanding of the segregation of impurities into the different growth sectors (Collins 1989a, b).

The major impurity in synthetic diamond is isolated substitutional nitrogen; a small fraction of natural diamonds also have nitrogen present predominantly in this form (Dyer *et al* 1965). Such diamonds are referred to as type Ib. In the majority of natural diamonds, most of the nitrogen is present in aggregated form (see Woods (1986) for

a recent description). Experimental batches of synthetic diamond produced by the temperature-gradient method have been studied previously, and it was shown that the nitrogen concentration is significantly lower in the cubic {100} growth sectors than in the octahedral {111} sectors (Woods and Lang 1975). More recent investigations (Kanda *et al* 1987, Dodge 1988, Welbourn 1988) have confirmed that result and shown that the nitrogen concentration is even lower in the minor {110} and {113} growth sectors. A conflicting result has been reported by Satoh *et al* (1989) who claim that, when the diamonds are grown at a relatively low temperature, the nitrogen concentration is highest in the {100} sectors.

Following radiation damage and annealing at about 300 °C, three vibronic systems with zero-phonon lines at 3.188, 2.807 and 2.156 eV are observed in the cathodoluminescence spectra of many type Ib diamonds. The latter system increases considerably in strength following annealing at 800 °C, and the luminescence observed by eye is then an intense orange. If the emission is examined before the diamond has been thermally annealed, in some samples the luminescence which is initially green, or blue, gradually changes with time to become predominantly pink, owing to the growth of the 2.156 eV system. This migration of the defects under the influence of the electron beam has been studied previously by Davies (1970) but is not properly understood.

Electron spin resonance measurements (Lomer and Wild 1973) suggest that the interstitial produced by the radiation damage is mobile at temperatures as low as 77 K and becomes trapped at various sites in the crystal. For annealing times around 1 h, there is little evidence for vacancy mobility until the diamond is heated to at least 550 °C; heating to around 800 °C is necessary to eliminate the GR1 and ND1 centres produced by the irradiation, and associated respectively with the neutral and negative vacancies (Davies 1977). In type Ib diamond this annealing produces an absorption band, with a zero-phonon line at 1.945 eV, which has been shown by Davies and Hamer (1976) to be due to a nitrogen–vacancy centre. Although photoluminescence in the 1.945 eV system can be generated by optical excitation in the absorption band, the system is absent from all cathodoluminescence spectra.

In the present investigation, we have studied the cathodoluminescence spectra associated with the 2.156, 2.807 and 3.188 eV centres. We show that, as with the 2.156 eV system, in a diamond that has not been thermally annealed the emission from the 2.807 and 3.188 eV systems, initially absent, grows as a function of time. From studies of the isotope shifts of the local-mode peaks in the spectra of the 2.807 and 3.188 eV systems, we conclude that each of the centres responsible for the luminescence involves the interstitial produced by the radiation damage together with a single nitrogen atom. The substantial increase in the 2.156 eV luminescence produced by annealing at temperatures above 550 °C, the response of the zero-phonon linewidth to random strains in the crystal and the absence of localised vibrational modes lead us to propose that this centre involves a vacancy (or vacancies) together with a single nitrogen atom.

2. Experimental details

The diamonds used in this work included a natural type Ib diamond with a polished surface, and the following batches of synthetic specimens:

- (i) standard diamonds about 1.5 mm across grown by the abrasive-grit process;
- (ii) diamonds about 0.6 mm across doped with nitrogen-15, grown by the abrasive-grit process;

(iii) standard diamonds about 2 mm across, grown by the temperature-gradient method;

(iv) diamonds about 1.5 mm across produced from ^{13}C , grown by the temperature-gradient method.

The isolated substitutional nitrogen concentration in a natural type Ib diamond is around 40 ppm. Previous measurements on the doped diamonds (Collins and Woods 1982) showed that they contain similar concentrations of ^{14}N and ^{15}N with a total nitrogen concentration of about 550 ppm. The diamonds grown from ^{13}C contain about 500 ppm of natural nitrogen, and the nitrogen content of the present 'standard' diamonds is somewhat less than this but has not been measured in the present investigation. (The nitrogen concentrations for the synthetic diamonds are average values based on infrared absorption measurements which assume that the nitrogen is homogeneously distributed. As discussed in § 1, the concentrations of nitrogen are very different in the different growth sectors.)

The diamonds were irradiated with typically 10^{22} electrons m^{-2} at 2 MeV, using the Van de Graaff accelerator at the University of Reading. Isothermal anneals were carried out for periods of 2 h in air for temperatures up to 500 °C and in vacuum at higher temperatures.

Cathodoluminescence spectra were measured using a custom-built electron gun operating at typically 45 kV and 10 μA , with a spot size about 300 μm in diameter. Measurements were made with the samples at 77 K, mounted in indium on the end of a cold finger. The excited surface of the large-area natural diamond was covered with a thin layer of graphite (using colloidal graphite in alcohol) and a number of small apertures were made in this film; this procedure is necessary to stop the specimen from charging up and deflecting the beam. Luminescence was collected from the excited face of the diamond with a spherical mirror and focused onto the entrance slit of a Spex 1500 monochromator fitted with a 1200 groove mm^{-1} grating blazed at 500 nm and an EMI 9789Q or 9558Q photomultiplier. A microcomputer system was used to collect the data, to perform signal averaging by multiple scanning, where necessary, and to replot the spectra on a linear energy scale. The spectra have not been corrected for the wavelength-dependent response of the optical system, and this will lead to a slight distortion of the shapes of the vibronic bands. Energies of sharp features in the spectra have been determined to an accuracy of ± 0.1 meV by superimposing, on the luminescence spectra, calibration lines which straddled the region of interest, and interpolating between these lines. The resolution is limited by the quality of the samples, and not by the spectroscopic instrumentation or techniques.

3. Results and discussion

The three cathodoluminescence bands studied in this work are shown in figure 1. The energy axes have been adjusted so that the zero-phonon lines are vertically one below the other. We notice that, although the vibronic bands are very different, each system has a sharp 'edge' at about 165 meV (the energy of the LO phonon) below the corresponding zero-phonon line. At energies just below this edge there are series of sharp lines in the 2.807 and 3.188 eV systems, but not in the 2.156 eV system.

Following radiation damage, and annealing at 800 °C, the intensity of the 2.807 eV zero-phonon line is about 30 times weaker than that of the 3.188 eV line. By examining

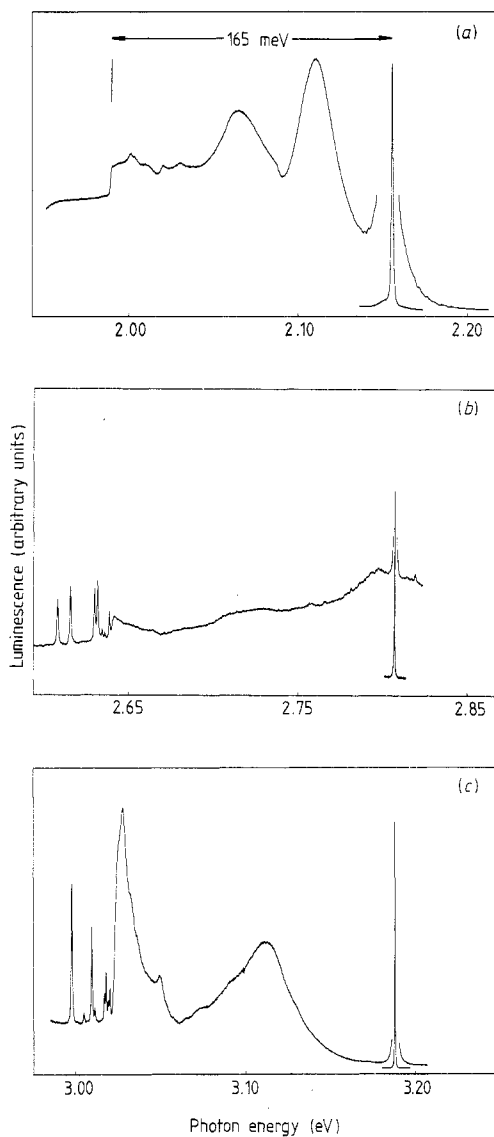


Figure 1. Cathodoluminescence spectra in the (a) 2.156 eV, (b) 2.807 eV and (c) 3.188 eV vibronic systems. The bands have been recorded at gains arbitrarily higher than those used for the zero-phonon lines. The energy axes have been shifted so that these lines are vertically one below the other. The vertical bar in (a) indicates the position of the LO edge, 165 meV lower in energy than the zero-phonon line. The intensity of the 2.807 eV zero-phonon line is only about one thirtieth of the 3.188 eV line, and the underlying luminescence in (b) is due to the tail of the 3.188 eV band. All spectra were recorded with the sample at 77 K.

the cathodoluminescence from different regions of the synthetic diamonds it was noticed that the widths of both zero-phonon lines vary considerably from one region of the crystal to another. For all diamonds except those from batch (iii)—see § 2—the lines were narrower in the {100} growth sectors than in the {111} sectors, and in all the specimens the lines were narrowest in the {110} sectors (this was not confirmed for the ^{13}C diamonds which had no suitable {110} facets). This phenomenon was particularly marked in the ^{15}N -doped diamonds (which have the highest average nitrogen concentration). The widths of the 3.188 eV line at half-height in a randomly selected group of {111}, {100} and {110} sectors for one ^{15}N sample were 2.2 meV, 0.77 meV and 0.46 meV, respectively; furthermore, in the major sectors there were broad wings at the base of the line which were absent in the {110} sector. These variations in linewidth

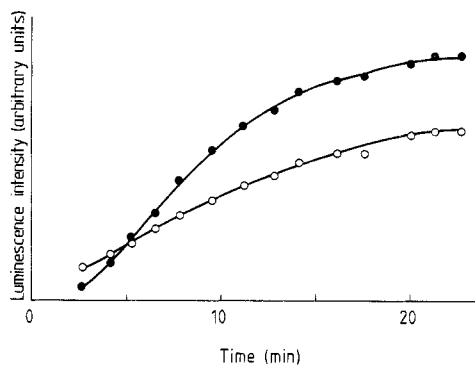


Figure 2. Growth in the cathodoluminescence intensity of the 2.807 eV zero-phonon line (●) and the underlying background due to the 3.188 eV band (○) plotted as a function of time. Data are for a natural type Ib diamond at 77 K.

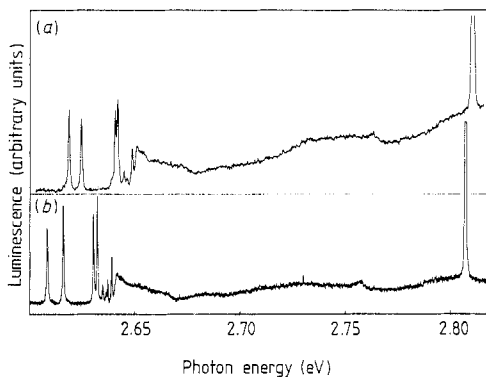


Figure 3. The 2.807 eV vibronic band for (a) a synthetic diamond grown from ^{13}C and (b) a diamond grown from ^{12}C . The spectra have been displaced vertically for clarity, and the zero-phonon lines are well off scale. The cathodoluminescence spectra were recorded with the diamonds at 77 K.

are almost certainly associated with the strain field produced by the nitrogen. (The distribution of nitrogen in the different growth sectors has been discussed in § 1. The diamonds in batch (iii) were grown at a lower temperature than the other specimens and may therefore have the highest nitrogen concentration in the {100} sectors (Satoh *et al* 1989.) The width of the 2.156 eV zero-phonon line varies in a similar way in the different regions of the diamonds, but in all cases the widths of the 2.807 and 3.188 eV lines are substantially narrower than that of the 2.156 eV line (by a factor of about 8).

By carefully selecting a growth sector which gives intense emission and, at the same time, the narrowest possible zero-phonon line for a given diamond, we have been able to examine in detail the local-mode structure associated with the 2.807 eV system which was overlooked by Collins and Woods (1987) in their similar study of the 3.188 eV system.

As part of this investigation we examined a natural type Ib diamond that had been irradiated but not annealed. As reported by Davies (1970), the colour of the luminescence was observed to change from blue to pink over a period of a few minutes, owing to the growth of the 2.156 eV system. By moving the sample to expose another aperture in the graphite film this observation could be repeated and extended to other optical centres. It was found that, as the colour of the luminescence changed from blue to pink, the intensities of the 2.807 and 3.188 eV systems grew in intensity from virtually zero to a saturated value, as illustrated in figure 2. (The 2.807 eV zero-phonon line is superimposed on the vibronic band of the 3.188 eV system and, by repeatedly scanning over the 2.807 eV line and noting the intensity of the background luminescence as a function of time, the growth of both systems could be measured simultaneously.) The curves in figure 2 are similar to those obtained by Davies (1970) for the 2.156 eV system, and we have not studied this phenomenon further in the present investigation.

In figure 3, we compare the 2.807 eV vibronic band for diamonds grown from ^{12}C and ^{13}C . We note that the energy separation between the LO edge and the zero-phonon line for the ^{13}C diamond is smaller than the corresponding separation in the ^{12}C diamond by a factor of about $(12/13)^{1/2}$ (i.e. 0.961) and also that all the sharp lines at energies just

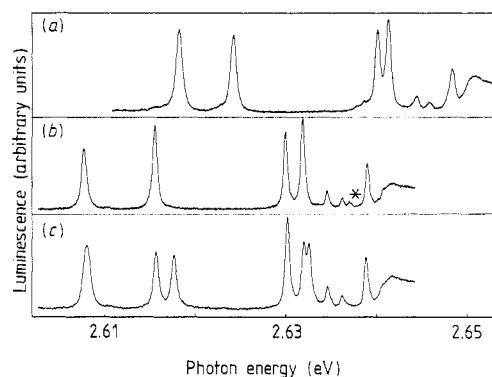


Figure 4. Cathodoluminescence spectra in the local-mode region of the 2.807 eV system for (a) a ^{13}C diamond containing ^{14}N , (b) a ^{12}C diamond containing ^{14}N and (c) a ^{12}C diamond containing roughly equal concentrations of ^{14}N and ^{15}N . (a) was obtained from a {100} growth sector, and (b) and (c) from {110} sectors. All spectra were recorded with the samples at 77 K and have been displaced vertically for clarity. The feature marked with a * in (b) is sample dependent and not part of the local-mode spectrum. (See also figure 3(b) where this line is relatively stronger.)

Table 1. Peak energies, phonon energies and isotope shifts for the sharp peaks in figures 4(a) and 4(b). The absolute peak energies are labelled $E(12)$ and $E(13)$ and the phonon energies as $\hbar\omega(12)$ and $\hbar\omega(13)$ for the ^{12}C and ^{13}C diamonds, respectively. The phonon energies are measured from the position of the corresponding zero-phonon line at 2806.6 meV for the ^{12}C diamond and 2810.0 meV for the ^{13}C diamond. The ratio R of $\hbar\omega(13)$ to $\hbar\omega(12)$ gives an indication of the isotope shift. For an isolated diatomic molecule executing harmonic vibrations, R would be 0.961 for a carbon-carbon vibration, and 0.979 for a carbon- ^{14}N vibration when the ^{12}C is changed to ^{13}C . Uncertainties in the energies are ± 0.1 meV, resulting in an uncertainty of rather less than ± 0.001 in R . Data for the table were processed with a higher precision than this and then rounded off; this occasionally leads to an apparent discrepancy of ± 1 least-significant digit.

$E(12)$ (meV)	$E(13)$ (meV)	$\hbar\omega(12)$ (meV)	$\hbar\omega(13)$ (meV)	R
2608.0	2618.2	198.6	191.8	0.966
2615.8	2624.0	190.8	186.0	0.975
2629.8	2640.2	176.7	169.8	0.961
2631.6	2641.4	174.9	168.6	0.964
2634.2	2644.3	172.4	165.7	0.961
2635.8	2645.7	170.8	164.2	0.962
2638.5	2648.3	168.1	161.7	0.962

below the LO edge have moved in energy by a similar amount. This immediately suggests that corresponding lines in the two spectra are local-mode replicas of the zero-phonon line. There is one additional line in the spectrum of the ^{12}C diamond, at 2.6366 eV which, in our diamonds, was sample dependent and, in a given sample, decreased in intensity during the measurements. This, clearly, is not part of the local-mode spectrum. The shift in energy of the zero-phonon line of the ^{13}C diamond, evident in figure 3, is a general feature of vibronic centres and has been discussed in detail by Collins *et al* (1988).

The local-mode lines of the ^{13}C diamond are not quite as sharp as those of the ^{12}C diamond (since they were obtained from a {100} rather than a {110} growth sector) but, even so, close examination of figure 3 shows that the fractional change in energy on changing isotopes is not the same for all the components. The local-mode replicas are shown in more detail in figure 4, and the energies of these features and their separations from the appropriate zero-phonon line are listed in table 1. The final column of that table gives the ratios of the phonon energies for each of the seven lines in the spectra

Table 2. Effect on the isotope shift of coupling a carbon–nitrogen diatomic molecule to a rigid lattice by springs with constants k_1 and k_2 attached to the carbon and nitrogen atoms respectively. R_1 and R_2 are the experimentally observed ratios of the energies of the local modes, when the carbon atom is changed from ^{12}C to ^{13}C or the nitrogen atom is changed from ^{14}N to ^{15}N , respectively, and R'_1 and R'_2 are the corresponding calculated values using the values of k_1 and k_2 shown (as multiples of k , the constant of the spring in the isolated diatomic molecule). By forcing R'_1 to equal R_1 , good agreement is also obtained between R'_2 and R_2 . A whole range of pairs of values of k_1 and k_2 is possible—those shown are simply examples. Local-mode energies are quoted for the ^{12}C diamond. The experimental uncertainty in the values of R_1 and R_2 is less than 0.001.

Local-mode energy (meV)	R_1	R_2	R'_1	R'_2	k_1	k_2
Harmonic oscillator	—	—	0.979	0.985	0	0
2608.0	0.966	>0.995	0.966	0.996	0.2	3
2615.8	0.975	0.989	0.975	0.989	0.8	1.5
2631.6	0.964	0.995	0.964	0.998	0.25	5.3

shown in figures 4(a) and 4(b). For four of the lines the ratios are close to 0.961, as expected for a carbon–carbon vibration. For the peak at 2.6158 eV in the ^{12}C diamond (the second peak from the left in figure 4) the ratio is approaching the value of 0.979 calculated for a carbon–nitrogen vibration when the mass of the carbon is changed from 12 to 13. It is clear from the spectra in figures 4(a) and 4(b) that this peak exhibits a smaller isotope shift than the other features do. To confirm that this effect is indeed due to nitrogen, we show in figure 4(c) the spectrum for a ^{12}C diamond containing roughly equal concentrations of ^{14}N and ^{15}N . The {110} facet on this diamond had dimensions of only $25 \times 100 \mu\text{m}$, and it was necessary to signal-average eight scans to obtain an adequate combination of resolution and signal-to-noise ratio.

The spectrum in figure 4(c) is almost the same as in figure 4(b); however, the second peak from the left now has a companion peak of comparable intensity, and with an isotope shift of 0.989, compared with the value of 0.985 calculated for a carbon–nitrogen vibration on changing the isotope of the nitrogen atom. We also note that the fourth peak from the left in figure 4(b), which exhibits a smaller isotope shift in figure 4(a) than expected for a carbon–carbon vibration, is also a doublet in figure 4(c) which indicates that it, too, is associated with a carbon–nitrogen vibration. The fact that we have *doublets* in figure 4(c) indicates that we are dealing with a centre which contains a *single* nitrogen atom.

The values calculated for the expected isotope shifts in the preceding two paragraphs are based on the assumption that we have an isolated diatomic molecule executing harmonic oscillations. It is not surprising, therefore, that we do not obtain precise agreement between the measured and calculated shifts. Collins *et al* (1987) have described a slightly more realistic model which considers the carbon–nitrogen diatomic molecule with spring constant k coupled to a rigid lattice by springs with constants k_1 and k_2 attached to the carbon and nitrogen atoms, respectively. By adjusting the ratio of k_1 to k_2 it is obviously possible to make the calculated shift on changing from ^{12}C to ^{13}C agree with the experimental data. Quite frequently these same values of k_1 and k_2 yield a better agreement between the measured and calculated shift for a given vibrational mode when the ^{14}N is replaced by ^{15}N in a ^{12}C diamond (Collins *et al* 1988). As shown in table 2, that is also true in this work for the modes

at 2.6080, 2.6158 and 2.6316 eV. (The energies quoted are for the ^{12}C diamond.) The 2.6080 eV line is the first from the left in figure 4(b), and we note in figure 4(c) that, although no splitting is observed, this peak has almost twice the width of the other features in the spectrum; furthermore, its mean spectral position is displaced from the corresponding peak in figure 4(b) by 0.8 meV to higher energy. We infer from this that two components *are* present, but that they are not resolved. The nitrogen isotope splitting of the mode at 2.6316 eV is just resolved at an R_2 value of 0.995 (see table 2). On this basis we have assigned $R_2 > 0.995$ for the 2.6080 eV mode, and this is consistent with a calculated value of 0.996.

4. Conclusions

We have compared three vibronic bands, with zero-phonon lines at 2.156, 2.807 and 3.188 eV, observed in the cathodoluminescence spectra of irradiated and annealed type Ib diamond and have described a detailed study of the isotope shifts of sharp lines in the spectral region between 2.60 and 2.64 eV when the carbon and nitrogen isotopes of the diamonds have been changed. This work has shown unambiguously that the sharp lines in this region are local-mode phonon replicas of the zero-phonon line at 2.807 eV and that the optical centre concerned involves a radiation damage product and a single nitrogen atom. The local-mode structure of this centre shows striking similarities to that of the 3.188 eV centre studied earlier by Collins and Woods (1987). The coupling of the 2.807 eV electronic transition to *lattice* modes is, however, very much weaker than for the 3.188 eV transition (compare figures 1(b) and 1(c)).

The widths of the 2.807 and 3.188 eV zero-phonon lines are small compared with that of the 2.156 eV line, and indeed with those of many other lines in diamond. The relatively small shifts of the former zero-phonon lines when stress is applied (inferred from the narrow linewidths) suggests that these centres do *not* contain a vacancy (Zaitsev *et al* 1982). On the contrary, the dramatic increase in the relative intensity of the 2.156 eV system, when annealing temperatures above that at which the vacancy becomes mobile are used, suggests that this centre *is* vacancy related, and this is consistent with the much greater width of the zero-phonon line. Intuitively, localised vibrational modes, with frequencies higher than those allowed by the perfect lattice, are more probable at centres involving trapped interstitials (which would increase the local spring constants) than at centres with a trapped vacancy. Again we have the evidence that the 2.156 eV system does *not* have local-mode structure in the luminescence spectrum. Collins *et al* (1987) reported that minor features in the 2.156 eV vibronic band, at 2.021 and 2.031 eV (see figure 1(a)) shift to slightly higher energy in diamonds doped with ^{15}N . Such a shift might have been expected if the features were pseudo-local-modes, but we have been unable to reproduce that result in the present investigation. However, the dominance of the cathodoluminescence spectrum by the 2.156 eV system in synthetic diamonds that have been subjected to radiation damage and annealed at 800 °C leaves little doubt that single nitrogen atoms are contained in the 2.156 eV centres.

We conclude therefore that the 2.807 and 3.188 eV vibronic bands are associated with optical centres involving a single nitrogen atom and an interstitial and that the 2.156 eV centre contains a single nitrogen atom and a vacancy (or vacancies). Our work, however, does not allow us to obtain a more detailed description of the atomic structure of these centres. As stated in § 1, the major end product of radiation damage

and annealing at 800 °C, in a type Ib diamond, is the nitrogen vacancy centre. Cathodoluminescence is a very sensitive technique for studying defects in diamond since most of the centres giving rise to vibronic bands have very short luminescence decay times (Collins 1974). The decay times of the 3.188 and 2.807 eV systems have not been measured, but that for the 2.156 eV system is only 24 ± 2 ns (Crossfield 1981). Although these three systems dominate the cathodoluminescence spectra, the concentrations of centres are probably relatively low.

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