The effects of isotope substitution in diamond studied by optical spectroscopy

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Modern synthesis techniques allow high-quality diamond crystals to be grown from isotopically enriched carbon and doped with isotopically enriched nitrogen. The vibrational frequencies and the energies of electronic transitions associated with point defects are modified by these isotopic substitutions. In this paper we review the spectroscopic measurements that have been carried out on diamonds grown from 99% ^{13}C, and from mixed isotopes of carbon, together with work carried out on diamonds with the natural abundance of carbon isotopes doped with 50 to 70% ^{15}N, and show how this has led to a better understanding of the optical centres. In addition the interpretation of the isotope structure produced by the natural abundance of ^{13}C on the hydrogen-related absorption bands in the infrared spectral region is presented.

1. INTRODUCTION

Isotope substitution is a powerful method of studying point defects in diamond. In simple cases vibrational frequencies are changed in inverse proportion to the square root of the mass of the isotope (or the reduced mass in a diatomic vibration). In addition the energies of electronic transitions are changed slightly, and such a change is manifested, for example, in the shift or splitting of a zero-phonon line in a vibronic band.

Carbon has two stable isotopes, ^{12}C and ^{13}C, with natural abundances of 98.9 and 1.1 atomic %, respectively. Diamonds with different isotopic compositions may readily be grown by high-pressure synthesis (Kamo *et al* 1988; Hass *et al* 1992). Nitrogen in single substitutional form is usually the dominant impurity in high-pressure synthetic diamond, although its concentration may be reduced to negligible levels by adding nitrogen getters to the growth capsule. The isotopic abundances of ^{14}N and ^{15}N are 99.7 and 0.3 atomic %, respectively, but the proportion of the latter can be increased to 70%, or more, by doping with isotopically enriched nitrogen compounds (Woods and Collins 1982).

Changes in vibrational frequencies are most apparent in those optical systems which exhibit localised vibrational modes. These are seen as sharp absorption lines in the infrared spectrum at frequencies just above the Raman frequency (1332.5 cm^{-1} in standard diamond), or, in certain vibronic bands, as sharp absorption or emission lines at an energy separation from the zero-phonon line which is somewhat larger than the Raman energy (165 meV). In this paper we review spectroscopic measurements that have been carried out on diamonds doped with ^{15}N or grown from ^{13}C, or mixtures of ^{12}C and ^{13}C.

1.1. Radiation damage

With two exceptions the optical centres which are the subject of this paper have been created by radiation damage, followed, in some cases, by annealing at temperatures up to 1500° C.

2. INTRINSIC CARBON ISOTOPE EFFECTS

Kamo *et al* (1988) and Collins *et al* (1988) have shown that when diamond is grown from 99% ^{13}C the Raman frequency is decreased by about 50 cm^{-1}. From the small difference between the measured value and the value expected from the average mass Collins *et al* inferred that there was a fractional change in the lattice constant of -3.3 x 10^{-4}. This estimate was critically dependent on the exact isotopic composition of the diamond, as well as the underlying assumption that the Raman frequency varies exactly as the reciprocal of the square root of the average mass. Later measurements by Holloway *et al* (1991) showed that the change is

rather smaller at -1.5×10^{-4}. Hass *et al* (1992) and Chrenko (1988) have measured the Raman frequency for diamonds with a range of isotopic compositions from 0.07 to 99% ^{13}C and shown that the change is not linear with composition. Near the middle of the range the frequency is around 5 cm^{-1} higher than would be expected from the average mass. Similar results have been obtained by Hanzawa *et al* (1992). Hass *et al* were able to obtain a good fit to their own experimental data by using a coherent-potential approximation with a small correction to take account of the observed lattice contraction.

Optical absorption and luminescence measurements have shown that the indirect energy gap is 13.6 ± 0.2 meV higher for ^{13}C than for ^{12}C diamond (Collins *et al* 1990). These authors showed that most of the change is produced by the isotopically induced change in the electron-phonon interaction. Using experimental data for the temperature dependence of the energy gap this contribution was calculated to be 13.5 ± 2 meV. A second contribution comes from the volume change produced by changing the isotope. Collins *et al* estimated this component to be 3 ± 1.3 meV, but the experimental measurement of the change in lattice parameter by Holloway *et al* (1991) suggests this term should be reduced to 1.2 ± 0.5 meV. The total calculated change of 14.7 ± 2.1 meV is then fully consistent with the measured value.

3. HYDROGEN IN DIAMOND

Many natural type I diamonds (i.e. those containing nitrogen) exhibit a series of absorption lines in the near infrared spectral region between 2700 and 3400 cm^{-1} associated with the presence of hydrogen (Woods and Collins 1983). The strongest of these lines is at 3107 cm^{-1} and, although in most specimens the intensity of this line is less than 1 cm^{-1}, diamonds are occasionally found in which the peak absorption coefficient is greater than 10 cm^{-1}. For these diamonds a small, ill-defined, peak is always present on the low wavenumber side of the main line. By using empirical curve-fitting procedures Woods and Collins were able to show that the small peak had the same shape and width as the 3107 cm^{-1} line, and was located at 3098 cm^{-1} with a relative intensity of 1.4%. Although the latter figure is slightly higher than the natural abundance of 13C,

the measured position of the peak agrees exactly with that expected for the vibration of an isolated diatomic C-H molecule. This is the most compelling evidence that the 3107 cm^{-1} absorption is produced by hydrogen bonded to carbon, rather than to nitrogen, although it is curious that it is only observed in nitrogen-containing diamonds.

The 3107 cm^{-1} line has never been detected in diamonds grown by high-pressure synthesis, and it has therefore not been possible to investigate the absorption system further by studying it in diamonds enriched with ^{13}C or doped with deuterium. Hydrogen-related absorption is frequently observed in diamond grown by chemical vapour deposition (CVD) but the peak widths are too broad to compare with those in natural diamond, or to make isotope studies worthwhile. The absence of this absorption in high-quality CVD diamond (Sussmann 1993) is consistent with the proposal made by Woods and Collins (1983) that the hydrogen in natural diamond is not incorporated into the diamond crystal structure, but is bonded at internal surfaces such as sub-microscopic cavities or inclusion/diamond interfaces.

4. NITROGEN RELATED DEFECTS

Isolated substitutional nitrogen in diamond produces an absorption band in the defect-induced one-phonon region with a maximum at 1130 cm^{-1} and a localised vibrational mode at 1344 cm^{-1}. When the diamonds are doped with a mixture of ^{14}N and ^{15}N the peak of the band shifts to lower wavenumbers, but the frequency of the local mode peak is unchanged (Collins and Woods 1982). In diamonds grown from 99% ^{13}C the frequency of the local mode peak changes by a factor of 0.961, close to the value $(12/13)^{0.5}$ expected if the vibrating atoms are carbon (Collins *et al* 1988). Collins *et al* (1987) proposed that the local mode peak corresponds to a vibration in which the nitrogen atom is virtually stationary. Recently Sangster *et al* (1993) have examined the behaviour of this peak in diamonds grown from mixed carbon isotopes. The bond between the nitrogen atom and one of its surrounding carbon atoms is substantially shortened, and Sangster *et al* have shown that the isotope splitting is consistent with the vibration of this carbon atom and its three nearest-neighbour carbon atoms.

5. RADIATION DAMAGE

Figure 1 shows absorption spectra of standard synthetic diamonds produced using (a) radiation damage by 2 MeV electrons, (b) subsequent annealing at 450° C and (c) further annealing at 800° C.
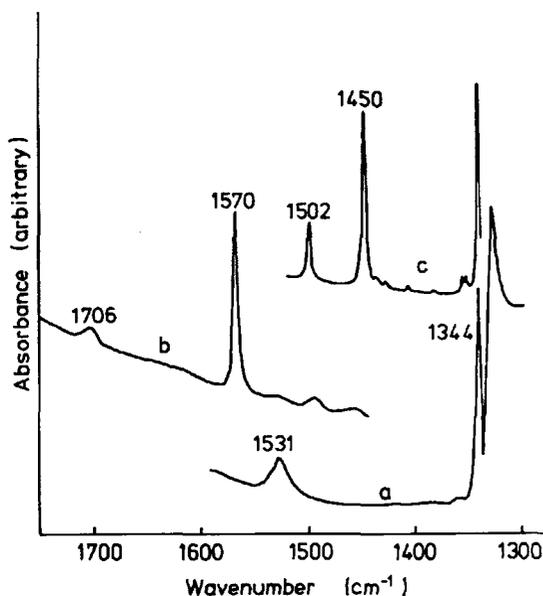

Figure 1. Absorption associated with localised vibrations, at frequencies just higher than the one-phonon band, produced by (a) radiation damage, (b) subsequent annealing at 450° C and (c) further annealing at 800° C.

The peaks at 1531 and 1570 cm^{-1} appear in all diamonds, regardless of nitrogen content, while the remaining peaks are absent in diamonds containing no nitrogen (Woods 1984; Collins *et al* 1988). In diamonds doped with a mixture of ^{14}N and ^{15}N each of these latter peaks is accompanied by a second peak with an isotope shift close to that expected for the vibration of a diatomic C-N molecule (Woods and Collins 1982; Woods 1984). In diamonds grown from 99% ^{13}C the frequencies of the 1531 and 1570 cm^{-1} peaks are reduced by a factor close to 0.961, showing they are associated with the vibration of a carbon atom.

Nisida *et al* (1992) have recently measured these infrared vibrational lines in diamonds grown from mixed carbon isotopes. They find that the 1450 cm^{-1} peak splits into 2 and the 1570 cm^{-1} peak splits into 3. From this, and the earlier results of Woods (1984) and Collins *et al* (1988), they conclude that these two absorption peaks are produced by a C-N split interstitial and a carbon split interstitial, respectively. The 1706 cm^{-1} peak also splits into 2 and Nisida *et al* conclude that this, too, is due to a C-N split interstitial. Collins *et al* (1987) had previously suggested that this peak was due to the stretching of a C=N double bond. Nisida *et al* find that the 1530 cm^{-1} peak broadens, but does not split. The best fit to the lineshape is for a defect comprised of five C atoms, and they propose that the line is produced by an interstitial C atom in a tetrahedral site.

The analyses of these data look very plausible but there are problems in that the carbon split interstitial is not expected to be stable at temperatures up to 900°C, and neither should it be infrared active. The former point also applies to the 5RL defect discussed below.

5.1. A di-nitrogen centre

A localised mode absorption peak is produced at 1856 cm^{-1} in natural type Ia diamonds (diamonds containing significant concentrations of nitrogen in pairs and higher aggregates) by neutron irradiation and heating at temperatures above 500° C, with a secondary annealing stage above 900° C. In synthetic diamond, in which the nitrogen is present as isolated substitutional atoms, the absorption does not occur until the specimen is heated for several hours at temperatures above 1400° C. As a result of this treatment a substantial fraction of the single nitrogen atoms group together in pairs through a vacancy-enhanced aggregation mechanism. To investigate the possibility that the 1856 cm^{-1} line is associated with a defect containing two nitrogen atoms Collins and Woods (1982) examined the absorption spectra of neutron irradiated synthetic diamonds containing different proportions of ^{14}N and ^{15}N, following such a high temperature anneal. They found that the 1856 cm^{-1} line was accompanied by two additional lines at 1833 and 1820 cm^{-1}, with the intensities expected for the vibration of a pair of nitrogen atoms. No model for the centre was proposed by Collins and Woods, but it is possible that one or both of the nitrogen atoms are in interstitial

sites, following an exchange with a carbon interstitial produced by the radiation damage.

5.2. Vibronic bands

Following radiation damage and annealing at about 400°C, diamonds with low nitrogen concentrations exhibit the 5RL and TR12 vibronic bands in absorption and luminescence, with zero-phonon lines (ZPL) at 4.582 and 2.638 eV, respectively. The latter has a local mode peak at about 200 meV from the ZPL, and the former has a series of local mode peaks spaced at about 237 meV in the luminescence band. In both cases the energy separation of the local mode peak is reduced by a factor of about 0.961 in diamonds grown from 99% ^{13}C (Collins *et al* 1988; Lawson 1991).

Figure 2 shows the first local mode region in the 5RL cathodoluminescence band for diamonds grown using 40/60 and 50/50 mixtures of ^{12}C and ^{13}C.
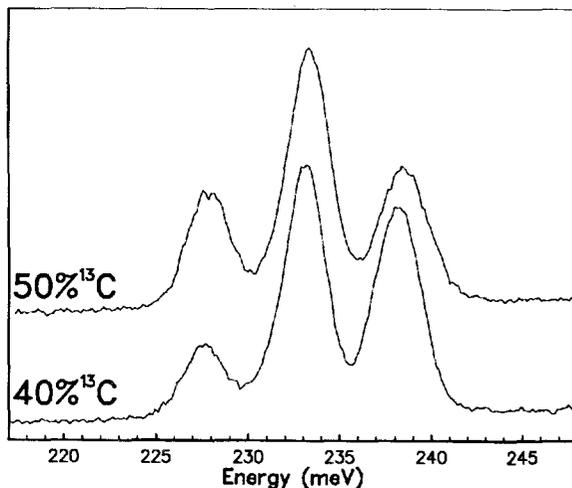
Figure 2. The first localised vibrational mode in the 5RL cathodoluminescence band for synthetic diamonds grown using 40% and 50% ^{13}C.

The behaviour is exactly as expected for a carbon split interstitial (Collins *et al* 1993). There are three types of pair that can form, namely ^{12}C-^{12}C, ^{12}C-^{13}C and ^{13}C^{13}C, and the relative intensities of the corresponding peaks should be 4:12:9 for the 40/60 specimen and 1·2:1 for the 50/50 specimen, as observed

experimentally. However, the 5RL band is stable to thermal annealing at temperatures up to 800° C and, as with the 1570 cm^{-1} infrared peak discussed above, this does not seem reasonable for the interstitial. Stoneham (1992) has therefore suggested that the split interstitial is trapped at a benign impurity.

Figure 3 shows the TR12 local mode in cathodoluminescence for a 40/60 ^{12}C/^{13}C diamond, compared with that for a 99.9% ^{12}C diamond.
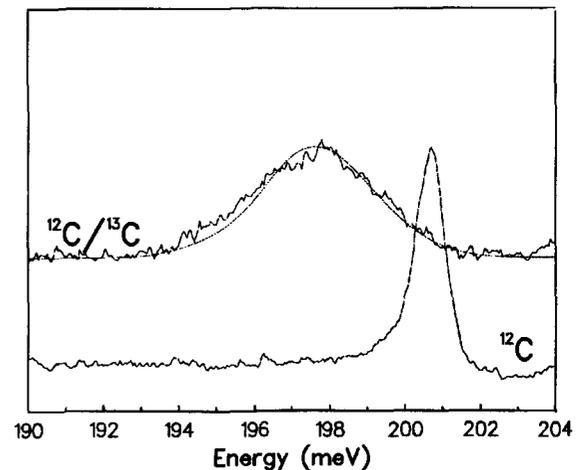
Figure 3. The localised vibrational mode in the TR12 cathodoluminescence band for synthetic diamonds grown using pure ^{12}C (bottom spectrum) and a mixture of 60% ^{12}C and 40% ^{13}C (top spectrum). The dotted curve shows a theoretical fit to the latter.

Here the local mode feature is a broad peak, and the dotted line through the data is based on a valence force model using a periodic cluster of 64 unit cells (Mainwood *et al* 1993). The fit was carried out by strengthening 6 bonds in the cluster. This would be the requirement if the defect comprised a carbon interstitial in a hexagonal site, but there is, at present, no evidence to support this suggestion.

When the synthetic diamonds contain isolated substitutional nitrogen the cathodoluminescence spectra, following radiation damage and annealing at 400° C, exhibit the vibronic bands with zero-phonon lines at 3.188 and 2.807 eV. Each of these systems has a group of local mode peaks in the energy range 168 to 200 meV from the ZPL (Collins and Woods 1987;

Collins and Lawson 1989). Studies of these bands in diamonds doped with ^{15}N, or grown from 99% ^{13}C indicated that these optical centres consist of one nitrogen atom and involve one or more carbon interstitials. The local mode spectra are extremely complex in diamonds grown from mixed isotopes of carbon, probably indicating that several carbon interstitials are involved (Collins *et al* 1993).

When nitrogen-containing synthetic diamonds have been subjected to heavy radiation damage, followed by annealing at temperatures around 1700°C, the H2 vibronic band is produced, with a zero-phonon line at 1.257 eV (Satoh 1988). From optical bleaching measurements Mita *et al* (1990) have proposed that the H2 centre is a negatively charged H3 centre, which has the structure N-V-N. In ^{12}C diamonds the absorption band has a localised vibrational mode at 1.424 eV, and figure 4 shows the energy separation of this peak from the corresponding zero-phonon line in ^{12}C, ^{13}C and 40/60 ^{12}C/^{13}C diamonds. Accurate measurements show that the energy separations are 167.1 meV for the ^{12}C specimen and 160.9 for the ^{13}C diamond (Lawson *et al* 1992).
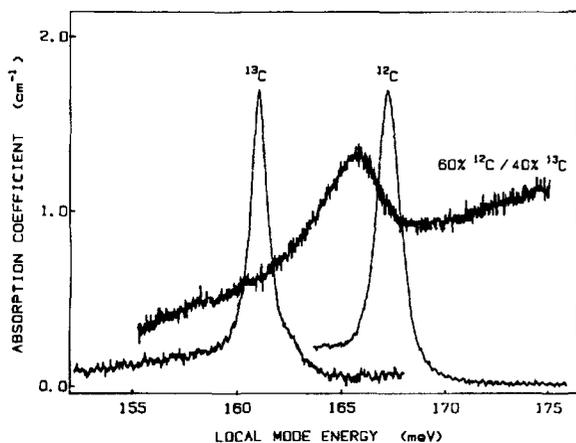
The ratio of these energies is about 0.963, suggesting that the localised mode is associated with the vibration of carbon atoms. The isotope shift of the peak in the mixed isotope diamond is smaller than would be expected from a linear interpolation (Collins *et al* 1993). Because of the proximity of the local mode energy to the Raman energy there will be considerable coupling of this vibration to the band modes. Hass *et al* (1992) have shown that the the Raman frequency does not vary linearly with ^{13}C concentration, and that the deviation at a concentration around 40% is approximately 5 cm^{-1}. We therefore expect the local mode peak in the H2 band to be up to 0.6 meV higher in energy than determined by a linear interpolation. A lineshape very like the experimental one is generated by cluster calculations in which the two carbon back bonds are strengthened (Mainwood *et al* 1993).

6. ZERO-PHONON LINES

Shifts of the zero-phonon lines of the common optical centres in diamond range from -0.5 to 8.0 meV when the host lattice is (almost) completely changed from ^{12}C to ^{13}C, where the minus sign indicates that the shift is to lower energies in the ^{13}C crystals (Collins *et al* 1988, Collins and Lawson 1989, Lawson *et al* 1992). In most cases the isotope shift is positive. In diamonds containing x% ^{13}C the shift of the ZPL is x% of the total shift observed in 99% ^{13}C (Collins *et al* 1993, Woad 1993).

For a given optical centre the shift is produced by the isotope-induced change in the lattice constant, the different zero-point energies in the two electronic states to the transition and vibronic effects. In principle these contributions to the overall isotope shift can be estimated if the temperature-dependence of the zero-phonon line energy, and the parameters describing the behaviour of the line with applied uniaxial stress, are known. Calculations of the isotope shift have been carried out for 8 optical centres by Collins *et al* (1988), for the H2 system by Lawson *et al* and for the 1.883 eV system by Nazaré and Rino (1993). In most cases the calculated shift is comparable with the experimental value, but the method of analysis is not sufficiently refined to predict the isotope shifts exactly. The contribution of the change in lattice constant to the isotope shifts was overestimated by Collins *et al* (1988)

Figure 4. The H2 local mode peak in a ^{12}C diamond, a ^{13}C diamond and diamond grown using 60% ^{12}C and 40% ^{13}C. The absorption coefficient scale is shown for the ^{12}C diamond which had the strongest absorption.

who used a fractional change of -3.3×10^{-4}, compared with the more recent experimental value of -1.5×10^{-4} obtained by Holloway *et al* (1991).

6.1. Nitrogen centres

Studies of nitrogen ion implantation have been reported by Zaitsev *et al* (1982) and Gippius *et al* (1982). They observed the 3.188 eV and 2.807 eV zero-phonon lines immediately after implantation, and the 2.156 eV, 2.463 eV (H3) and 2.985 eV (N3) lines after various heat treatments. All the lines shifted to shorter wavelengths when the implantation was carried out with ^{15}N. These optical centres (except N3) have also been studied by the author in synthetic diamonds doped with ^{15}N during growth, with up to 70% of the nitrogen being present as this isotope. In these diamonds no isotope shift due to the ^{15}N could be detected.

As with changing the carbon isotope, any shift in the zero-phonon line is a result of the change in the zero-point energy of the crystal. However, the impurity atoms are only a small part of the total system, which consists of a considerable amount of diamond lattice in addition to the atoms of the impurity centre itself. Even if the masses of all the impurity atoms are changed, shifts in the zero-phonon line are therefore expected to be very small. By considering a simple model of a nitrogen atom placed at the centre of a linear chain of carbon atoms Davies (1983) estimated that the shift for the N3 zero-phonon line would not exceed 0.1 meV. Most zero-phonon lines in diamond are substantially wider than this, and the effects of nitrogen isotope substitution are difficult to detect. The results of Zaitsev *et al* (1982) and Gippius *et al* (1982) should therefore be treated with caution.

7. SUMMARY

In this article we have reviewed the major spectroscopic investigations that have been carried out to study isotope effects in natural and synthetic diamond. Synthetic diamonds have been grown using various ratios of ^{12}C to ^{13}C or doped using various ratios of ^{14}N to ^{15}N, and the effects of these isotopic substitutions on the variety of optical centres produced by radiation damage and annealing have been investigated in detail. These programmes of work have led to a greater understanding of many of the defect centres in diamond,

and also raised a number of questions that will be addressed by ongoing experimental and theoretical studies in this area.

REFERENCES

R M Chrenko, J. Appl. Phys., 63 (1988) 5873.

A T Collins, G Davies, H Kanda and G S Woods, J. Phys. C, 21 (1988) 1363.

A T Collins and S C Lawson, J. Phys.: Condens. Matter, 1 (1989) 6929.

A T Collins, S C Lawson, G Davies and H Kanda, Phys. Rev. Lett., 65 (1990) 891.

A T Collins, M Stanley and G S Woods, J. Phys. D, 20 (1987) 969.

A T Collins, P J Woad, G S Woods and H Kanda, Diam. and Related Mater., 2 (1993) 136.

A T Collins and G S Woods, Phil. Mag. B, 46 (1982) 77.

A T Collins and G S Woods, J. Phys. C, 20 (1987) L797.

G Davies, Diamond Conference, Cambridge, UK (1983).

H Hanzawa, N Umemura, Y Nisida, H Kanda, S Sato and T Nakashima, presented at ICDIM '92, Nordkirchen, Germany (1992).

K C Hass, M A Tamor, T R Anthony and W F Banholzer, Phys. Rev. B, 45 (1992) 7171.

H Holloway, K C Hass, M A Tamor, T R Anthony and W F Banholzer, Phys. Rev. B, 44 (1991) 7123.

M Kamo, H Yurimoto and Y Sato, Appl. Surf. Sci., 33/34 (1988) 553.

S C Lawson, PhD thesis, University of London (1991).

S C Lawson, G Davies, A T Collins and A Mainwood, J. Phys.: Condens. Matter, 4 (1992) 3439.

A Mainwood, A T Collins and P Woad, presented at the 17th International Conference on Defects in Semiconductors, Gmunden, Austria, 19 - 23 July (1993).

Y Mita, Y Nisida, K Suito, A Onodera and S Yazu, J. Phys.: Condens. Matter, 2 (1990) 8567.

M H Nazaré and L M Rino, Diamond Conference, Bristol, UK (1993).

Y Nisida, Y Yamada, H Kanda, T Nakashima, S Sato, S Kobayashi and M Okada, presented at ICDIM '92, Nordkirchen, Germany (1992).

M L J Sangster, I Kiflawi and G S Woods, Diam. and Related Mater. 2 (1993) 1243.

S Satoh, European Patent No. 88121859.8 (1988).

A M Stoneham, personal communication (1992).

R S Sussmann, Indust. Diam. Review 53 (1993) 63.

P J Woad, personal communication (1993).

G S Woods, Phil. Mag. B, 50 (1984) 673.

G S Woods and A T Collins, J. Phys. C, 15 (1982) L949.

G S Woods and A T Collins, J. Phys. Chem. Solids, 44 (1983) 471.