

Absorption spectra of hydrogen in ^{13}C diamond produced by high-pressure, high-temperature synthesis

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 3163

(<http://iopscience.iop.org/0953-8984/15/19/316>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 09:43

Please note that [terms and conditions apply](#).

Absorption spectra of hydrogen in ^{13}C diamond produced by high-pressure, high-temperature synthesis

Filip De Weerd^{1,2}, Yuri N Pal'yanov³ and Alan T Collins²

¹ Diamond High Council, Hoveniersstraat 22, 2018 Antwerpen, Belgium

² Wheatstone Physics Laboratory, King's College London, Strand, London WC2R 2LS, UK

³ Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Sciences, Academician Koptyug Prospect 3, 630090 Novosibirsk, Russia

Received 7 March 2003

Published 6 May 2003

Online at stacks.iop.org/JPhysCM/15/3163

Abstract

Sharp absorption lines produced by hydrogen in diamond have been studied in diamonds grown from ^{13}C by high-pressure, high-temperature synthesis. Analyses of the two-phonon intrinsic absorption and of the Raman shift have shown that the ^{12}C content of the diamond is 13.5%. This value is entirely consistent with the relative intensities of the absorption lines at 3107 and 3098 cm^{-1} , confirming that they are due to a strongly localized C–H stretching vibration. A correlated line, observed at 1405 cm^{-1} for natural diamond, and attributed to the C–H bending vibration, exhibits both an isotope shift and a shift due to weak coupling with the one-phonon modes. By analogy with natural diamond, lines for the ^{13}C diamond at 2757 and 4469 cm^{-1} are assigned to the combinations $2\hbar\omega_b$ and $\hbar\omega_s + \hbar\omega_b$, respectively, where $\hbar\omega_s$ and $\hbar\omega_b$ are the stretch and bend frequencies. The frequency invariance, on carbon isotope substitution, of a hydrogen-related line at 3237 cm^{-1} is not inconsistent with the proposal that this is produced by a N–H vibration.

1. Introduction

Sharp absorption lines at 1405 and 3107 cm^{-1} in the infrared absorption spectra of natural diamond were tentatively attributed to hydrogen by Charette (1961) and have subsequently been studied by several researchers. Recently the role of hydrogen in diamond has acquired a technological importance; it is frequently incorporated in diamond grown by chemical vapour deposition (CVD) and can passivate boron acceptors in doped material (Chevallier *et al* 1998, Zeisel *et al* 1999, Uzan-Saguy *et al* 2001). In the present investigation we have studied the absorption spectra associated with hydrogen, in diamond produced from ^{13}C by high-pressure, high-temperature (HPHT) synthesis, in order to obtain a better understanding of the defects involved.

Table 1. Positions, intensities and assignments of the hydrogen-related absorption peaks of natural diamond (Davies *et al* 1984, Fritsch *et al* 1991 and this work). The fundamental bend and stretch frequencies are respectively $\hbar\omega_b$ and $\hbar\omega_s$. The very weak component at 5555 cm^{-1} has been observed only by Fritsch *et al*.

Line position (cm^{-1})	Relative peak height	Assignment
1405	400	$\hbar\omega_b$
2786	34	$2\hbar\omega_b$
3107	1000	$\hbar\omega_s$
4169	4	$3\hbar\omega_b$
4499	29	$\hbar\omega_s + \hbar\omega_b$
5555	~ 0.1	$4\hbar\omega_b$
5889	~ 0.6	$\hbar\omega_s + 2\hbar\omega_b$
6070	~ 1.2	$2\hbar\omega_s$

Runciman and Carter (1971) found that the absorption peaks at 1405 and 3107 cm^{-1} correlated in intensity, and assigned them, respectively, to the bending and stretching modes of either N–H or C–H bonds. Woods and Collins (1983) drew attention to a very weak shoulder that is always present near the base of the 3107 cm^{-1} peak. A manual deconvolution of this feature showed that it had the correct position (3098 cm^{-1}) and approximately the correct intensity (1.4%) to be associated with the stretching of ^{13}C –H. In reaching this conclusion Woods and Collins assumed that the main peak was due to ^{12}C –H, and that the ratio of the vibration frequencies could be calculated by treating the C and H as an isolated diatomic molecule. (The natural abundance of ^{13}C is 1.1%.)

When the intensity of the 3107 cm^{-1} peak is moderately high ($\sim 10 \text{ cm}^{-1}$), two additional minor features at 2786 and 3237 cm^{-1} are easily observed on either side of the main peak. The intensity of the 3107 cm^{-1} peak correlates reasonably well with that of the 2786 cm^{-1} peak (Davies *et al* 1984) but there is no correlation with the 3237 cm^{-1} peak (Woods and Collins 1983). Other, even weaker, peaks have been found which correlate with the main peaks, and are listed in table 1. These have been attributed (Davies *et al* 1984, Fritsch *et al* 1991) to overtones and combinations of the fundamental vibrational modes. The frequencies at which such peaks are observed are slightly lower than those given by the arithmetic sums of the fundamental frequencies because of slight anharmonicity in the vibrations (Davies *et al* 1984). The combinations at 5555, 5889 and 6070 cm^{-1} were not detected by Davies *et al* (1984), but can be seen (Fritsch *et al* 1991) in specimens with very strong hydrogen-related absorption, using the more-sensitive technique of Fourier transform infrared (FTIR) spectroscopy. We have confirmed in the present investigation, by comparing absorption spectra for three separate diamonds, that the peaks at 5889 and 6070 cm^{-1} are indeed correlated with the other peaks listed. However, we were not able to detect the peak at 5555 cm^{-1} observed by Fritsch *et al*.

Some diamonds, particularly those in which the H-related absorption is very strong, exhibit many additional peaks in the vicinity of the 3107 cm^{-1} peak. Woods and Collins (1983) show some of these, and attribute them to N–H vibrations.

Although the measurements of Woods and Collins appeared to be consistent with the interpretation that the 3107 cm^{-1} peak and the correlated features listed in table 1 are due to C–H vibrations, they were unable to detect these absorption features for type IIa (nitrogen-free) diamonds, although the features were present for all but one of the 50 type Ia diamonds that they investigated. (Type Ia diamonds contain nitrogen in aggregated forms.) Later, Mendelssohn *et al* (1986) obtained two-dimensional maps of the infrared absorption spectra from a polished slice of type Ia diamond that also exhibited strong hydrogen-related absorption. The distribution of nitrogen in the diamond that they studied was very inhomogeneous, and

the measurements showed that, although there was no one-to-one correlation, the intensity of the 3107 cm^{-1} peak varied in sympathy with the concentration of the A aggregate of nitrogen. (The A aggregate is a nearest-neighbour pair of substitutional nitrogen atoms.)

De Weerd and Collins (2002) characterized 60 type Ia and mixed type Ia—type Ib diamonds using FTIR spectroscopy. (For an exclusively type Ib diamond, all the nitrogen is present on isolated substitutional sites.) For the mixed-type diamonds the 3107 cm^{-1} line could be detected when at least 20% of the nitrogen was aggregated in A defects. The 3107 cm^{-1} line was also seen, sometimes in considerable strength, in diamonds in which virtually all the nitrogen was fully aggregated into the B form (4 nitrogen atoms surrounding a vacancy). For those diamonds in which the hydrogen-related absorption could be detected, the intensity of the 3107 cm^{-1} line tended to be stronger in specimens with a high nitrogen concentration.

Diamond grown by HPHT synthesis from a metal solvent–catalyst, at typically 1400°C , contains nitrogen in isolated substitutional positions at an average typical concentration of 200 ppm. No hydrogen-related absorption is observed in such specimens. However, if the diamonds are annealed at $>2100^\circ\text{C}$, a substantial fraction of the nitrogen forms A aggregates, and in some cases hydrogen-related absorption is also observed (Kiflawi *et al* 1996). To maximize the amount of hydrogen-related absorption, Kiflawi *et al* annealed their specimens at 2650°C for 5 h. For a diamond grown by HPHT synthesis the concentrations of nitrogen are very different in the different growth sectors, and vary within each growth sector, depending on the growth conditions. From a two-dimensional infrared absorption map, of a hydrogen-containing specimen, Kiflawi *et al* (1996) showed that the intensity of the 3107 cm^{-1} peak correlated approximately with the concentration of the A aggregate of nitrogen. The origin of the hydrogen in those diamonds that exhibited this absorption was not known.

Borzdov *et al* (2002) showed that it is possible to grow diamonds by HPHT synthesis using Fe_3N as the solvent–catalyst. Typical growth conditions use a temperature of 1700°C and a pressure of 7 GPa maintained for 20 h. The use of a nitride results in a much higher nitrogen concentration (up to 3300 ppm) in the specimens, compared with the typical 200 ppm in commercial synthetic diamonds grown using a metal solvent–catalyst. The higher nitrogen concentration, combined with the high temperature and long growth time, results in most of the nitrogen being present in the form of A aggregates in the as-grown material. Furthermore, many of the specimens show the hydrogen-related absorption peaks at 1405 and 3107 cm^{-1} . Measurements on different diamonds, from the same growth run, but containing different nitrogen concentrations, showed that the intensity of the 3107 cm^{-1} peak increased as the nitrogen concentration increased. The source of the hydrogen in these diamonds is assumed to be the Fe_3N solvent–catalyst which itself was synthesized using NH_3 gas (Borzdov *et al* 2002).

Kiflawi *et al* (1996), faced with the apparent nitrogen dependence of the 3107 cm^{-1} peak, examined this feature for high-temperature-annealed synthetic diamonds doped with ^{15}N , but found no shift of the peak. They therefore concluded that the absorption is not due to N–H centres. Instead they proposed that the conditions that produce the A aggregate of nitrogen also favour the formation of C–H centres. However, Chevallier *et al* (2002) correctly point out that the absence of an isotope shift of the line does not disprove the suggestion that the centre producing the line contains nitrogen. They give examples known in Si and GaP where changing the isotope of an impurity does not result in a change of the vibrational frequency. They could also have drawn attention to the lack of an isotope shift of the sharp 1344 cm^{-1} line in diamond. This absorption arises at a localized vibrational mode produced by the presence of single-substitutional nitrogen, but shows no detectable shift in diamonds grown using ^{15}N (Collins and Woods 1982). Chevallier *et al* therefore propose that the centre producing the 3107 cm^{-1} absorption is a H–C–N complex containing at least one nitrogen atom. Since the

3107 cm^{-1} system is only seen in type Ia diamonds, the H–C–N complex would probably contain two or more nitrogen atoms.

To date the only evidence that the 3107 cm^{-1} peak is due to a C–H vibration comes from the work of Woods and Collins (1983), based on an extremely weak feature of relative intensity $\sim 1\%$ at the base of the 3107 cm^{-1} peak and believed to be due to ^{13}C . In the present investigation we have therefore examined the hydrogen-related absorption in diamonds with a high nitrogen concentration grown from ^{13}C .

2. Experimental details

Amorphous carbon powder, isotopically enriched to 98–99% ^{13}C , was placed into a Pt ampoule and partially graphitized by heating to 1400 °C under a pressure of 5 GPa, using a split-sphere-type multi-anvil apparatus (Pal'yanov *et al* 1997). This was used as the source material to grow diamonds from a Fe_3N solvent–catalyst, as described by Borzdov *et al* (2002). The diamond growth time was 20.5 h, with a pressure fixed at 7 GPa and a temperature of 1850 °C. A few spontaneously nucleated diamonds recovered from the growth run were of sufficient size (approximately 100 μm across) and clarity to enable their infrared absorption spectra to be measured.

Specimens were mounted over a hole in a piece of aluminium foil and placed at the focus of a $5\times$ beam condenser in a Bruker Equinox 55 FTIR spectrometer. Spectra were obtained at a resolution of 0.5 cm^{-1} over the range 400–4500 cm^{-1} . Closely spaced peaks were deconvoluted into Lorentzian sub-components using the Grams/32 software. Deconvolutions could be carried out using either a linear or a quadratic baseline correction; for a given peak the calculated intensities were the same for both backgrounds, within the experimental uncertainty.

Raman spectra were recorded with a Renishaw 2000 Raman spectrophotometer, with an uncertainty in the Raman shift of $\pm 2 \text{ cm}^{-1}$. The 514.5 nm line of an Ar-ion laser was used with the sample mounted in a near-normal backscattering geometry. Shifting of the Raman line due to laser-induced heating of the sample was prevented by mounting the sample on a copper heat sink.

3. Results and discussion

The full absorption spectrum is shown in figure 1. The shape of the one-phonon absorption indicates that virtually all of the nitrogen is present in the A-aggregate form at an approximate concentration of 800 ppm. It is also clear that there is hydrogen-related absorption present at ~ 1400 and at $\sim 3100 \text{ cm}^{-1}$. Various features in the spectrum are considered in more detail below.

3.1. Absorption near 3100 cm^{-1}

Figure 2 shows that the absorption near 3100 cm^{-1} is comprised of two peaks at 3098 and 3107 cm^{-1} , together with some minor features which are just above the noise level. The two major components are at the identical frequencies determined by Woods and Collins (1983), but now the 3098 cm^{-1} peak is dominant. This confirms beyond doubt that the absorption is produced by the vibration of a C–H structure. Because the frequencies are more than twice that of the maximum vibrational frequency of the diamond lattice (1332.5 cm^{-1}), the stretching vibration of the bond is highly localized, and there is an insignificant coupling to the lattice modes.

Considering only the 3107 and 3098 cm^{-1} peaks, the former, due to the ^{12}C –H vibration, comprises $(11.4 \pm 0.3)\%$ of the total absorption, whereas the starting material contained only

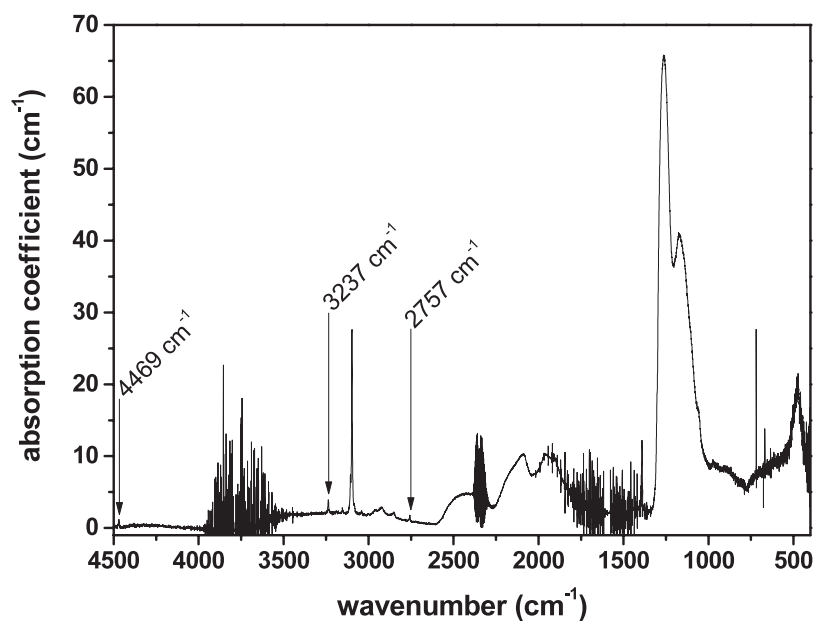


Figure 1. The absorption spectrum of an HPHT synthetic diamond grown from ^{13}C and containing hydrogen-related features. Because of the small size of the specimen it has not been possible to eliminate the atmospheric absorption completely. Most of the spectrum of interest lies in the atmospheric windows. The three weak peaks, labelled, have been identified from expanded plots of the spectrum.

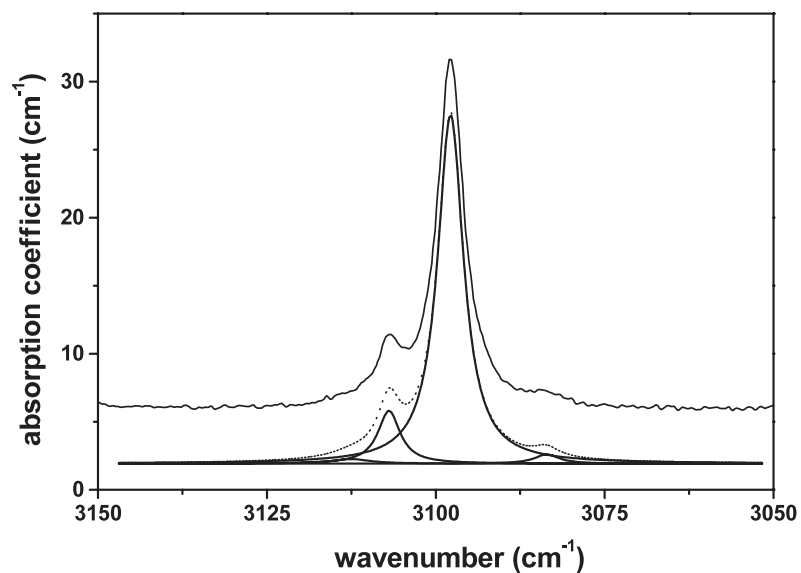


Figure 2. The absorption spectrum of the hydrogen-related peaks near 3100 cm^{-1} in an HPHT synthetic diamond grown from ^{13}C and the best-fitting Lorentzian components (continuous curves) of the spectrum, together with the sum of these components (dotted curve). The experimental spectrum has been shifted for clarity.

1–2% ^{12}C . We attribute this difference to the diffusion of carbon into the growth capsule from the graphite heater. We show below that the relative intensities of the two absorption peaks are consistent with the isotopic composition of the diamond.

3.2. Intrinsic two-phonon absorption

The absorption bands between approximately 1400 and 2600 cm^{-1} (figure 1) represent the two-phonon combination bands. These are made up of frequencies which propagate through the diamond lattice. Consequently, when we have a mixture of ^{12}C and ^{13}C atoms, we can assume, to a good approximation, that the frequencies of sharp features in the spectrum are inversely proportional to the square root of the average mass. In natural diamond there are two sharp spikes in the two-phonon spectrum at 1977 and 2158 cm^{-1} . In the synthetic diamonds investigated here these features are less sharp, but, from the spectrum in figure 1, can be located at 1909 ± 3 and 2087 ± 4 cm^{-1} , respectively. The ratios of corresponding frequencies in the diamonds grown from ^{13}C to those in natural diamond are 0.9656 ± 0.0015 and 0.9671 ± 0.0019 , respectively. If P is the percentage of ^{12}C in the synthetic diamonds, then we expect the ratio, R , to be given by

$$R = \left(\frac{(98.9 \times 12) + (1.1 \times 13.00335)}{(P \times 12) + [(100 - P) \times 13.00335]} \right)^{1/2}.$$

Using a weighted average of $R = 0.9662 \pm 0.0012$ gives $P = (13.7 \pm 3.2)\%$ in good agreement with the value inferred from the relative amplitudes of the peaks in figure 2.

3.3. Raman measurements

The Raman line in natural type IIa diamonds, where the natural abundance of ^{13}C is 1.1%, is at 1332.5 cm^{-1} . The change in atomic mass when ^{12}C is replaced by ^{13}C induces a shift and an asymmetric broadening of the first-order Raman line (Hass *et al* 1992, Ruf *et al* 1998). From the shift, one can calculate the isotopic composition of the diamond from the relation (Vogelgesang *et al* 1996)

$$\hbar\omega_0 = 1332.82 - 34.77x - 16.98x^2.$$

In this equation, x is the fraction of ^{13}C , and $\hbar\omega_0$ is the position of the Raman line which, in this case, is at 1290 ± 2 cm^{-1} . This gives the fraction of ^{12}C as $(13.4 \pm 3.1)\%$, in excellent agreement with the previously calculated values.

3.4. Absorption near 1400 cm^{-1}

The 1405 cm^{-1} C–H bending vibration in natural diamond is close to the maximum one-phonon frequency (1332.5 cm^{-1}). The high-frequency limit of the one-phonon band decreases by approximately 50 cm^{-1} , on substituting for ^{12}C with ^{13}C . Because of weak interaction with the one-phonon modes, the C–H frequency is pulled somewhat lower than that predicted by the isotope shift for an isolated C–H defect. The vibration is still sufficiently localized that, in our diamond with mixed isotopes, the individual ^{12}C –H and ^{13}C –H peaks are seen at 1396 and 1391 cm^{-1} respectively (figure 3). The separation of these two peaks is 20% larger than that calculated for the vibration of an isolated diatomic molecule, and the intensity of the component due to ^{12}C is $(36 \pm 6)\%$, compared with 11.4% derived from figure 2. The latter figure was shown to be consistent with the isotopic composition of the diamond. We infer that the simplistic analysis which worked well for the highly localized stretching vibrations near 3100 cm^{-1} is less appropriate for the partially localized bending vibrations near 1400 cm^{-1} .

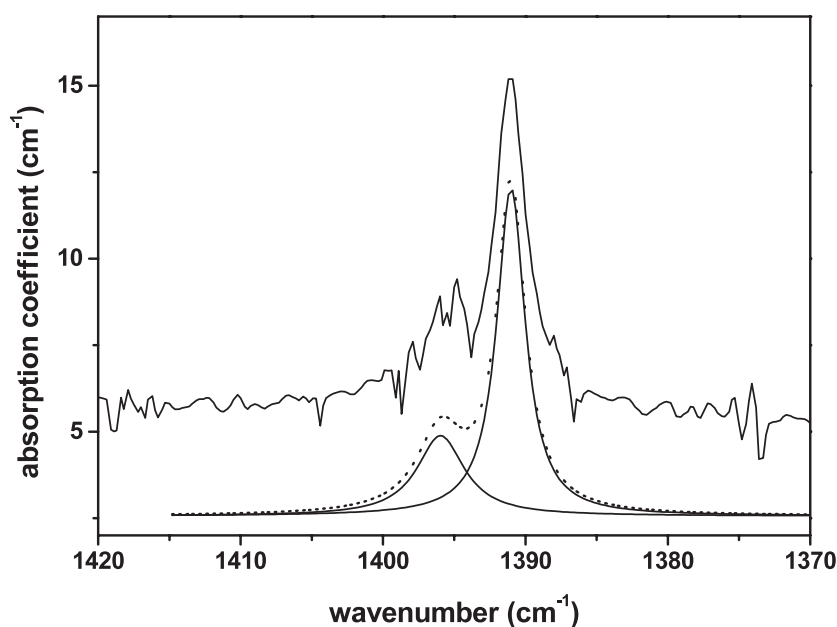


Figure 3. The absorption spectrum of the hydrogen-related peaks near 1400 cm^{-1} in an HPHT synthetic diamond grown from ^{13}C and the best-fitting Lorentzian components (continuous curves) of the spectrum, together with the sum of these components (dotted curve). The experimental spectrum has been shifted for clarity. Because of the residual water vapour absorption, the uncertainties in the fitting parameters are greater for the data in this figure than for the data in figure 2.

3.5. One-phonon absorption

The major absorption peak associated with A aggregates of nitrogen occurs at 1282 cm^{-1} in the defect-induced one-phonon region of natural diamond. There is no straightforward method of calculating the position of this peak for ^{13}C diamond. We see from figure 1 that in our diamond containing approximately 88% ^{13}C the maximum absorption occurs at 1260 cm^{-1} . The isotope shift is comparable with, but rather smaller than, the 32 cm^{-1} shift observed (Collins *et al* 1988) for the peak associated with isolated substitutional nitrogen which, for natural diamond, is located at 1130 cm^{-1} .

3.6. Combination bands

Three weak peaks at 2757 , 3237 and 4469 cm^{-1} can be observed in figure 1. By analogy with natural diamond (table 1), we attribute the 2757 cm^{-1} peak to the combination $2\hbar\omega_b$ ($2 \times 1391\text{ cm}^{-1}$) and the 4469 cm^{-1} peak to $\hbar\omega_s + \hbar\omega_b$ ($1391 + 3098\text{ cm}^{-1}$). As for natural diamond, because of slight anharmonicity, the positions of the combination bands are at slightly lower frequencies than those given by the arithmetic sums. Since the diamonds contain mainly ^{13}C , combinations involving ^{12}C with ^{13}C (and especially ^{12}C with ^{12}C) will be too weak to detect in these specimens.

The feature at 3237 cm^{-1} occurs at the same frequency as for natural diamond. Woods and Collins (1983) noted that this peak did not correlate in intensity with those attributed to C–H vibrations, and suggested that it was due to an N–H vibration. That proposal is not inconsistent with the absence of an isotope shift, observed here for diamonds grown from ^{13}C .

Because of the small sizes of the synthetic diamonds, and their relatively weak hydrogen-related absorption, the counterparts of the extremely weak combination bands seen in natural diamonds (table 1) could not be detected.

4. Conclusions

We have studied hydrogen-related absorption peaks in diamonds grown from ^{13}C and which contain approximately 800 ppm nitrogen in the A-aggregate form. The results show unambiguously that the absorption peaks at 3107 and 3098 cm^{-1} are due to the stretching vibrations of a C–H bond. The relative intensities of the two components are consistent with the isotopic composition of the diamond, determined from the shift of sharp features in the intrinsic two-phonon absorption band, and from the shift of the Raman peak. The isotopic splitting for the bending vibration is close to that calculated for isolated diatomic molecules comprised of $^{12}\text{C}\text{--H}$ and $^{13}\text{C}\text{--H}$, but both components are pulled to lower frequency because of weak coupling to the one-phonon lattice vibrations. The relative intensity of the $^{12}\text{C}\text{--H}$ peak, calculated using a simple model, is higher than expected from the isotopic composition. The first overtone, $\hbar\omega_0$, of the bend vibration, and the combination band $\hbar\omega_s + \hbar\omega_b$ have been detected; as in natural diamond the frequencies are slightly lower than those calculated from the arithmetic sum of the frequencies. The position of a feature at 3237 cm^{-1} has been shown to be independent of the isotopic composition of the diamond, and this is not inconsistent with the proposal that this feature is due to an N–H vibration.

References

- Borz dov Yu, Pal'yanov Yu, Kupriyanov I, Gusev V, Khokhryakov A, Sokol A and Efremov A 2002 *Diam. Relat. Mater.* **11** 1863–70
- Charette J J 1961 *Physica* **27** 1061–73
- Chevallier J, Jomard F, Teukam Z, Koizumi S, Kanda H, Sato Y, Deneuville A and Bernard M 2002 *Diam. Relat. Mater.* **11** 1566–71
- Chevallier J, Theys B, Lusson A, Grattapain C, Deneuville A and Gheeraert E 1998 *Phys. Rev. B* **58** 7966–9
- Collins A T, Davies G, Kanda H and Woods G S 1988 *J. Phys. C: Solid State Phys.* **21** 1363–76
- Collins A T and Woods G S 1982 *Phil. Mag.* **B 46** 77–83
- Davies G, Collins A T and Spear P M 1984 *Solid State Commun.* **49** 433–6
- De Weerd F and Collins A T 2002 *Diamond Conf. (Oxford)* (unpublished abstracts)
- Fritsch E, Scarratt K and Collins A T 1991 New diamond science and technology *Proc. 2nd Int. Conf. on the New Diamond Science and Technology* ed R Messier, J T Glass, J E Butler and R Roy (Pittsburgh, PA: Materials Research Society) pp 671–6
- Hass K C, Tamor M A, Anthony T R and Banholzer W F 1992 *Phys. Rev. B* **45** 7171–82
- Kiflawi I, Fisher D, Kanda H and Sittas G 1996 *Diam. Relat. Mater.* **5** 1516–18
- Mendelssohn M J, Milledge H J, Woods P A, Seal M, Boyd S R, Matthey D P and Pillinger C T 1986 *Diamond Conf. (London)* (unpublished abstracts)
- Pal'yanov Yu N, Khokhryakov A F, Borz dov Yu M, Sokol A G, Gusev V A, Rylov G M and Sobolev N V 1997 *Geol. Geofiz.* **38** 882–906 (Engl. transl. 1997 *Russ. Geol. Geophys.* **38** 920–45)
- Ruf T, Cardona M, Sternshulte H, Wahl S, Thonke K, Sauer R, Pavone P and Anthony T R 1998 *Solid State Commun.* **105** 311–6
- Runciman W A and Carter T 1971 *Solid State Commun.* **9** 315–17
- Uzan-Saguy C, Reznik A, Cytermann C, Brener R, Kalish R, Bustarret E, Bernard M, Deneuville A, Gheeraert E and Chevallier J 2001 *Diam. Relat. Mater.* **10** 453–8
- Vogelgesang R, Ramdas A K, Rodriguez S, Grimsditch M and Anthony T R 1996 *Phys. Rev. B* **54** 3989–99
- Woods G S and Collins A T 1983 *J. Phys. Chem. Solids* **44** 471–5
- Zeisel R, Nebel C E and Stutzmann M 1999 *Appl. Phys. Lett.* **74** 1875–6