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The effects of carbon and nitrogen isotopes on the ‘N3’ optical transition in diamond

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Abstract. The N3 centre in diamond consists of three nitrogen atoms and one vacancy. We show that the N3 zero-phonon line, at 2.985 eV in natural diamond, is shifted by $+0.2 \pm 0.1$ meV in ¹²C diamond doped with ¹⁵N, with no detectable change in the vibronic bandshape. In ¹³C diamond, the energies of all the phonons seen in the vibronic band appear to be reduced from ¹²C diamond in the ratio $\sqrt{12/13}$, and the zero-phonon is shifted by $+4.5 \pm 0.2$ meV. The carbon isotope shift can be understood in terms of contributions from the lattice expansion, of 0.36 ± 0.08 meV, 2.7 ± 0.4 meV from the different vibrational frequencies in the ground and excited electronic states, and ~ 1.1 meV from the Jahn–Teller effect in the excited state.

1. Introduction

Nitrogen is the most abundant impurity in natural diamonds and in diamonds synthesized at high temperature and pressure (HTHP). It is grown in as isolated substitutional atoms, but heating the diamonds, in nature or in the laboratory, allows the nitrogen to aggregate. The aggregation can produce pairs of substitutional nitrogen atoms (‘A’ centres) and clusters of four N atoms and a vacancy (‘B’ centres): see Woods (1994) for a review. Other aggregation processes produce small but significant concentrations of centres. Of particular interest here is the well-known ‘N3’ optical centre, which is observable also in EPR as the ‘P2’ resonance (Davies *et al* 1978). From EPR and ENDOR studies the centre is believed to contain three nitrogen atoms arranged on substitutional sites as nearest neighbours to one common atomic site, with a vacancy at that site (van Wyk 1982, van Wyk and Loubser 1993). These centres produce a characteristic optical band with its zero-phonon line at 2.985 eV in natural diamond. N3 centres can be produced by heating diamonds which contain A centres and isolated N (Chrenko *et al* 1977), by heating diamonds rich in B centres (Brozel *et al* 1978), or by heating diamonds which contain only isolated N atoms (Collins and Stanley 1985, Satoh and Sumiya 1995).

In this paper we use the ability to make N3 centres to examine the effects of isotope doping on the centres. Isotope effects on the optical bands of diamond have been studied extensively (e.g. Collins *et al* (1987) for ¹⁵N on local mode vibrations, Collins *et al* (1988) for ¹³C on various electronic and vibrational bands, Nazaré *et al* (1991) for Ni), but to the best of our knowledge there are no published data for the N3 centre. In section 2 we describe the experimental methods used in this work, and estimate the concentration of N3 centres generated in our samples by heat treatment. We also note that it is possible to destroy N3 centres by heat treatment. In section 3 we report the effects on the vibronic band

of isotopic substitution of the host lattice and of the nitrogen impurity, and in section 4 we show that the effect of ^{13}C doping can be understood in terms of other known properties of the centre if Jahn–Teller effects are included.

2. Experimental details

Diamonds with concentrations of between 4.5 and $6 \times 10^{19} \text{ cm}^{-3}$ dispersed nitrogen atoms were made by the high-temperature, high-pressure method. Synthetic diamonds with different isotope compositions have been used: standard $^{12}\text{C} + ^{14}\text{N}$ diamond, $^{13}\text{C} + ^{14}\text{N}$ diamond, and $^{12}\text{C} + ^{14}\text{N} + ^{15}\text{N}$ diamond. The ^{15}N samples were made by doping the synthesis capsule with ^{15}N -labelled aniline, but these samples were always contaminated with ^{14}N . The ratio of ^{15}N to ^{14}N was measured for samples from each batch using the relative intensities of the two isotopically shifted lines in the spectrum of the H1a centre (Woods and Collins 1982). In contrast, the ^{13}C samples were essentially pure isotope samples. All of the natural diamonds contained both A and B centres.

The infrared absorption spectra were measured at room temperature using a Perkin–Elmer 580B spectrometer to establish the concentrations of the single nitrogen and of the A and B nitrogen aggregates. Spectra in the visible and ultra-violet regions were measured at 77 K, using either a Perkin–Elmer model 330 spectrometer or a Hilger Monospek grating monochromator.

The synthetic and natural diamonds were annealed at temperatures between 2200 and 2700 °C under a stabilizing pressure using the equipment described by Evans and Qi (1982). We have not observed N3 centres after heating at 1750 °C synthetic diamonds which had been irradiated with 10^{18} to $3 \times 10^{18} \text{ cm}^{-2}$ electrons of energy 2 MeV to increase the mobility of the N atoms (Collins 1978). However, heating unirradiated synthetic diamonds between 2500 and 2700 °C caused the aggregation of the single N atoms to form A and B aggregates, as monitored by the infra-red absorption spectra (Woods 1986), and also created N3 centres. In samples with 4.5 to $6 \times 10^{19} \text{ cm}^{-3}$ dispersed N atoms we observed an integrated absorption in the zero-phonon line at 77 K of about 0.6 nm cm^{-1} (or 40 cm^{-2}) after heating at 2650 °C for four to five hours.

To estimate the concentrations of N3 centres produced in this way we use detailed-balance arguments (see, e.g., Stoneham 1975). They relate the strength of the absorption to the concentration of the centres using the radiative lifetime to calibrate the oscillator strength of the transition. In SI units, the concentration $[N]$ of centres is

$$[N] = \frac{9}{\pi^2} \frac{n^2}{(n^2 + 2)^2} \frac{E^2 \tau}{c^2 \hbar^3} \frac{g_f}{g_i} \int \mu(E) \text{d}E. \quad (1)$$

Here $n = 2.4$ is the refractive index of diamond. E is the mean energy of luminescence and is 2.8 eV ($4.5 \times 10^{-19} \text{ J}$). The radiative lifetime τ has been estimated at 150 ns by Davies and Thomaz (1978) allowing for the non-radiative de-excitations at the centre. The degeneracies g_f and g_i of the final and initial states of the luminescence band are known from the work of Crowther and Dean (1967), giving $g_f/g_i = 1/2$. The integral in equation (1) is over the absorption band, including its phonon sideband, and so is about 30 times the zero-phonon absorption (Halperin and Nawi 1967). Evaluating, a zero-phonon absorption at 77 K of 0.6 nm cm^{-1} corresponds to $2.5 \times 10^{16} \text{ cm}^{-3}$ N3 centres. Tests of equation (1) on defects in silicon suggest that it is accurate within a factor of 2 or 3 (Davies *et al* 1987). The nitrogen converted to N3 centres under these conditions is therefore about three orders of magnitude less than the total available nitrogen.

This conversion fraction is comparable with that found in most natural diamonds. For natural diamonds (examined without further heat treatment) Woods (1986) has observed that the absorption (in cm^{-2}) integrated across the N3 zero-phonon line measured at 77 K is usually related to the concentration of nitrogen in the B aggregates (in cm^{-3}) by

$$I(N3) = 1.9 \times 10^{17} N_B \text{ cm}^{-1} \quad (2)$$

using the nitrogen assay values of Sobolev and Lisoivan (1972), Burgemeister (1980) and Woods *et al* (1990). From equation (1), this implies that there is about 100 times less nitrogen in the N3 centres than in the B aggregates, and nitrogen may be present in aggregates other than the B form.

We note in passing that heating natural diamonds with a high concentration of N3 centres (zero-phonon absorption of 10 to 20 nm cm^{-1}) in the range 2300 to 2650 °C results in a decrease by up to a third in the N3 absorption, implying that the different forms of nitrogen, including the N3 centre, probably come to an equilibrium dependent on the annealing temperature, as reported for the major forms of nitrogen (Evans *et al* 1995).

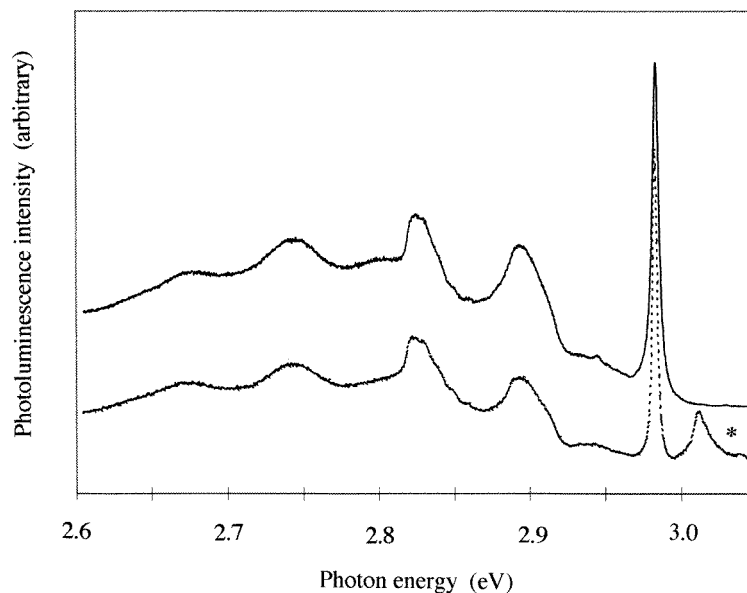


Figure 1. The photoluminescence measured at 77 K of the N3 centre in a natural diamond (upper curve) and a nominally $^{12}\text{C} + ^{15}\text{N}$ diamond (lower curve). The feature marked with an asterisk is independent of the N3 band.

3. Isotope effects on the N3 band

Figure 1 shows the photoluminescence of the N3 centre in a natural diamond and a nominally $^{12}\text{C} + ^{15}\text{N}$ diamond, and figure 2 shows spectra for a natural diamond and a $^{13}\text{C} + ^{14}\text{N}$ diamond. All of the spectra were measured at 77 K. We note that the height of the zero-phonon line relative to the vibronic band is affected by its width and also, in the natural diamond, by significant absorption of the zero-phonon luminescence by the zero-phonon absorption line. Otherwise, the bands in the $^{12}\text{C} + ^{14}\text{N}$ and $^{12}\text{C} + ^{15}\text{N}$ diamonds have extremely similar shapes, neglecting the independent features which are labelled with an

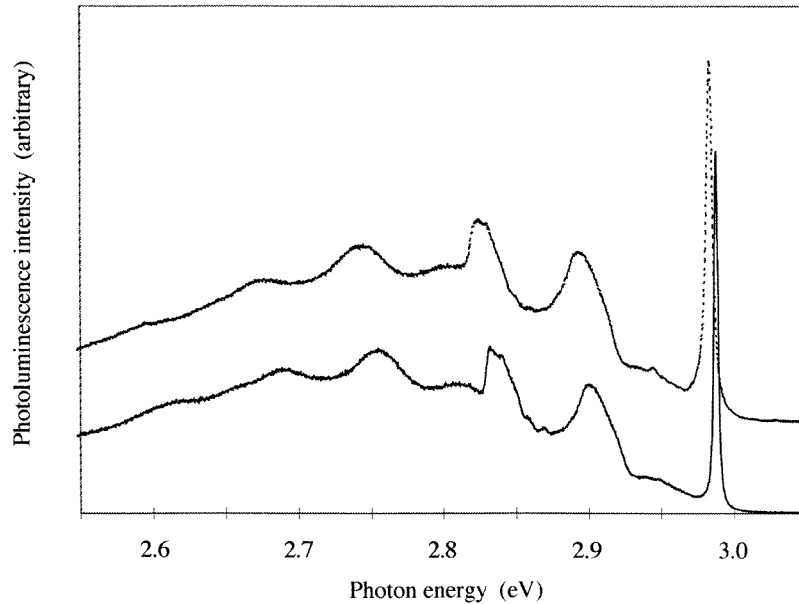


Figure 2. The photoluminescence measured at 77 K of the N3 centre in a natural diamond (upper curve) and a $^{13}\text{C} + ^{14}\text{N}$ diamond (lower curve).

asterisk. The only detectable difference in the N3 spectra is that the zero-phonon line is shifted to higher energy in the ^{15}N sample by 0.14 ± 0.07 meV. From the H1a absorption line (section 2) the ^{15}N diamond contained the isotopes in the ratio $^{15}\text{N}:^{14}\text{N} = 0.6:0.4$. The N3 centre contains three N atoms, so with this isotope ratio we would expect 0.22 of the centres to have all three atoms as ^{15}N , 0.43 of them to have two ^{15}N and one ^{14}N , 0.29 to have one ^{15}N and two ^{14}N , and 0.06 to have all three as ^{14}N . The observed peak therefore corresponds closely to the case of two ^{15}N and one ^{14}N . Consequently, the shift for complete replacement is expected to be 3/2 times larger than observed, giving

$$hv_{15} - hv_{14} = 0.2 \pm 0.1 \text{ meV.} \quad (3)$$

In the $^{13}\text{C} + ^{14}\text{N}$ diamond the shift in the zero-phonon energy is considerably larger:

$$hv_{13} - hv_{12} = 4.5 \pm 0.2 \text{ meV.} \quad (4)$$

Within experimental uncertainties, the energies (measured from the zero-phonon line) of all of the features in the vibronic sideband of the ^{13}C diamond are reduced by a factor $\sqrt{12/13}$ relative to those in the ^{12}C diamond. Consequently, at this level of measurement it appears that all of the modes of vibration of the centre are dominated by the motion of C atoms, and that we may ignore the N atoms. We will therefore assume in the following that the effective masses of all the modes of vibration of the N3 centre are changed by the ratio 13/12 in a ^{13}C diamond relative to a ^{12}C diamond.

4. Discussion of the ^{13}C isotope effects

The isotope dependence of the energy of a zero-phonon line is usually discussed in terms of two types of effect, often called the *static* and the *dynamic* terms (Hughes 1966). Here

it will also be necessary to introduce a third term derived from the Jahn–Teller effect.

The static shift occurs as a result of diamonds made from ^{13}C having a larger lattice spacing than those made from ^{12}C . The difference in lattice parameter is (Holloway *et al* 1991, 1992, Yamanaka *et al* 1994)

$$\frac{\Delta a}{a} = 1.5 \times 10^{-4}. \quad (5)$$

It produces a static shift of the zero-phonon line of

$$\Delta h\nu_s = 3L(c_{11} + 2c_{12}) \frac{\Delta a}{a} \quad (6)$$

where the sum of the elastic constants $c_{11} + 2c_{12} = 1326$ GPa (Grimsditch and Ramdas 1975, Ramdas *et al* 1993), and $3L = 1.8 \pm 0.4$ meV GPa $^{-1}$ (Crowther and Dean 1967, Wedlake 1970) is the response of the N3 zero-phonon line to a hydrostatic compressive stress. The effect can therefore be explicitly evaluated, and shifts the N3 line by 0.36 ± 0.08 meV to higher energy in ^{13}C .

The dynamic shift is less easy to calculate. It arises because the zero-phonon line is a transition between the zero-point energy states of all of the vibrational modes of the N3 centre. A detailed account of the dynamic shift has been given by Hughes (1966) for the situation where there is no Jahn–Teller effect. It is useful here to give a very simplified single-mode version of this case, so that we can later contrast the different behaviour of a Jahn–Teller system. The adiabatic potential in the electronic ground state is written, for a single mode, as $V_g = \frac{1}{2}m\omega^2 Q^2$ where m is the effective mass of the mode, ω its frequency and Q is the displacement coordinate. The zero-point energy level, from which the zero-phonon line originates at low temperature, has an energy $E_g^0 = \frac{1}{2}\hbar\omega$. In the excited state the potential becomes $V_e = E_0 + \frac{1}{2}m\omega^2 Q^2 + aQ$ where E_0 is the increase in electronic energy at $Q = 0$ and the term aQ represents the electron–lattice interaction which is linear in the displacement Q . Consequently

$$V_e = E_0 + \frac{1}{2}m\omega^2 \left(Q + \frac{a}{m\omega^2} \right)^2 - \frac{a^2}{2m\omega^2}. \quad (7)$$

It follows that the vibrations are harmonic, and the zero-point energy state in this electronic state has an energy $E_e^0 = E_0 - E_r + \frac{1}{2}\hbar\omega$ where the relaxation energy

$$E_r = a^2 / 2m\omega^2. \quad (8)$$

The zero-phonon transition occurs at the difference in energy of E_0^e and E_0^g , which is simply E , and E is independent of the mass m . With coupling to many modes the dynamic shift is still zero as long as the electronic state couples only linearly to the displacement modes. To obtain a dynamic shift it is necessary to include higher-order coupling, which changes the zero-point energies in the ground and excited states. The energy of the zero-phonon line is then, in the limit of zero temperature,

$$h\nu = E + \frac{1}{2} \sum_i (\hbar\omega_i^e - \hbar\omega_i^g) \quad (9)$$

where ω_i^e is the (angular) frequency of the i th mode of vibration in the electronic excited state of the N3 centre, and ω_i^g is the frequency of the mode in the ground electronic state. It is expected that $\omega^g \approx \omega^e$ for lattice modes. E continues to be independent of the isotope mass in the many-mode case (Hughes 1966). We have noted that the effect on the vibronic bandshape of changing the isotopes is that all of the modes of vibration are affected as though they only involve carbon atoms. In the harmonic approximation, which is adequate

here, the sum in equation (9) will therefore change by the ratio $\sqrt{12/13}$ when the lattice is changed from ^{12}C to ^{13}C , and $h\nu$ depends on the isotope:

$$h\nu_{13} - h\nu_{12} = \frac{1}{2}(\sqrt{12/13} - 1) \sum_i (\hbar\omega_i^e - \hbar\omega_i^g) \quad (10)$$

where $\hbar\omega_i^e$ and $\hbar\omega_i^g$ are for ^{12}C . It is convenient to write the sum in equation (10) in the form

$$\sum_i (\hbar\omega_i^e - \hbar\omega_i^g) = \int d\omega g(\omega) \quad (11)$$

where $g(\omega) d(\omega)$ is sum of the frequency shifts for all modes between frequencies ω and $\omega + d\omega$. Following Hughes (1966) we estimate $\int d\omega g(\omega)$ from the temperature dependence of the energy of the zero-phonon line, which is determined by two types of contribution. One is the effect of lattice expansion, which produces a shift in the zero-phonon line analogous to the static shift of equation (6), with the fractional change in lattice parameter replaced by the linear expansion of the crystal at the temperature of measurement. This contribution can be evaluated explicitly using the known expansion of diamond (Slack and Bartram 1975). The second contribution to the shift comes from the fact that in the ground and excited electronic states the vibrational quanta of each mode may be slightly different as a result of the changed chemical bonding. At temperature T a mode of energy $\hbar\omega$ has a mean occupation number of $n(\omega) = 1/(\exp(\hbar\omega/kT) - 1)$. The zero-phonon transition involving that mode occurs at an energy $n(\omega^g)(\hbar\omega^e - \hbar\omega^g)$, different from that of the transition at zero K. Consequently the contribution from all of the modes to the temperature dependence of the energy of the line is

$$\Delta h\nu(T) = \int d\omega g(\omega)n(\omega). \quad (12)$$

At low temperature this expression emphasizes the lowest-energy phonons, and the energy of the N3 zero-phonon line has only been measured over the limited temperature range 0 to 400 K (Halperin and Nawi 1967). We proceed empirically here by noting that over this range the shift of the N3 line, after allowing for the effects of lattice expansion, appears to be proportional to the temperature dependence of the lowest indirect energy gap of diamond, which is known over a significantly larger range of temperature, 0 to 700 K (Clark *et al* 1965). This implies that $g(\omega)$ for the N3 band is approximately proportional to the $g(\omega)$ that describes the temperature dependence of the energy gap of diamond. Allowing for expansion, between 0 and 400 K the N3 line shifts by 5.0 meV (Davies 1974) while the lowest-energy gap shifts by 24.7 meV (Collins *et al* 1990). The dynamic isotope shift of the energy gap is 13.5 ± 2 meV (Collins *et al* 1990) which scales to 2.7 ± 0.4 meV for the N3 line. This argument, calculating the isotope shift from the temperature dependence, would fail if there were high-energy local vibrational modes at the centre, since they would not be populated at usable temperatures. However, no such modes are observed at the N3 centre.

The final term comes from a re-examination of the zero-point energy in the ground and excited states. The N3 transition occurs between a non-degenerate electronic ground state and an excited orbital doublet in the trigonal point group (Crowther and Dean 1967). The excited doublet couples with modes of vibration which transform as the E representation in the point group. It has been suggested that the Jahn–Teller relaxation energy is $E_{JT} \approx 0.7\hbar\omega$ (Davies and Thomaz 1978, Davies 1981) where $\hbar\omega$ is the effective quantum of the E modes. The Jahn–Teller Hamiltonian for this problem can be written (Ham 1972, equations (2.2.1),

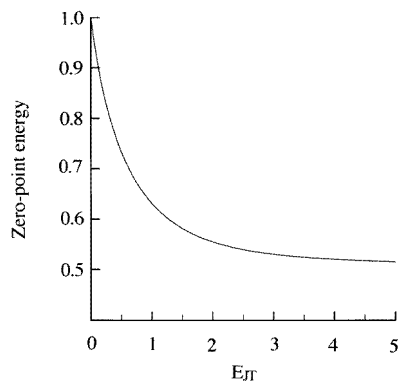


Figure 3. The zero-point energy in an $E \times e$ Jahn–Teller system as a function of the Jahn–Teller relaxation energy. The energy unit is the mode quantum $\hbar\omega$.

(2.2.6)) as

$$H = E_0 I + \frac{1}{2m} (P_\theta^2 + P_\epsilon^2) I + \frac{1}{2} m \omega^2 (q_\theta^2 + Q_\epsilon^2) I + k(Q_\theta U_\theta + Q_\epsilon U_\epsilon) \quad (13)$$

where the terms represent respectively the electronic energy E_0 of the excited state measured at the origin of the mode displacements ($Q_\theta = Q_\epsilon = 0$), the nuclear kinetic and the potential energy, and the linear electron–phonon coupling. The I - and U -terms are 2×2 matrices (Ham 1972). The Jahn–Teller relaxation energy is

$$E_{JT} = k^2 / 2m\omega^2. \quad (14)$$

E_{JT} has a very similar form to the relaxation E_r in the non-degenerate case, equation (8), and again is independent of the mass m . However, in contrast to the non-degenerate case, the zero-point energy is a function of the relaxation energy, and reduces as E_{JT} increases. Qualitatively, the optical centre moves in the ‘Mexican hat’ potential (figure 6 of Sturge 1967). In the limit of large k there is complete rotational freedom in the Q_θ , Q_ϵ space and the zero-point motion is reduced to a contribution of only $\frac{1}{2}\hbar\omega$ from the constrained radial motion in that space. The effect is shown in figure 3, as calculated numerically by diagonalization of the Jahn–Teller matrix, the results agreeing with the sparser tabulated data given originally by Longuet-Higgins *et al* (1958). For $E_{JT} = 0.7\hbar\omega$ the zero-point energy is $E_0^e = 0.68\hbar\omega$. In the electronic ground state, the two components of the E modes each contribute a zero-point energy of $\frac{1}{2}\hbar\omega$, giving a total zero-point energy of $E_0^g = \hbar\omega$. Consequently the zero-phonon line, which occurs between the zero-point levels, is lowered in energy by $|E_0^e - E_0^g| = 0.32\hbar\omega$ as a result of the reduced zero-point energy in the excited state. When the mass of the mode is changed from 12 to 13 units, this *reduction* in the zero-phonon energy is further decreased by a factor $\sqrt{12/13}$. Assigning again, from figure 1, the value of 90 meV to $\hbar\omega_{12}$, this effect increases the zero-phonon energy in ^{13}C relative to ^{12}C by $0.3(1 - \sqrt{12/13})\hbar\omega_{12} \sim 1.1$ meV.

Adding the effect of the static isotope shift of 0.36 ± 0.08 meV, the dynamic shift of 2.7 ± 0.4 meV and the Jahn–Teller term of 1.1 meV gives a total expected shift of

$$h\nu_{13} - h\nu_{12} \sim 4.2 \text{ meV} \quad (15)$$

which is similar to the measured value of equation (4).

This analysis necessarily contains approximations. We cannot determine $g(\omega)$ accurately. For example, it is not necessary for the changes in frequency in each mode to be

related to the strength of that mode as seen in the phonon sideband. Neither is the strength of the Jahn–Teller coupling known exactly, and its contribution varies between zero for no coupling to $(\sqrt{13/12} - 1)\frac{1}{2}\hbar\omega_{12}$ with strong coupling, i.e. from 0 to 3 meV for $\hbar\omega_{12} = 90$ meV. However, this term, which we are not aware of being necessary in the interpretation of any other isotope data for point defects in crystals, is probably significant at this centre.

It is striking that the isotope effects of nitrogen, at the core of the optical centre, are negligible. For the electronic ground state this is qualitatively consistent with the analysis of ENDOR data which place the active electron on the C atom next to the vacancy (van Wyk and Loubser 1993). Recent theoretical work (Goss and Jones 1997) also places the ground electronic state distant from the N atoms, but locates the excited state close to the N atoms.

5. Summary

We have established that the N3 centres in diamond can be destroyed as well as created by thermal treatment, and so in this respect they behave in a similar way to the major aggregates of nitrogen. Their production in specially synthesized diamonds has allowed the effects of isotope substitution to be investigated. There is little effect on the N3 bands shape when ^{15}N is substituted for ^{14}N , and the zero-phonon energy is perturbed by only 0.2 ± 0.1 meV; this value coincides with the only other report we are aware of for a shift of a zero-phonon line in diamond with nitrogen isotope substitution (the 389 nm line; Gippius *et al* 1982, Gippius 1997). The N3 optical spectrum shows a significant shift of 4.5 meV on substituting ^{13}C for ^{12}C , and this effect can be closely reproduced when the linear Jahn–Teller coupling is included.

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