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## Temperature dependence of optical absorption by the single-substitutional nitrogen donor in diamond

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Received 17 May 1991, in final form 17 September 1991

**Abstract.** In contrast to virtually all natural diamonds, synthetic diamonds show a considerable, reversible, change in colour upon heating. This colour change from yellow to reddish brown in the type Ib diamonds is especially noticeable above 500 K and is attributed to the interaction of optical transitions at the substitutional nitrogen impurity centres with lattice vibrations. Optical absorption spectra of homogeneous regions in several crystals were measured as a function of temperature (77–773 K) in the wavelength interval 200–700 nm. The spectra are interpreted in terms of an analytical model for electronic transitions from a deep donor level to a continuous range of levels in the conduction band, where strong electron–phonon coupling is taken into account. Numerical evaluation based on this model yielded a Huang–Rhys factor,  $S = 16 \pm 1$ , a phonon energy,  $\hbar\omega = 0.15 \pm 0.02$  eV and the temperature dependence of the nitrogen donor ionization energy. Upon a temperature rise to 750 K the latter showed a decrease of about 0.08 eV.

### 1. Introduction

During the production of high-pressure anvils and turning tools from monocrystalline, synthetic diamond, it was discovered that all the crystals turned into a darker, reddish brown colour while being polished (Moermond and Rutten 1987). This effect is caused by the increase in temperature during the diamond polishing process. After cooling, the crystals reacquired their original yellow colour. Repeated heating and subsequent cooling of the crystals in our laboratory showed that the process is reversible and reproducible.

Heating experiments of several, differently coloured type I, IIa and IIb (Walker 1979) natural diamonds showed that practically all the crystals kept their room-temperature colour, even at temperatures of about 800 K. The only exception was the rare class of natural type Ib diamonds, which behaved in the same manner as the synthetic specimens. Since synthetic diamonds are type Ib too (Chrenko *et al* 1971), it can be concluded that the influence of temperature on the transition probability of optical excitations at the single-substitutional nitrogen impurity centres in the crystals is responsible for the changes in colour.

The single-substitutional nitrogen donor is a well known and extensively studied defect in diamond. Electron paramagnetic resonance (EPR) studies (Smith *et al* 1959, Loubster and du Preez 1965) demonstrated that the fifth electron of N is unpaired and occupies an antibonding C–N orbital. Owing to a pseudo-Jahn–Teller effect the centre is trigonally distorted along the bond corresponding to this orbital. Since the pioneering

studies by Dyer *et al* (1965), several studies have been devoted to the optical properties of this defect. Four papers (Sobolev *et al* 1969, Chrenko *et al* 1971, Collins 1980, Woods *et al* 1990) have been concerned with the relation between single-substitutional nitrogen concentration and optical absorption. By means of photoconductance spectroscopy and the thermoelectric effect, Farrer (1969) and Vermeulen and Farrer (1975) proved that the above-mentioned fifth electron can be excited into the conduction band. The optical ionization energy of the nitrogen donor is about 2.2 eV (Walker 1979). Two recent investigations dealt with the occurrence of three bands, superimposed on the photoionization continuum, in the optical absorption spectrum of type Ib diamonds, which are labelled as A (3.3 eV), B (3.9 eV) and C (4.5 eV). Koppitz *et al* (1986) attributed the A and B features to transitions from the ground to excited states of the nitrogen centre, whereas the C band was assigned to a charge transfer from the valence band to a nitrogen donor level. Their interpretation of the C band is in conflict with the observation by Nazaré and Neves (1987), who found from low-temperature spectroscopy that the C band is mainly a vibronic system with its narrow zero-phonon line at 4.059 eV. This points to transitions between levels within the forbidden zone.

In the present paper the results of quantitative ultraviolet-visible (UV-VIS) absorption spectroscopic measurements of synthetic type Ib diamonds are reported. The spectra were recorded at different temperatures ranging from 77 to 773 K. The temperature dependence of the optical absorption cross section is interpreted in terms of a model for electronic transitions from a deep donor level to a continuous range of levels in the conduction band, where electron-phonon coupling plays a dominant role (Kukimoto *et al* 1973, Jaros 1977, Stoneham 1975). To facilitate interpretation, the experiments were complemented with UV-VIS photoconductance spectroscopy.

## 2. Experimental details

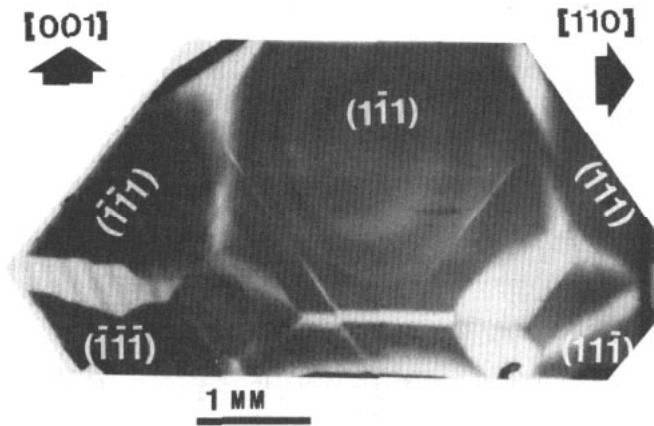
### 2.1. Measurements and data reduction

The absorption spectra in the UV-VIS region were recorded by making use of a single-pass Jobin-Yvon HR25 monochromator, fitted with a holographic grating (1200 grooves per millimetre) and a standard multi-alkali photomultiplier tube. As light sources, a tungsten lamp for the 400–700 nm wavelength interval and a xenon lamp for 200–400 nm range were used. The diamond specimens were clamped in a holder, which can be heated up to 800 K with an accuracy of  $\pm 4$  K. The low-temperature measurements at 77 K were carried out by mounting the crystals in a conventional liquid-nitrogen cryostat provided with quartz windows.

The optical transmission was measured at an absolute scale with an accuracy of 1–2%. Conversion of the transmission values to absorbance values was carried out after correction for multiple internal reflection. The necessary reflection coefficients were calculated from the refractive index data for diamond as given by Peter (1923).

To obtain information on the concentration of single-substitutional nitrogen in the specimen crystals, the absorption coefficient at  $1130\text{ cm}^{-1}$  (Chrenko *et al* 1971, Collins 1980) was determined with the help of a fast Fourier transform infrared spectrophotometer.

Photoconductance spectra were recorded with the above-described monochromator-light source combination as an excitation source. The photocurrents were measured with a pico/nanoampere meter, interfaced with a microcomputer. The bias voltage was



**Figure 1.** Ultraviolet ( $\lambda = 365 \text{ nm}$ ) absorption topograph of a  $(1\bar{1}1)$  synthetic diamond plate. The darker areas correspond to volumes of higher nitrogen impurity content. The large, uniform  $(1\bar{1}1)$  sector was used for spectroscopy.

kept at 45 V. To obtain light intensities capable of producing measurable photocurrents in the pico- and nanoampere range, the monochromator slits were opened widely. This has a negative effect on the resolution, which was lowered to 9 nm. To obtain a relative photocurrent per photon as a function of photon energy, corrections were made for the wavelength-dependent variations in output intensity of light from the monochromator.

## 2.2. Specimens

Diamonds are notorious for their optical inhomogeneity, which is caused by a non-uniform distribution of point defects (Raman 1944, Hanley *et al* 1977, Lang 1979, van Enkevort and Visser 1990, Burns *et al* 1990). To select volumes of homogeneous nitrogen concentration in the crystals, use was made of optical absorption topography (Woods and Lang 1975). This characterization technique, which employs the enhanced near-UV absorption by the single-substitutional nitrogen centres, is capable of imaging the distribution of this impurity in the diamonds. The topographs were obtained by photographing the specimen plates via an optical transmission microscope fitted with a monochromatic ultraviolet ( $\lambda = 365 \text{ nm}$ ) light source. Figure 1 shows a typical micrograph of one of the synthetic diamond specimens. The nitrogen concentration in the absorbing, darker,  $\{1\bar{1}1\}$  growth sectors is higher than in the weakly absorbing, brighter,  $\{100\}$ ,  $\{110\}$  and  $\{113\}$  sectors. The large volumes corresponding to the relatively uniform  $\{1\bar{1}1\}$  sectors were used for the present spectroscopic studies.

The synthetic diamonds for absorption spectroscopy were carefully polished to blocks of about 1 mm thickness or to plates of 0.15 mm thickness for investigation in the visible and the UV regions respectively. For photoconductivity measurements, cubes of side about 1 mm were cut and polished from large synthetic diamonds. To obtain ohmic contacts, two opposite faces were sputter-coated with a multi-metal layer of 40 nm Ti, 60 nm Pt and 1000 nm Au (Seal and van Enkevort 1988). All the specimen crystals were grown by Dr R Burns (De Beers Diamond Research Laboratory).

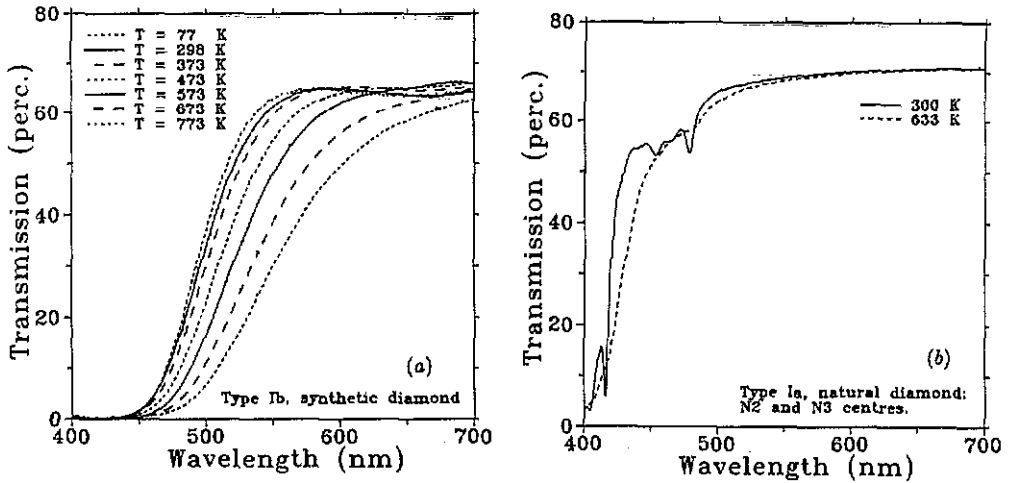


Figure 2. Transmission spectra of type I diamonds recorded at different temperatures: (a) synthetic Ib diamond; (b) Cape Yellow, natural type Ia diamond with N3 ( $\lambda = 416$  nm) and N2 ( $\lambda = 478$  nm) centres.

### 3. Results and discussion

#### 3.1. Optical absorption

Figure 2(a) shows a series of visible-light spectra measured for a thicker Ib diamond plate at temperatures ranging from 77 to 773 K. Especially at  $T > 500$  K and for wavelengths shorter than 650 nm the optical absorption increases strongly upon increase of temperature. This corresponds to the observed darkening and reddening of the natural and synthetic type Ib crystals at elevated temperatures. For comparison, figure 2(b) gives the optical transmission spectra of a natural, yellow type Ia diamond with N2 and N3 centres (Walker 1979) recorded at 300 and 633 K. Here the observed shift in optical absorption in the blue-violet is too low to be detected by eye. The change in colour of type Ib diamonds upon heating provides a simple means of distinguishing them from other classes of diamond crystals.

Figure 3 gives the dependence of the absorption cross section  $\sigma(h\nu)$  of the single-substitutional nitrogen centres on UV-VIS photon energy  $h\nu$  at different temperatures. This (dimensionless) cross section is defined as the ratio of the absolute optical absorption coefficient and the infrared (IR) absorption coefficient at  $1130\text{ cm}^{-1}$ . Since the latter is linearly related to the concentration of single-substitutional nitrogen in the crystals,  $\sigma(h\nu)$  is proportional to the optical absorption per unit of nitrogen concentration. The cross section defined in this manner circumvents the use of an absolute value for the nitrogen concentration, which has not yet been established unambiguously in relation to the IR absorption (Sobolev *et al* 1969, Chrenko *et al* 1971, Collins 1980). Very recently Woods *et al* (1990) obtained more reliable values on the basis of precision measurements.

The optical absorption plots in figures 3(a) and (b) show an overall increase of the cross section for increasing photon energies. At 77 K the onset of this increase occurs at 2.1 eV. Since at that temperature thermal broadening is not relevant, this transition energy provides a measure for the optical ionization energy of the donor centre. The present value agrees well with the value mentioned by Walker (1979), but is 0.4 eV

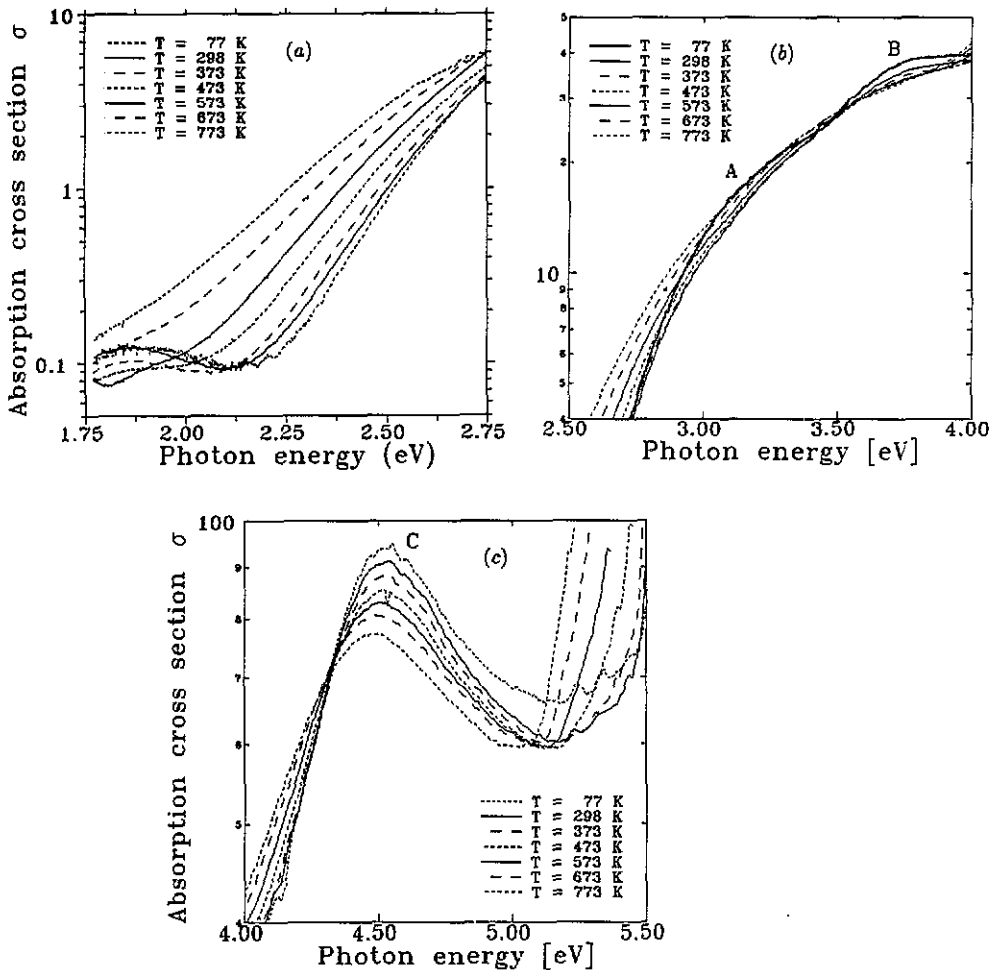


Figure 3. Optical absorption cross section of the nitrogen impurity in type Ib diamond as a function of photon energy and temperature: (a)  $1.75 \text{ eV} \leq h\nu \leq 2.75 \text{ eV}$ ; (b)  $2.50 \text{ eV} \leq h\nu \leq 4.00 \text{ eV}$ ; (c)  $4.00 \text{ eV} \leq h\nu \leq 5.50 \text{ eV}$ . The cross section  $\sigma(h\nu)$  is defined as the ratio of the optical absorption coefficient at photon energy  $h\nu$  and the IR absorption coefficient at  $1130 \text{ cm}^{-1}$ .

higher than the result obtained by Farrer (1969). At  $T < 400 \text{ K}$  a weak absorption band near  $1.85 \text{ eV}$  can be recognized in figure 3(a). This band, which will not be considered further, might tentatively be assigned to Ni impurities (Collins and Spear 1982, 1983). Since this feature possibly obscures the actual threshold of the absorption continuum, the ionization energy of the nitrogen donor might be somewhat lower than  $2.1 \text{ eV}$ .

At  $T < 600 \text{ K}$  the three bands A, B and C (Koppitz *et al* 1986), superimposed on the photoionization continuum, are well recognized in the spectra of figure 3. Around and above this temperature the A and B bands fade away, but the strongest peak C persists and shifts from  $4.52 \text{ eV}$  at  $77 \text{ K}$  to  $4.48 \text{ eV}$  at  $773 \text{ K}$ .

According to Bachelet *et al* (1981), the ground state of the unpaired electron at the N donor in its undistorted configuration is  $A_1(T_d)$ , while its first excited state is  $T_2(T_d)$ . Koppitz *et al* (1986) demonstrated that this  $T_2$  state is split into an  $A_1(C_{3v})$  and an  $E(C_{3v})$

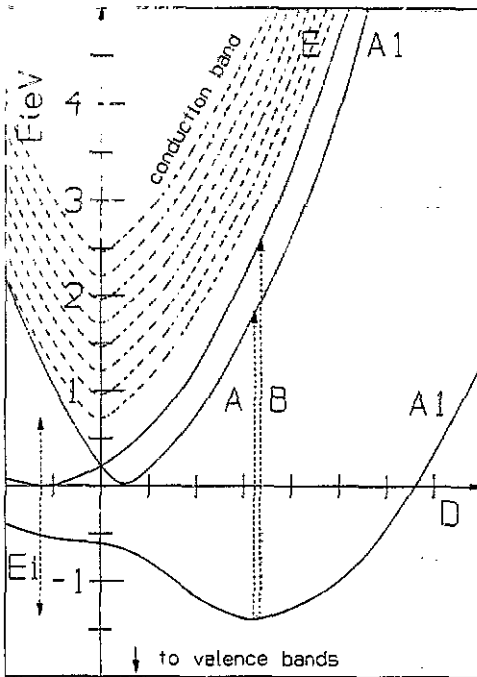
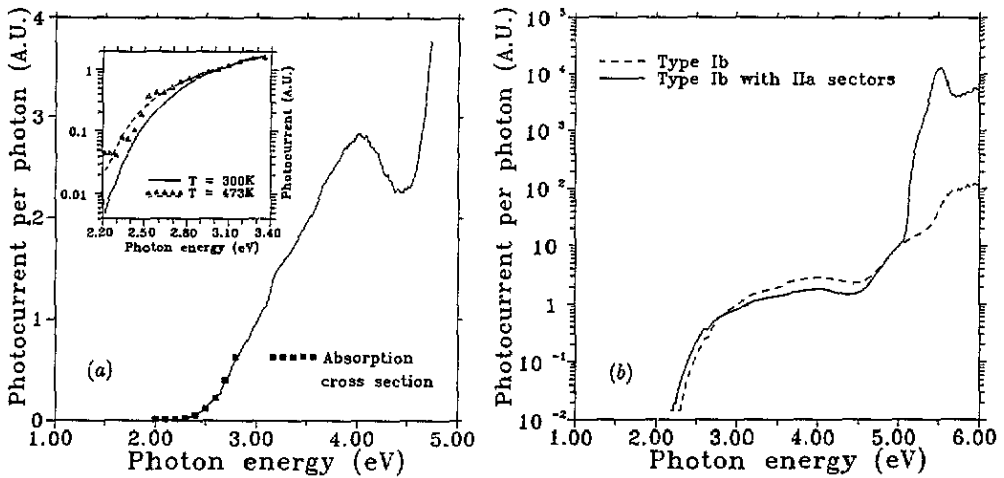


Figure 4. Configuration-coordinate diagram showing the energy levels of diamond:N with respect to trigonal distortions (Koppitz *et al* 1986). In this schematic representation the minima of the (upper) A1 and E parabolas have been arbitrarily set below the conduction band. The actual situation is not known.

state, owing to a pseudo-Jahn-Teller effect resulting from a shift of the N atom along one of the four C-N bond directions (figure 4). From their configuration-coordinate diagram it was derived that the A and B absorption bands are associated with the  $A_1(C_{3v}) \rightarrow A_1(C_{3v})$  and  $A_1(C_{3v}) \rightarrow E(C_{3v})$  vibronic transitions respectively. The expected zero-phonon energies of both transitions are equal to a Jahn-Teller energy  $E_{JT}$  of 1.4 eV and thus should be considerably less than the optical ionization energy of the nitrogen donor. However, during the present spectroscopic investigations, neither zero-phonon lines (see also Nazaré and Neves 1987) nor other optical absorption associated with the A and B bands were found in the photon range 1.4 to 2.1 eV. As mentioned in the introduction also for band C it is not clear whether optical transitions only occur via levels in the forbidden zone or whether levels in the valence band are also involved. To gather information on whether energy levels in the valence or conductance bands are playing a role during the optical transitions at the nitrogen centre, photoconductance spectroscopy was applied to three type Ib specimens.

### 3.2. Photoconductance

Figure 5 shows characteristic, normalized photoconductance spectra of two synthetic type Ib diamond blocks recorded at room temperature. Similarly to the optical absorption, the photocurrent also increases continuously (except for a dip near 4.5 eV) for larger photon energies. The onset of the increase near 2.2 eV is close to the donor ionization energy as estimated from the optical absorption spectra. In accord with an early observation by Farrer (1969), the dependences of photoconductivity and optical absorption on photon energy were found to be very similar in this study also (figure 5(a)). This indicates that both processes result from the same optical transitions at the nitrogen donor.



**Figure 5.** Photoconduction spectra of type Ib diamond: (a) linear scale; (b) logarithmic scale. To obtain a relative photocurrent per photon, corrections were made for the wavelength-dependent instrumental characteristics. In the interval  $2.0 \text{ eV} \leq h\nu \leq 3.0 \text{ eV}$  the optical absorption, indicated by squares in (a), matches well with the photocurrent. The inset in (a) gives the photoconduction spectra for the specimen without type IIa sectors, measured at room temperature and at 473 K.

To confirm that the temperature-dependent colour change of type Ib diamond is caused by a thermal broadening of its photoionization continuum, a photoconduction spectrum was also recorded at 473 K. The result is shown in the 'inset' in figure 5(a). It can clearly be seen that in the interval 2.0 to 3.5 eV a similar widening occurs as found for the optical absorption spectra. Owing to thermal ionization of the nitrogen donor, at higher temperatures the background electrical current becomes one to several orders of magnitude higher than the photocurrent. Therefore at  $T > 500 \text{ K}$  no photoconduction spectra could be measured.

The position of the weak band A cannot obviously be recognized in the photoconduction spectra. Band B almost coincides with the maximum at 4.0 eV, which is probably introduced by the minimum at 4.5 eV. Since no definite conclusion can be drawn whether the A and B bands appear as maxima or minima (Walker 1979, figure 12, case (2)) in the photocurrent spectra, it remains unclear whether the energy levels associated with the zero-phonon transitions of both systems are located in the forbidden zone or are resonant with the conduction band. If the band A and B zero-phonon transitions occur within the gap, then the influence of these bands on the temperature-dependent colour change must be minimal, because this phenomenon is dominated by transitions to the conduction band.

The strong absorption maximum C is replicated as a minimum in the photoconduction spectrum. This points to an absorption mechanism that is competitive with the direct ionization of the nitrogen donor. In other words, the transitions associated with C produce little or no photocurrent. This is in agreement with the work by Nazaré and Neves (1987), who interpreted band C as a result of vibronic transitions between two electronic levels with separation of 4.059 eV in the forbidden zone. The suggestion by Koppitz *et al* (1986) that band C is a result of hole creation leading to a negatively charged N state seems less probable. Since electron and hole mobilities are similar in diamond,



the photocurrent only goes to a minimum when the lifetime for holes is far less than that for electrons. Because of their totally different characters, the absorptions associated with band C (i.e.  $\alpha(h\nu)$  for  $h\nu > 4.0$  eV) are excluded from the analysis in section 4.

For photon energies around and above the fundamental absorption edge of diamond at 5.5 eV, a rise in normalized photocurrent of one to several orders of magnitude was encountered (figure 5(b)). This photoconductivity differed for different specimens and varied considerably upon change of the orientation of the diamond blocks with respect to the incident UV-light beam. Enhanced photoconductivity of type Ib diamond near 5.5 eV was also reported by Farrer (1969) for one of his specimens and by Seal and van Enkevort (1988) for synthetic diamonds with a low nitrogen content. The (intrinsic) photocurrent generated by far-UV photons is caused by valence-to-conduction band excitation. As observed by Keddy *et al* (1988) and Seal and van Enkevort (1988) this intrinsic photoconductivity decreases dramatically for increasing nitrogen concentrations. In other words, the single-substitutional nitrogen is a very effective recombination centre for electron-hole pairs. The photocurrent in the present case is almost certainly generated in the minor, low-nitrogen-content sectors {100}, {110} and {113} between the large, high-nitrogen-content sectors {111}. In view of the non-uniform distribution of these volumes with low nitrogen concentration and the limited penetration depth of  $>5.5$  eV radiation in the crystals, the variation of photocurrent with specimen orientation is easily understood. The association of intrinsic photocurrent with low-nitrogen-content volumes is confirmed by its long rise and decay times ( $1-10^2$  s), which are similar to those found for low-nitrogen-content synthetics during other investigations at our laboratory. The currents induced by radiations less than  $\approx 5.0$  eV showed no detectable delay in rise or decay. The intrinsic photoconductance will not be considered in the analyses given in section 4.

#### 4. Analysis of measured optical cross sections

The meaning and derivation of the transition probabilities  $G(h\nu, T)$  and other symbols used in this section are all given in the appendix. As shown in this appendix, from two absorption spectra  $\sigma(h\nu)/h\nu$ , recorded at different temperatures  $T_0$  and  $T_1$ , the thermal broadening  $\Delta G^*(h\nu, T_0, T_1)$  can be evaluated by searching for the appropriate Gaussian curve that gives  $G(h\nu, T_1)$  upon convolution with  $G(h\nu, T_0)$ . This was realized by a least-squares procedure in which

$$\sum_{h\nu=2.0}^{4.0\text{eV}} \{\ln[G(h\nu, T_1)] - \ln[G(h\nu, T_0) * \Delta G^*(h\nu, T_0, T_1)]\}^2$$

is minimized under variation of  $(ds^2(T)/dT)_{\bar{T}}$  and  $(d\varepsilon_i(T)/dT)_{\bar{T}}$  in  $\Delta G^*(h\nu, T_0, T_1)$ . In figure 6 it is demonstrated that, even for the very large temperature interval of about 700 K the high-temperature absorption spectrum matches well with the low-temperature one convoluted with a suitable Gaussian function. To avoid interference by the weak absorption band near 1.85 eV and the deviating band C, only data points in the interval 2.0 to 4.0 eV were considered.

Applying the above procedure to pairs of absorption spectra recorded at successive temperatures i.e.  $\Delta T$  is not too large,  $(ds^2(T)/dT)_{\bar{T}}$  and  $(d\varepsilon_i(T)/dT)_{\bar{T}}$  were derived for several temperatures  $\bar{T}$  ranging from 175 to 723 K. In figures 7 and 8 the results are presented as a function of temperature. A least-squares fitting of the experimental

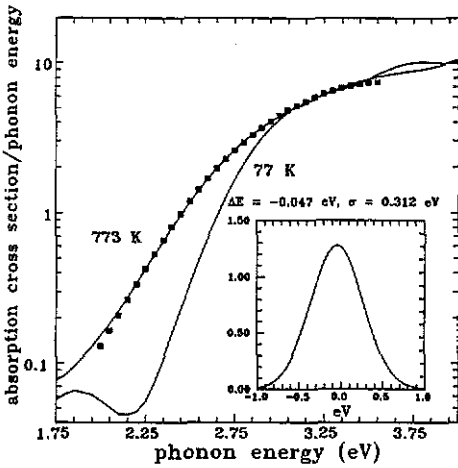


Figure 6. Convolution of  $G(h\nu, 77 \text{ K})$  with  $\Delta G^*(h\nu, 77 \text{ K}, 773 \text{ K})$  produces a new function, indicated by squares, which is almost identical to the experimental  $G(h\nu, 773 \text{ K})$ . The convolution mask  $\Delta G^*(h\nu, 77 \text{ K}, 773 \text{ K})$ , a Gaussian curve with its origin at  $-0.047 \text{ eV}$  and a standard deviation of  $0.312 \text{ eV}$ , is given in the inset.

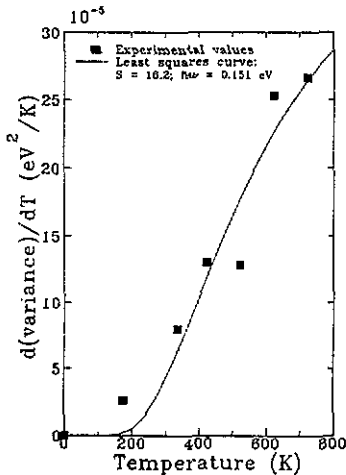


Figure 7. Temperature dependence of  $(ds^2(T)/dT)_{\bar{T}}$ . The squares denote the experimental points, whereas the full curve gives a least-squares fit using the theoretical temperature dependence of  $(ds^2(T)/dT)$  as formulated in equation (A12).

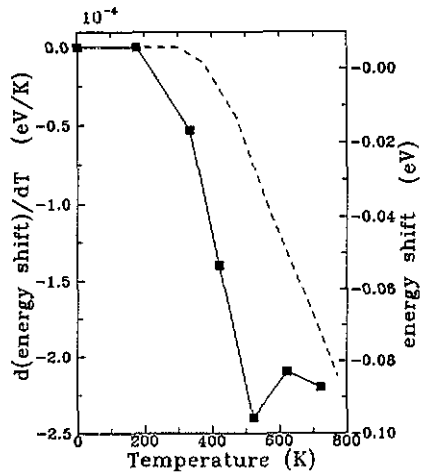


Figure 8. Experimental values for  $(de_i(T)/dT)_{\bar{T}}$  as a function of temperature. The broken curve gives the temperature shift  $s_i(T)$  of the optical ionization energy which was obtained by integration of the  $(de_i(T)/dT)_{\bar{T}}$  points.

$(ds^2(T)/dT)_{\bar{T}}$  points with the theoretical dependence (A12) gives values for the Huang-Rhys factor  $S = 16 \pm 1$  and the phonon energy  $\hbar\omega = 0.15 \pm 0.02 \text{ eV}$  (figure 7).

The Huang-Rhys factor deduced from the absorption spectra is large. This explains the considerable change in colour of the type Ib diamonds upon heating and confirms the validity of the Gaussian approximation of  $G^*(h\nu, T)$ . The phonon energy found from the above analysis matches closely with the Raman energy of diamond,  $\hbar\omega = 0.165 \text{ eV}$ , as well as with the maximum in the IR absorption spectrum of type Ib diamond,  $\hbar\omega = 0.140 \text{ eV}$ . This means that the electronic transitions at the nitrogen donor are coupled either with vibrations in the diamond lattice or with vibrations related to the nitrogen atom.

**Table 1.** Absorption cross section  $\sigma(T)$  as a function of temperature for three standard blue/green laser lines. The second-order polynomial description  $\sigma(T) = aT^2 + bT + c$  gives an excellent fit within the error interval of the experimental parameters.

Laser wavelength (nm)	$a$	$b$	$c$
He-Ne 543.5	$2.87 \times 10^{-6}$	$-1.10 \times 10^{-3}$	0.232
Ar 514.5	$4.20 \times 10^{-6}$	$-1.30 \times 10^{-3}$	0.491
Ar 488.0	$5.26 \times 10^{-6}$	$-1.20 \times 10^{-3}$	1.195

Figure 8 gives the experimental  $(d\varepsilon_i(T)/dT)_{\bar{T}}$  points as a function of temperature. In the same graph  $\varepsilon_i(T)$ , as obtained by integration of  $(d\varepsilon_i(T)/dT)_{\bar{T}}$ , is presented as a broken curve. The temperature dependence of the optical ionization energy is low: upon heating from 0 to 750 K,  $E_i(T)$  decreases by about 0.08 eV. This is about half the decrease of the indirect band-gap energy of diamond in the same temperature interval, which is estimated to be 0.15 eV by extrapolation of the full curve in figure 8 of Clark *et al* (1964).

## 5. Conclusions

Upon change of temperature from 77 K to about 800 K, the colour of type Ib diamonds changes reversibly from yellow to dark, reddish brown. This change in colour is explained by a 'red broadening' of the optical absorption band related to the photoionization of the single-substitutional nitrogen donors in the crystals. The UV-VIS absorption spectra of such diamonds, which were carefully measured for a range of different temperatures, were successfully interpreted in terms of a slightly modified Huang-Rhys model for electron-phonon coupling. This yielded a large value for the Huang-Rhys factor,  $S = 16 \pm 1$ , and a phonon energy,  $\hbar\omega = 0.15 \pm 0.02$  eV, close to the Raman energy of diamond.

The increase of optical absorption as a function of temperature might be utilized for temperature measurements in corrosive, hostile environments. This can be achieved by monitoring the change in transmission of a laser beam that passes the two plane-parallel windows of a polished synthetic diamond block placed at the locus of measurement. For this application, the temperature dependence of the absorption cross section is given in table 1 for three 'blue/green' standard laser wavelengths.

## Acknowledgments

The authors are grateful to Mr A Moermond and Mr Th Rutten for bringing to their attention the remarkable change in colour of synthetic diamond during polishing. Further, they are indebted to Dr M Seal for critically reading the manuscript and to Dr R Burns for producing the large, good-quality synthetic diamonds.

### Appendix. Electron-phonon coupling during photoionization of deep levels in semiconductor crystals

The influence of electron-lattice interaction on the probability of electron transitions between two discrete energy levels with separation  $E_0(T)$  at a crystal defect can often be described by the Huang-Rhys model (Huang and Rhys 1950, Stoneham 1975, Davies 1981). In this theory it is assumed that the electron transitions are linearly coupled to phonons with one single energy,  $\hbar\omega$ . For large coupling, i.e. large values for the Huang-Rhys factor  $S$ , the transition probability or the optical cross section divided by the photon energy,  $\sigma(h\nu)/h\nu$ , is proportional to the convolution

$$G(h\nu, T) = \delta(h\nu - E_0(T)) * G^*(h\nu, T)$$

with

$$G^*(h\nu, T) = [(2\pi)^{1/2}s]^{-1} \exp[-(h\nu - S\hbar\omega)^2/2s^2]$$

where

$$s^2 = S(\hbar\omega)^2 \coth(\hbar\omega/2kT). \quad (\text{A1})$$

In this equation  $\delta(h\nu - E_0(T))$  represents the sharp electronic transition at  $h\nu = E_0(T)$  and  $G^*(h\nu, T)$  gives its broadening due to coupling with lattice vibrations. The Gaussian function  $G^*(h\nu, T)$  is normalized over  $h\nu$ , or

$$\int_{-\infty}^{+\infty} G^*(h\nu, T) d(h\nu) = 1.$$

In the present case of a deep level in a semiconductor crystal, there is no question of a transition between two isolated defects. In the case of a donor, many levels in the conduction band are involved. This implies that the electronic transition probability in the absence of interaction with phonons should no longer be presented by a Dirac  $\delta$ -function but must be described by a continuous function  $G^0(h\nu, T)$ . Assuming that  $S$  and  $\hbar\omega$  are identical for all the possible transitions, it follows that  $\sigma(h\nu)/h\nu$  is proportional to the convolution:

$$G(h\nu, T) = G^0(h\nu, T) * G^*(h\nu, T). \quad (\text{A2})$$

For photon energies less than the optical ionization energy  $E_i(T)$ ,  $G^0(h\nu, T) = 0$ ; for  $h\nu \geq E_i(T)$  this transition probability is positive.

If it is assumed that the *shape* of  $G^0(h\nu, T)$  is temperature-invariant and its *position* is governed by the temperature change of the ionization energy, then

$$G^0(h\nu, T) = G^0(h\nu - \varepsilon_i(T))$$

with

$$\varepsilon_i(T) = E_i(T) - E_i(T = 0 \text{ K}). \quad (\text{A3})$$

From (A2) and (A3) it follows that

$$G(h\nu, T) = G^0(h\nu) * G^*(h\nu - \varepsilon_i(T), T). \quad (\text{A4})$$

In this equation the temperature-independent part  $G^0(h\nu)$  gives the no-phonon transition probability at 0 K. The temperature-dependent part

$$G^*(h\nu - \varepsilon_i(T), T) = [(2\pi)^{1/2}s]^{-1} \exp\{-[h\nu - S\hbar\omega - \varepsilon_i(T)]^2/2s^2\} \quad (A5)$$

is determined by  $S$ ,  $\hbar\omega$  and  $\varepsilon_i(T)$ , which are unknown for type Ib diamond. With some differences, equations of the same kind as (A2) and (A4) have been formulated earlier by Kukimoto *et al* (1973) and Jaros (1977) in their analysis of the temperature dependence of the optical cross sections associated with oxygen in GaP.

In section 4, numerical values for  $S$ ,  $\hbar\omega$  and  $\varepsilon_i(T)$  are extracted from the measured temperature broadening of the optical absorption band associated with nitrogen donors in diamond. To allow for such an analysis, knowledge of the relation between  $G(h\nu, T_0)$  and  $G(h\nu, T_1)$  with  $T_1 > T_0$  is necessary.

Given the fact that  $G^*(h\nu, T)$  is Gaussian and considering that the convolution of two Gaussian functions generates a new Gaussian with a variance equal to the sum of the variances of the starting functions, it follows that

$$G^*(h\nu - \varepsilon_i(T_1), T_1) = G^*(h\nu - \varepsilon_i(T_0), T_0) * \Delta G^*(h\nu, T_0, T_1). \quad (A6)$$

In this equation

$$\begin{aligned} \Delta G^*(h\nu, T_0, T_1) &= \{2\pi[s^2(T_1) - s^2(T_0)]\}^{-1/2} \\ &\times \exp(-\{h\nu - [\varepsilon_i(T_1) - \varepsilon_i(T_0)]\}^2/2[s^2(T_1) - s^2(T_0)]) \end{aligned} \quad (A7)$$

is a Gaussian function with variance  $s^2(T_1) - s^2(T_0)$ , centred at  $\varepsilon_i(T_1) - \varepsilon_i(T_0)$ . Since convolution is associative

$$\begin{aligned} G(h\nu, T_1) &= G^0(h\nu) * G^*(h\nu - \varepsilon_i(T_1), T_1) \\ &= G^0(h\nu) * G^*(h\nu - \varepsilon_i(T_0), T_0) * \Delta G^*(h\nu, T_0, T_1) \\ &= G(h\nu, T_0) * \Delta G^*(h\nu, T_0, T_1). \end{aligned} \quad (A8)$$

Hence a relation between the transition probabilities at different temperatures has been obtained.

For not too large a difference between  $T_1$  and  $T_0$

$$s^2(T_1) - s^2(T_0) \approx \left(\frac{ds^2(T)}{dT}\right)_{\bar{T}} \Delta T \quad (A9)$$

and

$$\varepsilon_i(T_1) - \varepsilon_i(T_0) = \left(\frac{d\varepsilon_i(T)}{dT}\right)_{\bar{T}} \Delta T \quad (A10)$$

where  $\bar{T} = (T_0 + T_1)/2$  and  $\Delta T = T_1 - T_0$ . Combining equations (A7), (A9) and (A10) finally gives

$$\Delta G^*(h\nu, T_0, T_1) = \left[2\pi\left(\frac{ds^2(T)}{dT}\right)_{\bar{T}} \Delta T\right]^{-1/2} \exp\left(-\frac{\{h\nu - [d\varepsilon_i(T)/dT]_{\bar{T}} \Delta T\}^2}{2[ds^2(T)/dT]_{\bar{T}} \Delta T}\right) \quad (A11)$$

in which, after differentiating equation (A1),

$$ds^2(T)/dT = [S(\hbar\omega)^3/2k][T \sinh(\hbar\omega/2kT)]^{-2}. \quad (A12)$$

From equations (A8), (A11) and (A12) it is clear that the relation between  $G(h\nu, T_0)$  and  $G(h\nu, T_1)$  is solely determined by  $S$ ,  $\hbar\omega$  and  $\varepsilon_i(T)$ . This implies that, from a given series of optical absorption spectra recorded at different temperatures these three parameters can be evaluated.

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