The polarised absorption and cathodoluminescence associated with the 1.40 eV centre in synthetic diamond

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Abstract. Synthetic diamonds that are grown using nickel or a nickel alloy as the solvent–catalyst contain 1.40 eV centres which are strongly segregated in the {111} growth sectors. Absorption and cathodoluminescence measurements made using polarising optics show that the dipole moment of the centre is preferentially aligned with the {111} growth planes. The absorption and luminescence systems have a zero-phonon doublet at 1.4008 and 1.4035 eV, and, surprisingly, the high-energy component exhibits a much higher degree of polarisation than the low-energy line. Polarisation-dependent structure is also observed in the vibronic absorption and luminescence bands. The zero-phonon splitting is due to a splitting of the electronic ground state, and a speculative model is proposed that may form a basis for understanding the different polarisation behaviours of the two lines.

1. Introduction

In this paper we present the first detailed investigation of the polarisation phenomena associated with the absorption and cathodoluminescence spectra of the 1.40 eV system in synthetic diamond. The cathodoluminescence is strongest in diamonds grown using Ni or Fe–Ni as the solvent–catalyst, and in some of these diamonds the 1.40 eV system may also be observed in absorption (Collins and Spear 1983, Collins 1989). A limited number of observations suggest that, for a given synthesis process, the absorption band is more intense in samples with a low nitrogen concentration (Collins 1989). The 1.40 eV centres are strongly segregated in the {111} growth sectors, and cathodoluminescence measurements on a polished slice of diamond, having its surface approximately normal to a set of {111} growth planes, show that the E vector of the infrared emission is preferentially aligned with the growth planes (Lang 1980, Collins 1989).

The 1.40 eV system, in both absorption and cathodoluminescence, has a zero-phonon doublet at 1.4008 and 1.4035 eV. From temperature dependence measurements of the absorption intensities of the two components, Collins and Spear (1983) have shown that the 2.7 meV splitting is in the electronic ground state.

In the present investigation we show that the degrees of polarisation of the two zero-phonon lines are very different; the high-energy component exhibits virtually 100% polarisation, with the dipole moment parallel to the growth plane, whereas the intensity of the low-energy line changes by less than 30% when a polariser is rotated in front of the crystal. Furthermore, structure present in the vibronic absorption band when the polariser is perpendicular to the growth plane is absent in the parallel position.

These phenomena which, to the author's knowledge, are uniquely observed in synthetic diamond, are believed to result from the anisotropic incorporation of the defects during growth. On this basis a speculative model is presented that successfully reproduces the observed polarisation behaviour of the zero-phonon doublet.

2. Experimental details

Two thin polished slices of diamond, synthesised by the temperature-gradient method, were employed in this investigation. One was the large De Beers diamond, grown using an Fe–Ni solvent–catalyst, studied earlier by Woods and Lang (1975) and Lang (1980). This sample was used for cathodoluminescence measurements, and the appropriate growth sectors were identified by reference to the diagrams published by Lang (1980). The second crystal was grown, using a Ni solvent–catalyst with nitrogen getters added, by Dr Hisao Kanda of the National Institute for Research in Inorganic Materials (NIRIM), Japan. Absorption measurements were made using this specimen, and the {111} growth sectors were readily recognised from their green coloration (Collins 1989).

Cathodoluminescence measurements were carried out using a custom-built electron gun operating at 45 kV, with a beam current of typically 10 μA. The electron beam was focused to a spot about 300 μm in diameter, and the sample was mounted in indium on a liquid nitrogen cold finger. The front surface of the diamond was covered with a layer of graphite (using colloidal graphite in alcohol) and small apertures were made in this film to reveal the {111} growth sectors. (This procedure is necessary to stop the large-area diamond from charging up and deflecting the beam.) Luminescence was collected from the excited face of the diamond with a spherical mirror and focused onto the entrance slit of a Spex 1500 monochromator, fitted with a 1200 groove mm^{-1} grating blazed at 500 nm and a North Coast E0817 cooled Ge detector.

Absorption measurements were made using a Spex 1701 monochromator fitted with a 1200 groove mm^{-1} grating blazed at 500 nm and an RCA 31034 A photomultiplier. The diamond was mounted in indium, either on a liquid nitrogen cold finger or in an Oxford Instruments CF100 continuous-flow cryostat. A {111} growth sector was masked off with indium, and growth striae visible in this sector, associated with the advancing {111} planes, were arranged to be approximately parallel to the spectrometer entrance slit. Light from a tungsten strip lamp was focused onto the sample with a spherical mirror, and the transmitted light was collected by a second mirror and focused onto the monochromator entrance slit, using a filter to absorb unwanted radiation that would otherwise be diffracted in second order.

The analogue signals from the detectors were digitised and processed using micro-computer systems, but the cathodoluminescence spectra have not been corrected for the transfer function of the optical system. For the absorption studies, the incident light spectrum $I_0(\lambda)$ and the transmitted light spectrum $I_t(\lambda)$ were stored in the computer for closely spaced values of the wavelength λ, and the approximate absorption coefficient calculated point by point from $t^{-1} \ln(I_0(\lambda)/I_t(\lambda))$ where t is the sample thickness. For measurements of the whole vibronic band the signal covered a very wide dynamic range because of the strong absorption and rapidly decreasing quantum efficiency of the photomultiplier at the longer wavelengths. Here, a switched-gain amplifier, controlled by the microcomputer, preceded the analogue-to-digital converter, giving the signal-processing system a dynamic range of 19 bits with a resolution of 12 bits.

Polarisation measurements on the zero-phonon doublet in both absorption and

cathodoluminescence, and the vibronic band in emission, were carried out by passing the transmitted or emitted light through a Polaroid type HR plastic film polariser, and then through a polarisation scrambler, before entering the monochromator. (The scrambler makes the measurements independent of polarisation effects produced by the monochromator.) The easy-transmitting direction (hereafter referred to as the 'axis') of the Polaroid could be continuously rotated with respect to the vertical slit of the monochromator.

A plastic film polariser that would satisfactorily cover the wavelength interval 550 to 900 nm was not available, and for polarisation studies of the 1.40 eV vibronic band in absorption a prism polariser was inserted between the exit slit of the monochromator and the photomultiplier. This allowed the plane of polarisation to be selected either parallel or perpendicular to the monochromator slit. In this configuration the polarisation scrambler is not used, and the wavelength-dependent polarisation effects produced by the monochromator are eliminated when the ratio $I_0(\lambda)/I_t(\lambda)$ is calculated. Clearly a different $I_0(\lambda)$ is required for each polarisation.

3. Results

3.1. Cathodoluminescence studies

Figure 1(*a*) shows cathodoluminescence spectra of the 1.40 eV vibronic band recorded from a {111} sector of the diamond slice examined photographically by Lang (1980). For the upper curve in figure 1(*a*) the polariser was adjusted to obtain the maximum signal; it was then rotated through 90° to obtain the lower spectrum. As noted by Lang, the total intensity changes by about a factor of 2 for this change in polarisation. Figure 1(*b*) shows that a quite different situation applies to the zero-phonon doublet. Although these two lines arise from a split ground state (Collins and Spear 1983), the intensity of the higher-energy component changes by about factor of 10 when the direction of polarisation is altered, whereas the intensity of the lower-energy component changes by less than 30%. A detailed study of the polarisation of the zero-phonon lines was made using the ($\bar{1}11$) sector of the top surface of the diamond. The growth surfaces of the planes in this sector make an angle of approximately 85° with the excited surface (Lang 1980). Figure 2 shows that as the polariser is rotated the intensities of the two components change in phase with each other, closely following an expected $\cos^2$ variation. The experimental data are shown by the points in figure 2 and the full curves have been calculated using the model presented in § 4.

Returning to figure 1(*a*), we note that there are some minor differences in the vibronic bands recorded for the two different polarisations. Vertical arrows show two of these; the peak at 1.3035 meV in the upper spectrum (approximately 100 meV from the zero-phonon region) is absent in the lower spectrum, and, at about 165 meV (the energy of the zone-boundary LO phonon) from the zero-phonon region, the upper spectrum has a maximum that almost coincides with the minimum in the lower spectrum. Similar, but more marked, phenomena are observed in the vibronic absorption bands, as reported below.

3.2. Absorption spectra

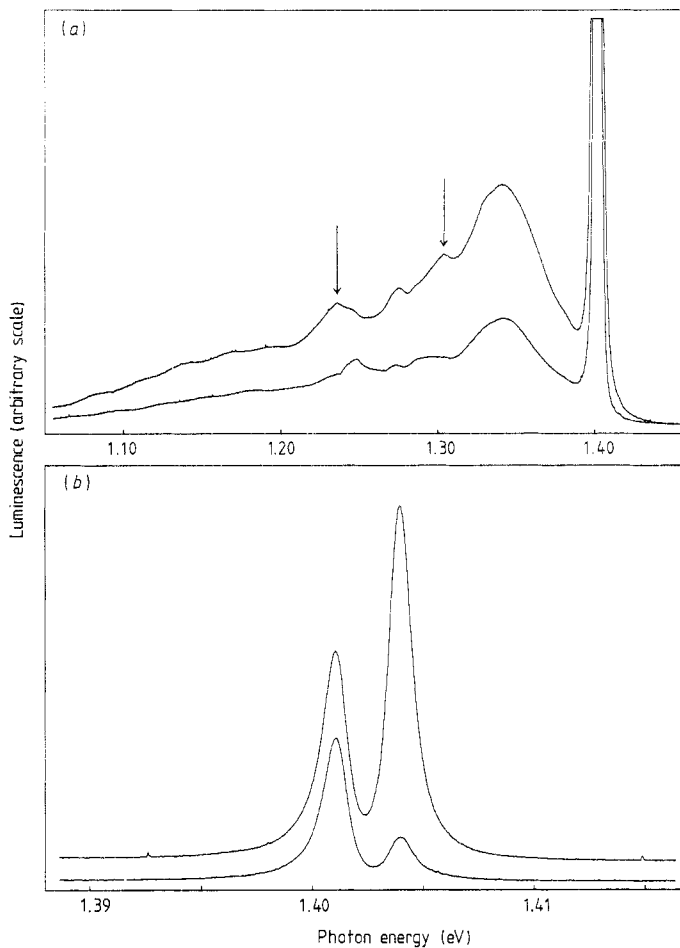Figure 3 shows the zero-phonon region of the 1.40 eV system in absorption. The spectra

Figure 1. (*a*) The polarised cathodoluminescence in the 1.40 eV vibronic band from a {111} growth sector of a polished slice of synthetic diamond. The upper spectrum was recorded by rotating the polariser to obtain the maximum signal; for the lower spectrum the polariser was then rotated through 90°. The spectra were recorded with the diamond at 77 K and the peak of the zero-phonon doublet is about 10× full scale. Vertical arrows indicate the positions of minor differences in the vibronic bands. (*b*) The 1.40 eV zero-phonon doublet obtained as in (*a*) for the two different polarisations; the spectra have been displaced vertically for clarity.

were obtained using one of the octahedral growth sectors of the near-central slice of the diamond grown at NIRIM. The growth planes are approximately normal to the surface of this slice. Figure 3(*a*) shows the spectra at 77 K, with the axis of the polariser set parallel (upper curve) and perpendicular (lower curve) to the direction of the advancing growth planes. As noted for the cathodoluminescence spectra (figure 1(*b*)), the intensity of the high-energy component changes by about a factor of 10, whereas that for the lower-energy line changes by less than 30%. For different settings of the polariser an approximate $\cos^2$ variation similar to that in figure 2 is obtained. The considerable absorption intensity in the parallel polarisation indicates that the 1.40 eV centres are present in quite high concentration. (It is difficult to make this statement quantitative
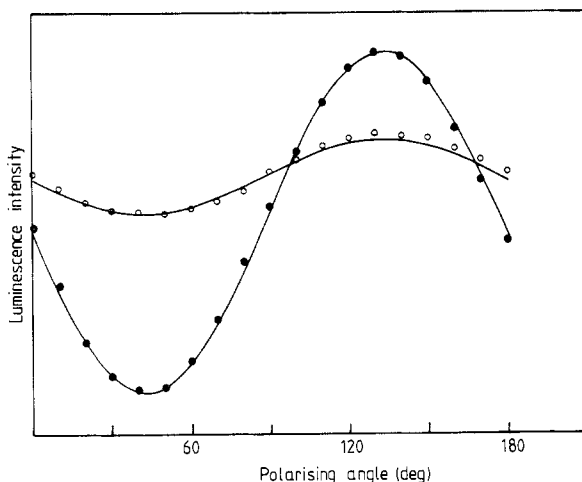
Figure 2. The variation with polarising angle of the intensities of the 1.4035 and 1.4008 eV components of the zero-phonon doublet, recorded using cathodoluminescence, from a sector in which the growth planes make an angle of approximately 85° with the surface. The data points are shown by full and open circles, respectively, and the curves are calculated using the model described in § 4. The diamond had been mounted on the cold finger in an arbitrary orientation with respect to the polariser axis, and the angle θ used in equation (3) is determined, by inspection, to be 133° less than the polarising angle.

since the oscillator strength is not known, but comparison with other vibronic bands in diamond—see, for example, data for the N3 centre by Davies *et al* (1978) and the 1.945 eV centre by Davies and Hamer (1976)—suggests that the defect concentration may be ~10^{24} m^{-3}).

The zero-phonon region at about 4 K is shown in figure 3(*b*). The diamond was moved between recording the spectra in figures 3(*a*) and 3(*b*) and, as the 1.40 eV absorption is quite inhomogeneously distributed in the growth sector examined, the absolute absorption intensities in figures 3(*a*) and 3(*b*) cannot be compared. The essential point is that, at about 4 K, the low-energy zero-phonon line is virtually frozen out in both polarisations (as expected from the work of Collins and Spear (1983)), and that the *E* vector associated with the high-energy line is still predominantly parallel to the growth planes. (The integrated intensity is about six times higher in the parallel polarisation; the ratio looks less than this because the line is only half as wide in the perpendicular polarisation.)

In figure 4 we show the 1.40 eV vibronic band measured at 77 K, together with the broad, structured band between about 1.75 and 2.1 eV that invariably accompanies the 1.40 eV system. In the parallel polarisation (upper curve) we see a clear, broad maximum in the vibronic band at about 60 meV above the zero-phonon region, corresponding to the maximum in the cathodoluminescence band (figure 1(*a*)) at 60 meV below the zero-phonon region. The absorption curve also shows a step at 1.570 eV, which is about 165 meV (the energy of the LO phonon) from the zero-phonon region. Several vibronic bands in diamond have a similar 'LO edge'.

Surprisingly, the absorption band is radically different for the perpendicular polarisation (the lower curve in figure 4). The 60 meV phonon mode is now too weak to detect with certainty, and two peaks (presumably phonon replicas) appear at 1.493 and
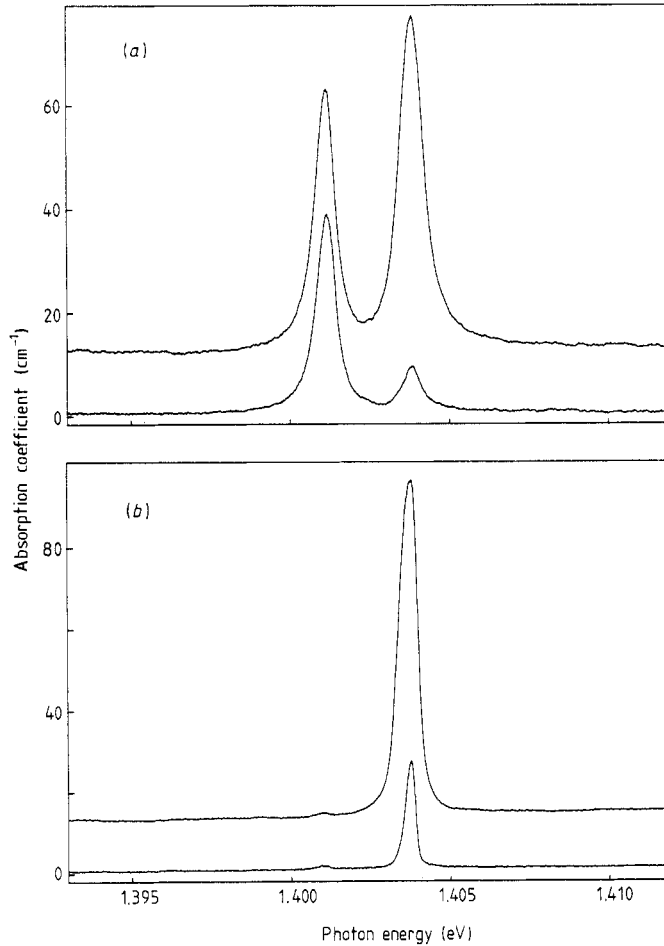
Figure 3. The 1.40 eV zero-phonon doublet recorded in absorption at (*a*) 77 K and (*b*) 4 K. The upper spectrum in each diagram is for the axis of the polariser set parallel to the growth planes; for the lower spectra the setting is perpendicular. The spectra have been displaced vertically for clarity.

1.505 eV that are not present in the parallel polarisation. The LO edge sharpens into a peak, and accurate measurement shows that the energy spacing of 165 meV is with respect to the *higher*-energy peak in the zero-phonon doublet (although this is relatively weak in the perpendicular polarisation).

Similar data to those in figure 4 are shown in figure 5 for a sample temperature of 4 K. Although the lower-energy zero-phonon line is now frozen out, the phenomena observed in the vibronic band are virtually the same as at 77 K. Comparison of figures 4 and 5 shows that the shape of the broad, structured, band with a maximum near 1.8 eV, is both polarisation- and temperature-dependent. This band always accompanies the 1.40 eV vibronic absorption system, but the relationship between the two remains obscure.
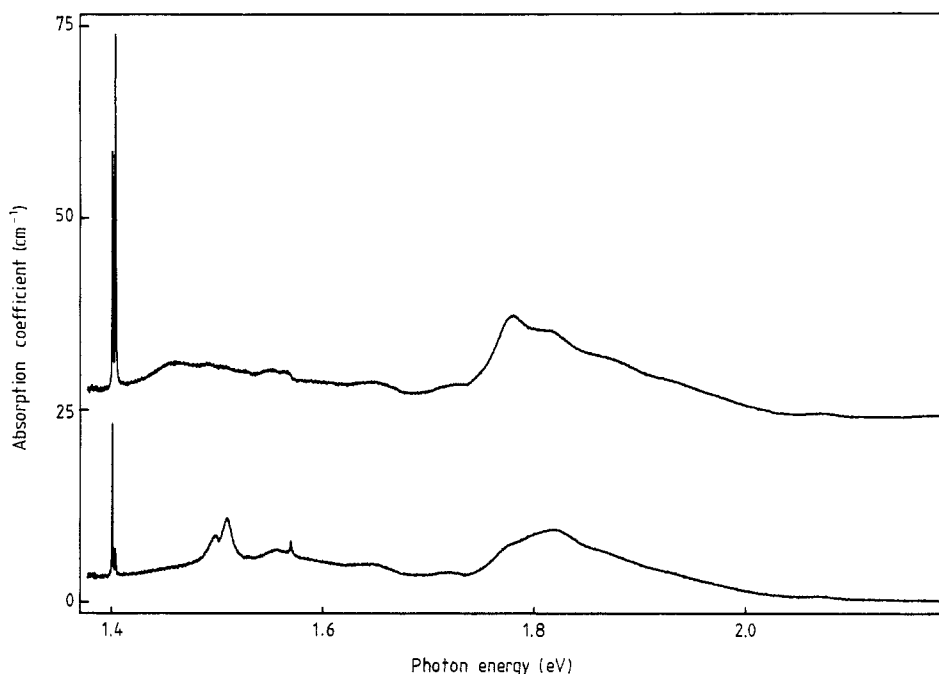
Figure 4. The 1.40 eV vibronic absorption band and related structure recorded with the sample at 77 K. The upper spectrum is for the axis of the polariser set parallel to the growth planes; for the lower spectrum the setting is perpendicular. The spectra have been displaced vertically for clarity.

4. Discussion

The growth-sector dependence of cathodoluminescence from synthethic diamond was first reported by Woods and Lang (1975). In that investigation, they noted that the green emission from the {100} growth sectors was linearly polarised, with the *E* vector parallel to the growth planes. Woods and Lang attributed this luminescence to the band A donor–acceptor pair recombination studied earlier by Dean (1965). However, Dodge (1986) points out that the donor–acceptor pair recombination is not expected to be polarised. Furthermore, he reports observing polarised green luminescence from {100} growth sectors in ballas (a naturally occurring, polycrystalline diamond), which his spectroscopic measurements showed was due to the H3 vibronic band. Dodge therefore *assumed* that the polarised cathodoluminescence observed in synthetic diamond by Woods and Lang was associated with H3 centres, and presented a plausible mechanism by which these centres could be *grown-in during synthesis*. Work by Collins (1989) has confirmed that the polarised green cathodoluminescence from the {100} growth sectors of synthetic diamond is indeed attributable to the H3 system.

The structure and symmetry of the H3 centre are known and this enables models for production of the centres during synthesis to be formulated. No such information is available for the 1.40 eV defect, but presumably a mechanism similar to that proposed by Dodge is responsible for the segregation of the centres into the {111} growth sectors. In the absence of a detailed atomic model for the 1.40 eV centre, we speculate briefly
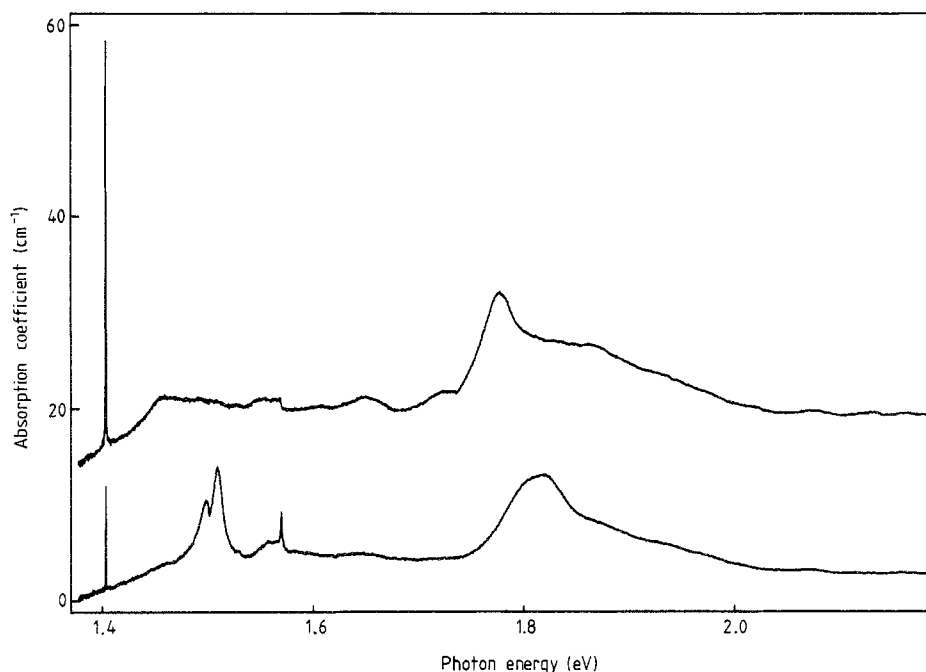
Figure 5. The 1.40 eV vibronic absorption band and related structure recorded with the sample at 4 K. The upper spectrum is for the axis of the polariser set parallel to the growth planes; for the lower spectrum the setting is perpendicular. The spectra have been displaced vertically for clarity.

on a process that could account for the different polarisation behaviours of the two components of the zero-phonon doublet.

In figure 6(a) we show the arrangement of atoms in two parallel adjacent $\{111\}$ growth planes of a perfect diamond. We will suppose that the incorporation of an impurity (probably nickel) during growth produces a 1.40 eV centre with its dipole moment pointing along a general direction such as OX, from a lattice site to a point which, in the perfect crystal, lies about a quarter of the way along an adjacent bond. We will look later at the physical significance of this configuration. We will suppose further that the anisotropy produced by the growing-in of the defects favours dipoles lying along directions such as OX, rather than those lying along crystallographically equivalent directions such as OX' shown in figure 6(b). Thus far the picture is analogous to that for the growing-in of H3 centres during synthesis; in that case the H3 dipoles occupy only those $\langle 110 \rangle$ directions that are parallel to the $\{100\}$ growth plane (Dodge 1986).

For the 1.40 eV centre we shall assume that if the crystal is given a small amount of thermal energy the dipole can 'flip'—reversibly—(by a currently unspecified process) from the orientation OX to the orientation OX', and we shall identify the 2.7 meV ground-state splitting with the energy required to produce this reorientation. In this model, absorption and luminescence transitions at dipoles such as OX will, therefore, be associated with the zero-phonon line at 1.4035 eV, whereas those at dipoles like OX' will be associated with the zero-phonon line at 1.4008 eV.

Let the OX- and OX'-type dipoles make angles of φ and φ' with the $\{111\}$ growth plane. The discussion that follows applies to either angle, and we will consider the angle
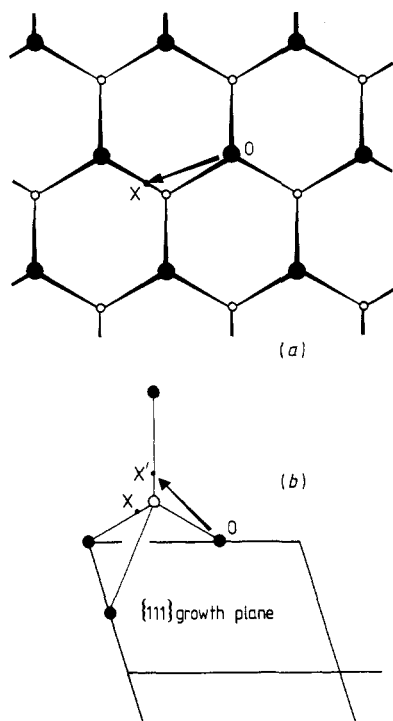
Figure 6. (*a*) The atomic arrangement in two adjacent parallel {111} growth planes viewed from a direction normal to the planes. The shaded 'atoms' are in front of the unshaded 'atoms'. The electric dipole moment is considered to lie along a direction such as O*X*. (*b*) The atomic arrangement as in (*a*) viewed obliquely. Anisotropic incorporation of the 1.40 eV centres during growth favours the dipole pointing along directions such as O*X*, rather than the crystallographically equivalent direction O*X'*. It is proposed that the dipole can flip reversibly from O*X* to O*X'* and that the thermal activation energy for this process can be equated with the ground-state splitting of 2.7 meV

φ'. The resolved component in the growth plane is $p \cos \varphi'$ and that perpendicular to the plane is $p \sin \varphi'$, where p is the dipole moment. There are three possible orientations of these resolved moments in the {111} growth planes. When luminescence from the growth planes is examined edge-on, the relative intensity observed parallel to the planes can be determined by considering three representative resolved dipole moments that make angles α, $\alpha + 120°$ and $\alpha + 240°$ to the direction defining the edge of the crystal. The total intensity is

$$[\cos^2 \alpha + \cos^2(\alpha + 120°) + \cos^2(\alpha + 240°)]p^2 \cos^2 \varphi'$$

that is

$$I(\text{parallel}) = \tfrac{3}{2}p^2 \cos^2 \varphi'. \tag{1}$$

The intensity perpendicular to the plane is simply

$$I(\text{perpendicular}) = 3p^2 \sin^2 \varphi'. \tag{2}$$

We note from equations (1) and (2) that provided $\sin^2 \varphi' < \tfrac{1}{2}\cos^2 \varphi'$ the light will be polarised preferentially in the parallel direction. This inequality requires that $\varphi' < 35.2°$.

If the polariser is rotated in front of the crystal, with the axis making an angle θ to

the parallel direction, the total intensity observed, $I(\theta)$, is

$$I(\text{parallel}) \cos^2 \theta + I(\text{perpendicular}) \sin^2 \theta.$$

Hence

$$I(\theta) = \tfrac{3}{2}p^2 \cos^2 \varphi' \cos^2 \theta + 3p^2 \sin^2 \varphi'(1 - \cos^2 \theta)$$

or, in general

$$I(\theta) = A[(\tfrac{1}{2}\cos^2 \varphi' - \sin^2 \varphi') \cos^2 \theta + \sin^2 \varphi'] \qquad (3)$$

where A is a scaling factor.

To fit the experimental data we note that, provided the light is preferentially polarised parallel to the growth planes, the maximum and minimum intensities are

$$I_{\max} = \tfrac{1}{2}A \cos^2 \varphi' \qquad I_{\min} = A \sin^2 \varphi'.$$

Hence

$$\tan \varphi' = (I_{\min}/2I_{\max})^{1/2}. \qquad (4)$$

Applying equation (4) to the data shown in figure 2 for the *higher-energy* zero-phonon line we find $\varphi = 13.17°$. Using the diagram in figure 6, straightforward geometry allows us to relate φ to φ' and we find that when $\varphi = 13.17°$, $\varphi' = 31.5°$.

The curves in figure 2 have been calculated using the above angles in equation (3), with the same scaling factor A for each curve. The plot for the high-energy zero-phonon line follows the data closely, as we would expect, since the experimentally observed minimum and maximum intensity values were used to calculate φ. That value of φ has been used to determine φ', using the known atomic arrangement in the diamond crystal structure. The pleasing feature of the model is how closely the curve for the low-energy zero-phonon line, calculated using the dependent value for the angle φ', matches the experimental data.

Because of the highly speculative nature of the model, no attempt has been made to recalculate the behaviour for the precise situation relating to the data in figure 2, for which the crystal is polished at an angle of about 85° to the ($\bar{1}11$) planes, or to investigate the effect of collecting the luminescence over a range of angles. (The collection mirror in the cathodoluminescence equipment has a numerical aperture of $f/0.5$.) The intention has been simply to explore a possible mechanism to account for the very different polarisation behaviour of the two components of the 1.40 eV zero-phonon doublet, in the light of the known anisotropic incorporation of H3 centres during diamond synthesis (Dodge 1986). In this respect the model has been very successful and it is reasonable to ask whether it has any physical significance. We know that when a single nitrogen atom substitutes for a carbon atom, a localised distortion occurs so that one C–N bond is about 10% longer than the others (Smith *et al* 1959). A larger distortion (about 25%) at the 1.40 eV centre would allow the unshaded 'atom' in figure 6(b) to sit at either X or X', with the site X being preferred energetically; the slight inequivalence between sites X and X' is then attributed to a growth anisotropy. Clearly this is very simplistic interpretation that will probably require revision when a detailed atomic configuration for the centre has been established.

It is not obvious at this stage how to account for the different phonon coupling in the two different polarisations shown in figures 4 and 5, but there is one further interesting point that emerges from the proposed model. When cathodoluminescence is collected *normal* to a {111} growth surface (e.g. an external octahedral face), it is expected to be unpolarised because of the threefold symmetry (see figure 6(*a*)). Experimentally this is found to be nearly true—intensities change by only a few per cent as the polariser is rotated. However, the low-energy zero-phonon line is always less intense than the high-energy component (see, for example, figure 1 of Collins and Spear (1983)). This is exactly what one would expect from the model proposed in the present paper. The ratio of the intensity in the low-energy line to that in the high-energy line is determined by the corresponding projected dipole moments on the {111} plane and is calculated to be $[\cos(31.5°)/\cos(13.17°)]^2$, i.e. about 77%. This is reasonably close to the value observed experimentally.

5. Summary

The polarisation behaviour of the 1.40 eV zero-phonon doublet and the vibronic band has been examined in both absorption and cathodoluminescence. The 1.40 eV centres are segregated in the {111} growth sectors and the spectra have been obtained using thin slices of diamond with one or more {111} sectors approximately normal to the polished surface. The absorption and luminescence systems have a zero-phonon doublet because of the splitting in the electronic ground state (Collins and Spear 1983). In both absorption and luminescence the high-energy component of the doublet (at 1.4035 eV) is almost 100% polarised, with the *E* vector parallel to the {111} growth planes, but the intensity of the low-energy component (at 1.4008 eV) only varies by about 30% when a polariser is rotated in front of the crystal. The structure observed in the vibronic absorption band when the polariser axis is perpendicular to the {111} growth planes disappears when the polariser is rotated to the parallel position. Minor changes are also noted in the cathodoluminescence band as the plane of polarisation is changed.

Polarised H3 luminescence from the {100} growth sectors of synthetic diamond has been successfully accounted for by assuming that the H3 centres are grown-in during synthesis (Dodge 1986). In the light of this proposal a speculative model has been described in the present paper that closely reproduces the observed polarisation behaviour of the two zero-phonon lines in the 1.40 eV system.

References

Collins A T 1989 *Proc. First Int. Conf. New Diamond Science and Technology (Tokyo) 1988*
Collins A T and Spear P M 1983 *J. Phys. C: Solid State Phys.* **16** 963–73
Davies G and Hamer M F 1976 *Proc. R. Soc.* A **348** 285–98
Davies G, Welbourn C M and Loubser J H N 1978 *Diamond Res.* 23–30
Dean P J 1965 *Phys. Rev.* **139** A588–602
Dodge C 1986 *PhD Thesis* University of Reading
Lang A R 1980 *Phil. Mag.* B **41** 689–98
Smith W V, Sorokin P P, Gelles I L and Lasher G J 1959 *Phys. Rev.* **115** 1546–52
Woods G S and Lang A R 1975 *J. Cryst. Growth* **28** 215–26