

EXCITED STATES OF THE «H3» CENTRE IN DIAMOND

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ABSTRACT — We report the effects of uniaxial stress perturbations on the H13 absorption lines in diamond. These lines are transitions to higher excited states of the well-known H3 optical centre. We show that, in common with other centres in diamond, the symmetry of the H3 centre is the same in each of its electronic states. However, there are large differences in responses of the different states to stresses. This suggests that each of the electronic states at the H3 centre is highly localised at the centre. The vibronic interactions between these spatially localised states produce significant effects on the optical spectra, even for states of very different energies.

1 — INTRODUCTION

When different experimental techniques are used to probe a defect in a crystal, they often produce data on different electronic states (including different charge states) of the defect. Because the equilibrium atomic configuration of the defect depends on the electron distribution, the defect may be observed with very different structures by the different experimental techniques. For example, recent work on a carbon-carbon defect in silicon has shown that the two carbon atoms occupy equivalent sites

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in the lattice when the defect is examined using optically detected magnetic resonance [1], but the two C atoms are grossly inequivalent when the defect is investigated by electron paramagnetic resonance [2].

Structural changes like these are of interest in themselves. They also cause practical problems. For example, they make it difficult to be certain whether the same defect is being observed in different experiments.

In diamond there are only a few published sets of optical studies made on significantly different states of centres. These studies are of:

- a) *The neutral vacancy.* The lowest energy optical transition (zero-phonon line at 1.673 eV) has been studied in detail, particularly, e.g. [3], by the technique of uniaxial stresses which will concern us throughout this paper. A series of higher transitions nearer 3 eV has also been investigated by uniaxial stresses [4]. In all the electronic states the neutral vacancy has the same point group symmetry: tetrahedral.
- b) *The negative vacancy.* An optical transition at 3.150 eV ascribed to the negative vacancy [5] has been investigated by uniaxial stresses [6]. The symmetry of the centre is again tetrahedral: evidently changing the charge state of the vacancy in diamond from neutral to singly negative does not change its symmetry. This contrasts strongly with the different symmetries observed for different charge states of the vacancy in silicon [7].
- c) *The 594 nm centre.* This centre is known to produce both the 2.086 eV (594 nm) and the 2.917 eV zero-phonon lines [8]. In both cases uniaxial stress measurements have shown the centres to be trigonal [8, 9]. In addition, paramagnetic resonance measurements on optically excited states (e.g. data on the nitrogen-vacancy centre, by J. A. van Wyk, private communication 1984) also show the same symmetries as those deduced from the optical studies.

Present evidence suggests then that defects in diamond probably have the same symmetry, regardless of electronic state.

The purpose of this paper is to examine another optical centre, the well-known "H3" centre with its main zero-phonon line at 2.463 eV. The centre is believed to be formed from two substitutional nitrogen atoms and one vacancy [10]. Recently [11] Collins has shown that the "H13" absorption line at 3.361 eV most probably also occurs at the H3 centre. This result is intriguing for the 2.463 eV transition has been shown [12] to occur at a rhombic I centre (point group C_{2v}), while the 3.361 eV line has been shown [13] to occur at a trigonal centre (point group C_{3v} , D_3 or D_{3d}). In this paper we present new data on the effects of uniaxial stresses on the 3.361 eV transition (and neighbouring lines). In § 3 we show that the 3.361 eV line does occur at a rhombic I centre, as for the 2.463 eV line: again the point group of a centre is the same for different excited states. We show that there are significant differences in the effects of stress on each excited state. In § 4 we suggest that these differences can produce interesting vibronic effects, and we show that unusual features in the absorption spectra of the H3 centre may be explained.

2 — EXPERIMENTAL DATA

Natural diamonds were used throughout. The samples were cut to cuboids with linear dimensions of 1 to 2 mm, and were oriented so that stresses could be applied along the main crystallographic axes. The crystals were irradiated with about $5 \times 10^{21} \text{ m}^{-2}$ 2 MeV electrons and annealed at about 1100 K for two hours.

The 3.361 eV line is relatively weak. Throughout this work measurements were therefore made using the luminescence excitation technique with the samples at liquid nitrogen temperature. The specimen was excited by light from a 1 kW Xenon arc, focussed through a 3/4 m grating monochromator. Luminescence from the sample was detected in a direction perpendicular to the exciting beam. Fig. 1 shows the zero-stress luminescence excitation spectrum recorded with all the visible luminescence being detected from the diamond at photon energies $h\nu < 2.5$ eV. This luminescence occurs from the H3 band (i.e. the 2.463 eV zero-phonon line and all its phonon sidebands [11]). This is confirmed

by the broken line on Fig. 1 which shows the luminescence excitation spectrum recorded at the same resolution but using a second monochromator to select only H3 luminescence (defined as the difference between the luminescence intensity at the peak of the H3 one-phonon sideband and the intensity at the minimum

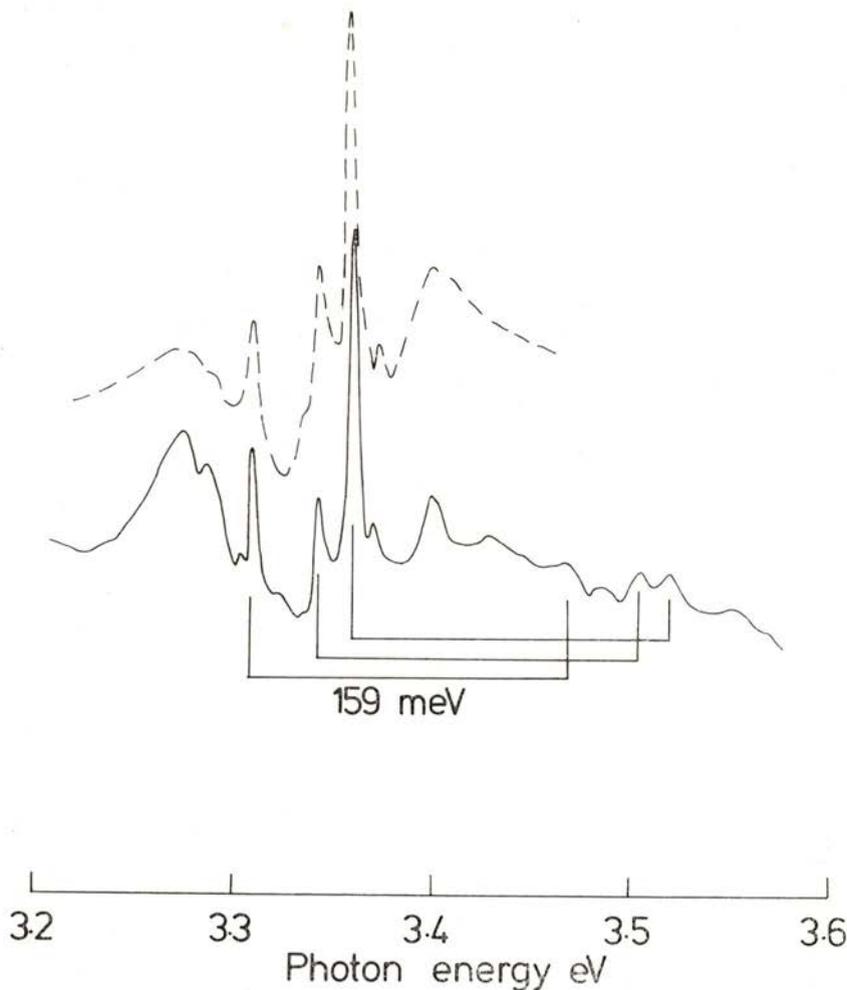


Fig. 1 — Luminescence excitation spectrum of the «H13» region at liquid nitrogen temperature. The solid line shows the spectrum recorded when all the emission in the H3 region is detected. The broken line shows the spectrum detected when a second monochromator was used to select only H3 emission, and is a higher resolution version of the spectrum given in reference [11].

between the first and second H3 phonon sidebands). The total luminescence excitation spectrum evidently arises predominantly from the H3 band. In the stress experiments the total emission with $h\nu < 2.5$ eV was detected.

Fig. 2 shows the spectra recorded under uniaxial compressions along the $\langle 001 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ axes. The energies of the stress-split components are shown as functions of the applied stress in Fig. 3. When detecting the luminescence from a resonantly excited defect, the observed stress-splitting pattern should depend on the experimental geometry [18]. However, in these experiments using small specimens it was not feasible to mask the crystals so as to closely define the optical geometry without seriously decreasing the already small signal. The polarisation of the spectra we recorded were very similar to those reported in the earlier absorption measurements [13].

3 — ANALYSIS OF THE EXPERIMENTAL DATA

The exact form of the spectrum near 3.3 eV is sample dependent. In particular, the broad line near 3.32 eV shown in the sample for $\langle 001 \rangle$ and $\langle 110 \rangle$ stresses (figure 2) is independent of the H3 centre: it is associated with the similar «H4» centre [14]. Allowing for these independent lines there are still many transitions in figure 1 occurring at the same centre. The 3.344 eV line has been correlated with the 3.361 eV line [13]. Other transitions at 3.310 and 3.373 eV, and the doublet at 3.403 eV always appeared in our samples in very similar strengths relative to the 3.361 eV line. Further evidence that the 3.310, 3.344, 3.361 and 3.403 eV lines occur at the same centre comes from what appear to be their one-phonon sidebands, all involving a well-defined phonon peak energy 159 ± 0.7 meV. The assigned one-phonon (and in some cases two-phonon) sidebands are linked to their zero-phonon lines in figure 1. The different intensities of the one-phonon sidebands relative to the zero-phonon lines will be discussed in § 4.

The presence of all these closely spaced transitions creates problems in interpreting the uniaxial stress data. Stress induced interactions must be expected to occur producing shifts that are non-linear functions of the applied stress. In addition some of the

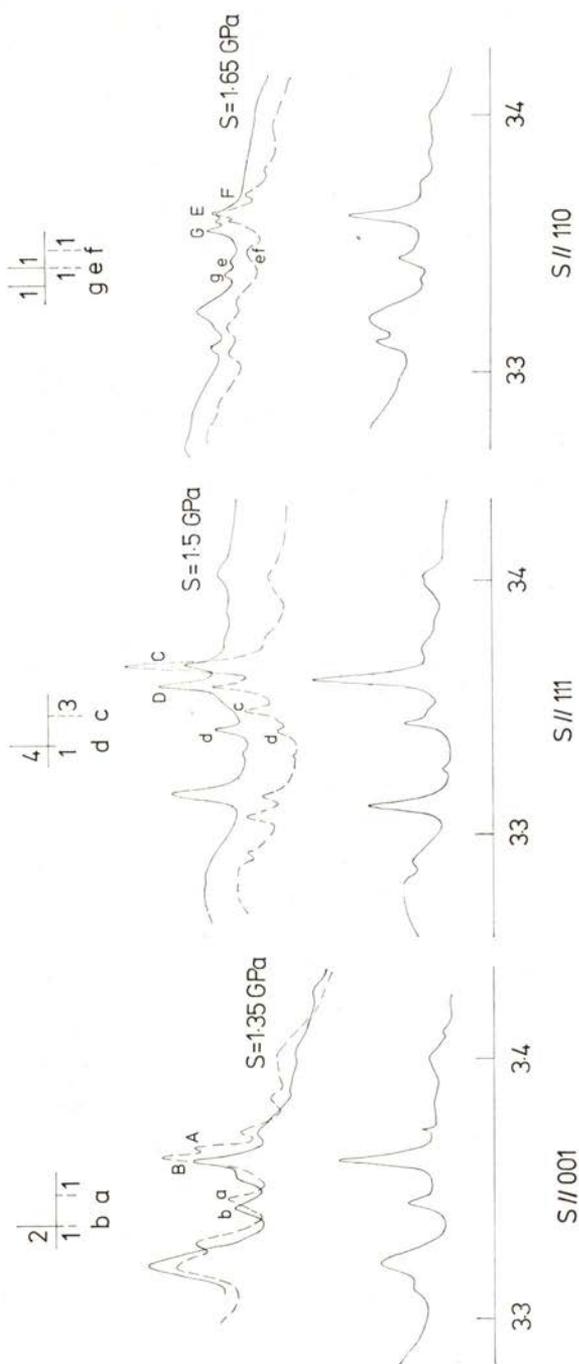


Fig. 2 — Effect of uniaxial stresses on the luminescence excitation spectrum in the H13 region. For each stress axis, the bottom spectrum was recorded at zero stress. The two upper spectra were recorded at the indicated stresses — the solid line is for the exciting light polarised parallel to the stress axis and the broken line is for exciting light polarised perpendicular to the stress axis. For [110] stress the perpendicular polarisation has its electric vector parallel to [110]. All spectra were recorded at liquid nitrogen temperature. The spike spectra show the predicted splitting patterns for the transition at a rhombic I centre, as discussed in § 3.

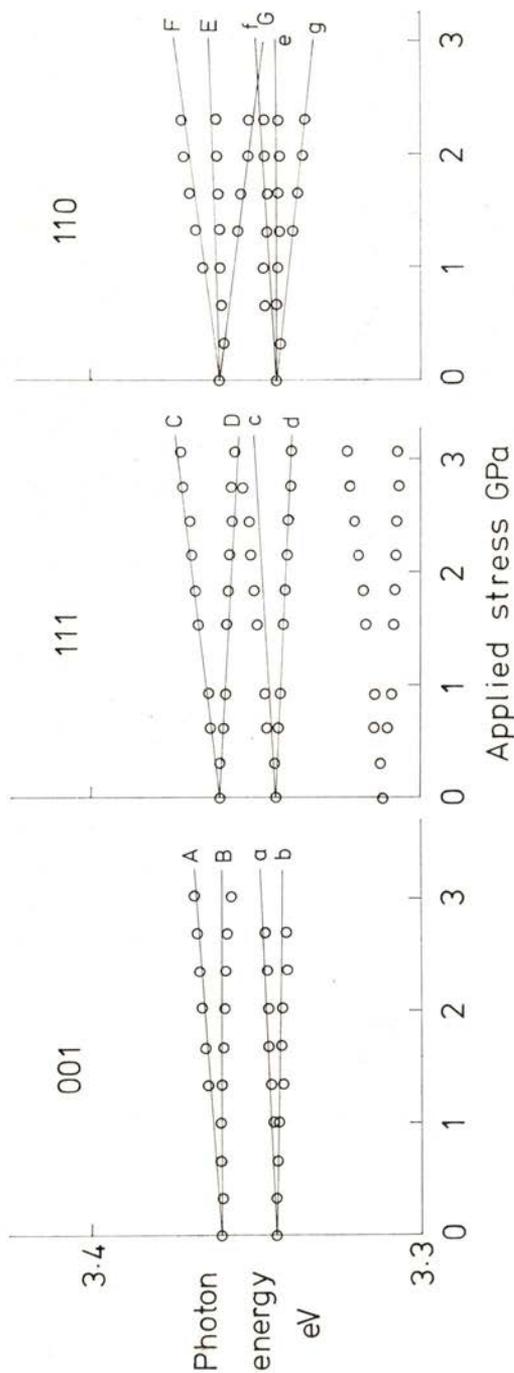


Fig. 3—The energies of the stress-split components from the 3.344 and 3.361 eV lines as a function of stress. The points are experimental data recorded at liquid nitrogen temperature. The solid lines are calculated as in § 3 using first order theory only. The 3.310 eV H3-associated line is only clearly resolved in our data for [111] stress: in this case the shift rates appear to be similar to those of the 3.344 and 3.361 eV lines.

(non-interacting) components become superimposed with increasing stress (e. g. components C and D on figure 2). The widths of the lines (~ 4 meV at zero stress and low temperature) are sufficiently large compared to some of the large separations of the lines that a fully detailed analysis is not feasible.

The effects of stresses in all three stress directions are clearest for the 3.344 eV line. This splits into the number of components with the polarisations and relative intensities only as expected for a transition at a C_{2v} centre (see insets to figure 2 and reference [15]) or an A to E transition at a tetragonal centre [16, 17]. The latter assignment requires the E state not to split under stress; the simplest assignment is that the 3.344 eV line occurs in the same C_{2v} symmetry as the 2.463 eV line of the centre.

Under uniaxial stress, a transition at a C_{2v} centre oriented with its C_2 axis along the [001] crystal axis is perturbed *to first order* in the stress tensor components by [15]:

$$\Delta(h\nu) = A_1 s_{zz} + A_2(s_{xx} + s_{yy}) + A_3 s_{xy} \quad (1)$$

where the s_{ij} are defined with respect to the crystal axes x, y, z . By "first order perturbation" we mean that the stress is sufficiently small that there is negligible stress-induced mixing of the states involved in the transition with any other state of the centre.

Under $\langle 001 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ the energy dependence of each stress-split component is given in terms of the unknown "stress parameters" A_1 , A_2 and A_3 as shown in Table 1. The unweighted least squares fit of the theoretical shift rates to the observed shift rates (denoted a for line a etc.) is obtained when A_1 and A_2 satisfy

$$25A_1 + 149A_2 = 36b + 24(c+d) + 36(f+g) + 18e$$

and

$$53A_1 + 25A_2 = 36a + 12(c+d) + 18e,$$

and when

$$26A_3 = 6(d-c) + 9(g-f).$$

The least squares fit is shown by the lines on figure 3, using the parameters listed in Table 1. The fit appears to be plausible.

TABLE 1

a) Comparison of the experimental and theoretical shift rates for the 3.344 and 3.361 eV lines.

Stress axis	Linear shift rates	Shift rates (meV / GPa)					
		3.344 eV			3.361 eV		
		Compt	Expt	Fit	Compt	Expt	Fit
001	A_1	a	1.1	1.4	A	2.7	2.5
	A_2	b	-1.2	-0.7	B	-0.8	0.1
111	$1/3 (A_1 + 2A_2 - 2A_3)$	c	3.6	2.1	C	4.0	4.1
	$1/3 (A_1 + 2A_2 + 2A_3)$	d	-1.6	-2.0	D	-1.5	-2.2
110	$1/2 (A_1 + A_2)$	e	-0.2	0.4	E	0.6	1.3
	$A_2 - A_3$	f	1.8	2.4	F	5.6	4.9
	$A_2 + A_3$	g	-3.6	-3.7	G	-4.4	-4.6

 Typical uncertainties are ± 0.3 meV / GPa.

b) Stress parameters used in the fit (meV / GPa).

Line (eV)	A_1	A_2	A_3
3.344	1.5	-3.1	-0.7
3.361	2.5	-4.7	0.1
2.463 (H3)	-8.7	6.9	6.7

The uncertainties in the parameters for the 3.344 and 3.361 eV lines are $\sim \pm 0.2$ meV / GPa. This large uncertainty is caused by the relatively small perturbations of the closely spaced lines.

From the polarisation of the stress-split components, the 3.344 eV line occurs from a ground state whose irreducible representation in the C_{2v} point group is A_1 to the excited B_1 state, or any other transition which can occur under a $\langle 110 \rangle$

electric dipole moment. (A complete tabulation of equivalent transitions is given in reference [12]). Since the 3.344 eV transition occurs from the same ground state as the 2.463 eV line, which we will assume for definiteness is an A_1 state, there are only two possibilities for the excited state of the 3.344 eV line, B_1 or B_2 , which are consistent with our stress data.

The 3.361 eV line behaves in a similar way to the 3.344 eV line (figures 2 and 3). The main difference is that the stress-split components of the 3.361 eV line are not polarised as fully as expected for an isolated A_1 to B_1 transition. For example, under $\langle 111 \rangle$ stress component C is not fully polarised with its electric vector perpendicular to the stress axis. Possibly this is an effect of the nearby 3.373 eV line, whose stress-split components overlap (and probably interact with) those of the 3.361 eV line. We cannot separate these effects in the experimental data. However, in the limit of large stress, similar states which interact weakly with each other split with shift rates equal to the non-interacting states. We have therefore fitted the theory of equation (1) to the 3.361 eV line. The shift rates are shown in figure 3. There is a plausible fit to the experimental data using the stress parameters listed in table 1. These parameters are very similar to those of the 3.344 eV line, also listed in the table. In the most clearly resolved spectra, taken under $\langle 111 \rangle$ stress, the H3-related line near 3.31 eV also appears to split with a similar shift rate to the 3.344 and 3.361 eV lines (figure 3).

We have shown that the 3.344 and 3.361 eV transitions occur at a C_{2v} symmetry, the same as for the lower energy 2.463 eV line. The earlier assignment of the 3.344 and 3.361 eV lines to a trigonal centre [13] arose through misinterpreting the complex experimental data resulting from the many, nearly degenerate, excited states of the centre.

4 — VIBRONIC COUPLING

We have shown that the symmetry of the «H3» defect is the same in the «H13» excited states (near 3.36 eV) as in the «H3» excited states (at 2.463 eV). However, the stress parameters show that substantial relaxations occur between the H3 and H13 states. The stress parameters of table 1 only give the

difference in perturbation of the excited and ground zero-phonon states (equation 1). The differences between H13 and H3 are of the same order as the H3 parameters (last line, table 1). Evidently the electronic orbitals in the 2.463 eV and 3.361 eV excited states are both still sufficiently localised that the electron-lattice coupling is strongly dependent on the electronic state. It follows that these compact electronic orbitals may interact with each other vibronically as the atoms of the defect vibrate.

As an example of the vibronic coupling we consider the 3.344, 3.361 eV pair of zero-phonon lines. These lines are observed in the intensity ratio (figure 1):

$$I_{3.344} / I_{3.361} \approx 0.2 .$$

Their one phonon sidebands involving the 159 meV phonons are very weak, but are almost equal in intensity. This difference does not arise from different electron-lattice interaction of the two electronic states, for their stress parameters are closely similar (table 1). A more likely cause is that the 3.344 and 3.361 eV states are interacting vibronically, the interaction transferring intensity from the 3.361 eV zero-phonon line to the one-phonon sideband of the 3.344 eV line. The amount of the intensity transferred is about 0.1 of the intensity of the 3.361 eV line, assuming that in the absence of the interaction the one-phonon sidebands of the 3.344 and 3.361 eV lines would have had intensities in proportion to the zero-phonon lines.

For a quantitative discussion we denote the electronic excited state of the 3.344 eV line by $\phi_1(r)$, and that of the 3.361 eV line by $\phi_2(r)$, where r represents all the electronic co-ordinates. The harmonic oscillator wave-functions for the n th quantum level of the 159 meV mode is denoted $\chi_n(Q)$, where Q is the mode's coordinate. Since the 3.344 and 3.361 eV lines have similar stress parameters (table 1) we will assume that the equilibrium values of Q for these two states are the same. Then, in the absence of any vibronic interaction, the vibronic wavefunctions and energies for the two states are simply

$$\begin{aligned} \psi_{1,n}(r, Q) &= \phi_1(r) \chi_n(Q), \quad E = W_1 + (n + 1/2) \hbar \omega \\ \psi_{2,n}(r, Q) &= \phi_2(r) \chi_n(Q), \quad E = W_2 + (n + 1/2) \hbar \omega \end{aligned}$$

where W_1 and W_2 are the energies of the two electronic states.

We now introduce a vibronic coupling perturbation energy

$$C = c Q . \quad (2)$$

Here c is an electronic operator with a matrix element

$$C = \int dr \phi_1 (r) c \phi_2 (r) \quad (3)$$

between the two states. This perturbation couples vibronic states differing by one in the quantum number:

$$\begin{aligned} \int dr dQ \psi_{1,n} c Q \psi_{2,n+1} &= C (\hbar / m\omega)^{1/2} \sqrt{(n+1)/2} \\ \int dr dQ \psi_{1,n-1} c Q \psi_{2,n} &= C (\hbar / m\omega)^{1/2} \sqrt{n/2} \end{aligned} \quad (4)$$

This coupling mixes the $\psi_{1,n}$ and $\psi_{2,n}$ to form new vibronic states

$$\psi_p (r, Q) = \sum_n a_{pn} \psi_{1,n} (r, Q) + \sum_n b_{pn} \psi_{2,n} (r, Q)$$

The coefficients a_{np} , b_{pn} are given by the secular matrix whose elements are as given in equation (4), in terms of the unknown $C (\hbar / m\omega)^{1/2}$ and

$$W_2 - W_1 \simeq 17 \text{ meV} .$$

From the coefficients the transition probability to the p th vibronic level is

$$T_p = (t_1 a_{p0} + t_2 b_{p0})^2 \quad (5)$$

where from the measured zero phonon intensities

$$(t_1 / t_2)^2 = 0.2 .$$

Numerical diagonalisation shows that 0.1 of the 3.361 eV absorption would be transferred to the one-phonon sideband of the 3.344 eV line when

$$C (\hbar / m\omega)^{1/2} \simeq 50 \text{ meV} \quad (6)$$

with about a $\pm 20\%$ uncertainty.

To give this interaction energy some physical meaning we can compare it to the stress parameters of table 1. From equations (2) and (3), C is the interaction energy between ϕ_1 and ϕ_2 for a unit displacement in Q . Multiplying C by a bond length in diamond, $a_0 = 0.154$ nm, gives the interaction energy per unit strain in the crystal. Division by an appropriate elastic constant e for diamond then gives an interaction energy per unit stress. The choice of elastic constant depends on the mode of vibration (e.g. whether it is a shearing mode or produces compressions on any particular axis). The type of mode is not known. We will use a simple mean of the elastic constants C_{11} , C_{12} and C_{44} with the value $e \approx 600$ GPa per unit strain. Using the mass of one carbon atom for m and $\hbar\omega = 159$ meV, from equation (6) the interaction energy per unit stress is

$$C_s = Ca_0 / e \approx 2.7 \text{ meV / GPa} .$$

This is within the range of the stress parameters for the H3 centre (table 1). The interaction will lead to stress-induced mixing of the 3.344 and 3.361 eV lines in the stress experiments. On figure 3 the stress-split components of the 3.344 eV line move almost parallel to the components of the 3.361 eV line they are interacting with, reducing the effects of the interaction. At 2 GPa, two states 17 meV apart interacting through C_s would have their energies changed by ~ 1.6 meV as a result of their mutual repulsion: an effect less than the width of the 3.344 and 3.361 eV lines. The repulsion would be primarily seen as an apparent change of slope of the stress-split components and probably accounts for some of the deviations between experiment and theory on figure 3.

The same idea of vibronic coupling can be used to explain the unusual peak at 3.28 eV in figure 1, which is associated with the H3 centre [11]. The 3.28 eV line has an integrated intensity of the order of 10^{-2} of the intensity of the H3 vibronic band. The 3.28 eV line is very wide, 43 meV at low temperature, over ten times wider than typical zero-phonon lines in diamond. We suggest that it is the one-phonon sideband of a forbidden transition at the H3 centre; the line is observed through vibronic mixing with the H3 band. We assume (and we will support this below) that the phonon mode has again $\hbar\omega = 159$ meV. The energy of

the forbidden zero-phonon line producing the 3.28 eV line is therefore ~ 3.12 eV, ~ 470 meV higher than the centroid of the H3 band. Repeating the vibronic calculations with

$$W_2 - W_1 = 470 \text{ meV,}$$

and with the transition probabilities $t_1 = 1$, $t_2 = 0$ in equation (5), we find that 10^{-2} of the absorption would be transferred to the 3.28 eV line when the vibronic interaction term

$$C (h/m\omega)^{1/2} \simeq 160 \text{ meV}$$

(see figure 4). The resulting stress parameter $C_s \simeq 8.6$ meV / GPa is still within the range observed at the H3 centre (table 1).

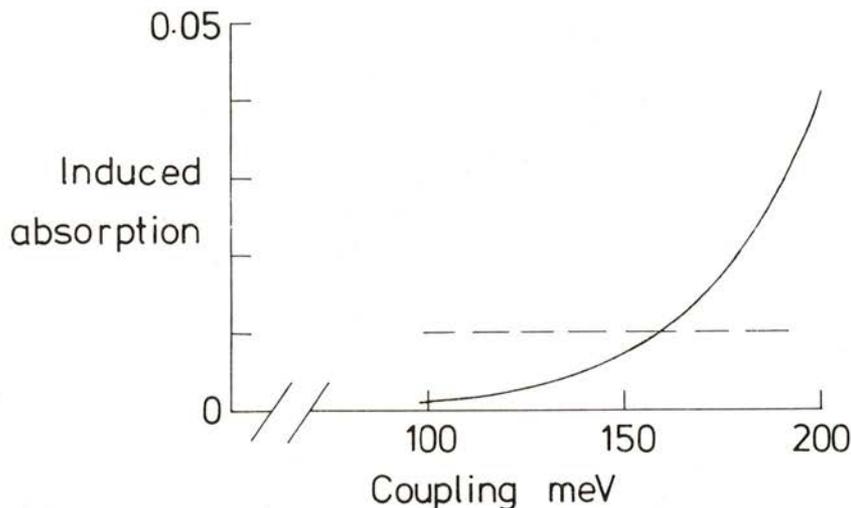


Fig. 4 — The solid line shows the calculated fraction of the absorption transferred from an allowed to a forbidden transition when the excited states of the allowed and forbidden lines are separated by 470 eV. The broken line shows the experimental value for the 3.28 eV H3-associated line relative to the H3 band; this value is obtained at a vibronic coupling (defined in § 4) of 160 meV, equivalent to a typical stress parameter for the H3 centre.

The same mechanism can explain the 3.32 eV H4 associated line seen on figure 2. This line again is 10^{-2} of the H4 band, and

again its electronic state lies ~ 460 meV above the centroid of the allowed (H4) band. In this case a further peak, ~ 150 meV above the 3.32 eV line, can be resolved in favourable samples [14]; this is interpreted as the two-phonon sideband of the forbidden line, giving direct evidence for a mode quantum $\hbar\omega \sim 150$ to 160 meV.

Paul Spear (private communication 1983) has shown that the 3.32 eV line is a transition at a monoclinic I centre, the same symmetry as the H4 centre, as would be expected in this model.

Vibronic interactions between states separated by considerable energies are clearly possible in diamond, producing the features like the 3.28 eV line. Vibronic interactions like these can occur essentially because the amplitudes of the vibrations are equivalent to considerable strains. For example, a 159 meV mode involving one vibrating carbon atom has a root mean square amplitude in its zero-point ($n=0$) motion of

$$[\langle Q^2 \rangle]^{1/2} = (\hbar / m\omega)^{1/2} = 3.3 \times 10^{-12} \text{ m}$$

This is equivalent to a 2 % strain of a 0.154 nm bond length, very large compared with the 0.3 % strains typical in uniaxial stress experiments.

5 — SUMMARY

We have shown that the excited states of the H3 centre, giving transitions near 3.35 eV, occur at a C_{2v} centre, the same symmetry as the basic 2.463 eV H3 transition. Nevertheless substantial differences occur in the response to stresses of the different excited states of the H3 centre. These lead to vibronic coupling, modifying the form of the optical spectra. In particular, isolated broad lines may occur, as observed in the experimental spectra, as a result of the vibronic coupling. Measurable bands may be induced even when the forbidden line is several hundred meV distant from the allowed line. We have suggested that this is the origin of the broad 3.28 eV line associated with the H3 centre. With this assignment, a phenomenological explanation has

now been given for all the H3-associated lines observed in the visible and ultra-violet spectra of irradiated and annealed diamond.

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