EFFECTS OF UNIAXIAL STRESS ON THE 27084 cm^{-1} AND 26942 cm^{-1} ABSORPTION LINES IN DIAMOND

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ABSTRACT — This note reports uniaxial stress measurements on the 27084 cm^{-1} and 26942 cm^{-1} zero phonon absorption lines in type I_a diamond. The centre where these transitions occur is shown to be trigonal.

1 — INTRODUCTION

The absorption line at 27084 cm^{-1} (Fig. 1) was first reported by Clark et al [1] in irradiated and annealed type I_a diamond and afterwards named H_{13}. According to Clark and Norris [2] this transition could occur at the H_3 defect.

During the present study it was observed that the H_{13} absorption band was present both in natural and treated type I_a diamond and was not detected in type II_a diamond.

The occurrence of the band in natural specimens is enough to cast some doubt about its origin being at the H_3 defect. We know now that the H_3 defect is produced when a radiation damage defect is trapped at the A centre and has a C_{2v} point group (Davies et al [3]), although we must point out that even the H_3 centre has been detected in natural I_{aA} diamonds and thought to have been produced through a process of natural irradiation and annealing. However the H_{13} band can not have its origin at the H_3 defect, since, as it is shown in the following sections, it occurs at a centre with trigonal symmetry, while the H_3 defect has a rhombic I symmetry. (Davies et al [3]).

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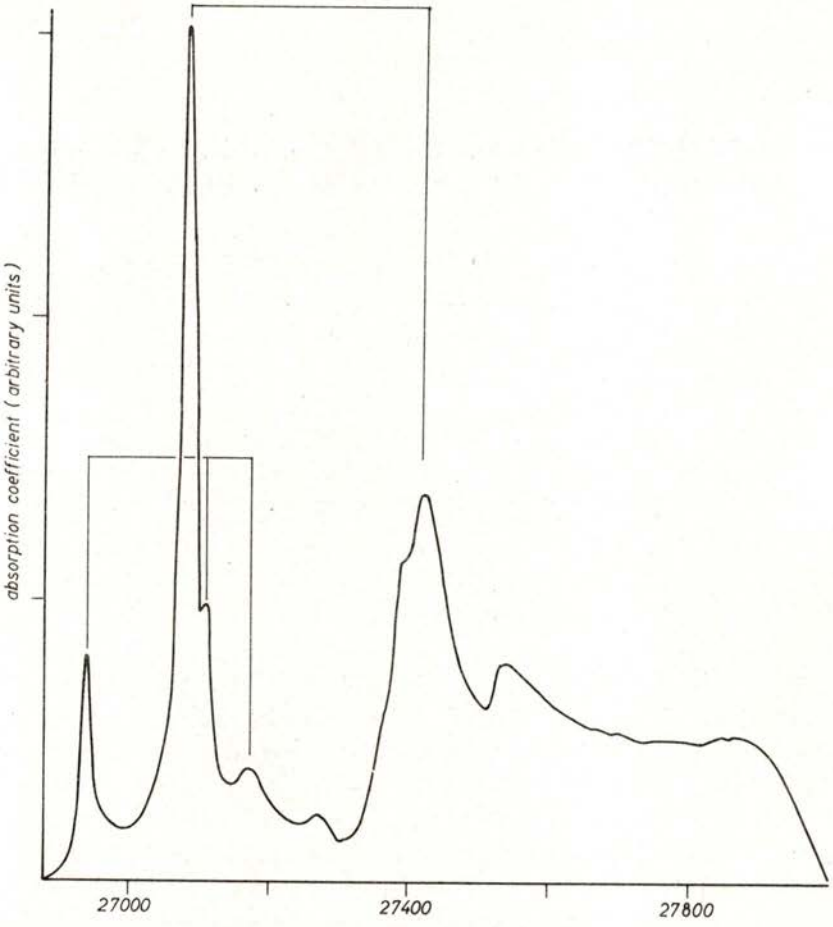

Fig. 1 — The H_{13} absorption spectrum at liquid nitrogen temperature in a type I_a diamond, after electron-irradiation and annealing. Features connected by lines are the 26942 cm^{-1} zero-phonon line and one-phonon band with $\hbar\omega \sim 170$ cm^{-1} and $\hbar\omega \sim 230$ cm^{-1}, and the 27084 cm^{-1} zero-phonon line and one-phonon band with $\hbar\omega \sim 350$ cm^{-1}.

2 — EXPERIMENTAL DETAILS

In the study of the 27084 cm^{-1} and the 26942 cm^{-1} absorption lines a set of seven samples was used. All of them were natural I_a diamond. Uniaxial stress measurements have been made at liquid nitrogen temperature. In all cases a Spex 1704

monochromator fitted with a 1200 lines mm^{-1} grating was used. Light from a 150 W Xe arc lamp was polarized by a calcite prism and detected by an R C A C31034 photomultiplier.

3 — RESULTS AND DISCUSSION

3.1 — *The H_{13} absorption band*

The H_{13} absorption band is shown in Fig. 1. The widths, spacings and splitting patterns under uniaxial stress suggest that the lines at 26942 cm^{-1} and 27084 cm^{-1} are zero-phonon lines. It is apparent from Fig. 1 that the zero-phonon line at 26942 cm^{-1} is replicated by its one phonon-side band of $\hbar\omega \sim 170$ cm^{-1} and $\hbar\omega \sim 230$ cm^{-1} while the zero phonon line at 27084 cm^{-1} is replicated by the one phonon side band of $\hbar\omega \sim 350$ cm^{-1}.

During the present study we measured the integrated strength of the two zero-phonon lines at 77 K and observed that a correlation could be established in a set of seven diamonds (Fig. 2a).

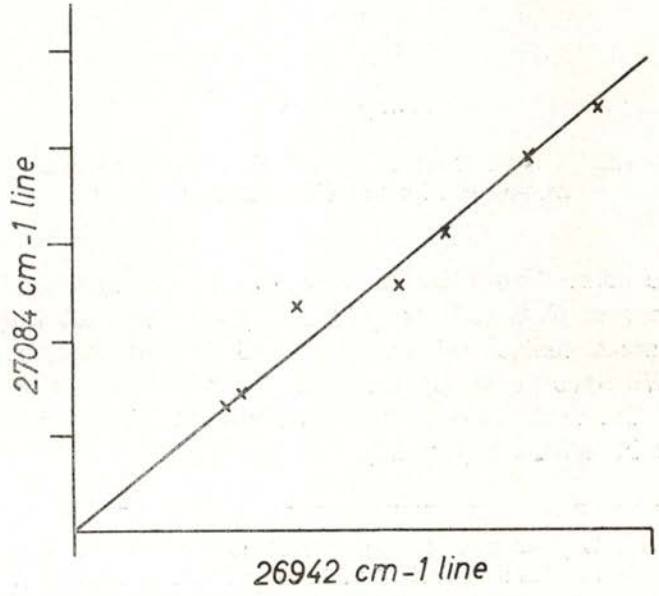

Fig. 2 a — Correlation of the intensities of the 27084 cm^{-1} and 26942 cm^{-1} zero-phonon lines in seven specimens, all of them natural I_a diamond; data taken at 77 K. Notice the different scales used for the two line intensities.

All the specimens were natural I_a diamond; two of them had been irradiated at room temperature with 2 Mev electrons and then annealed at 800°C for about 30 minutes. The H_{13} absorption band was not detected in type II_a diamond.

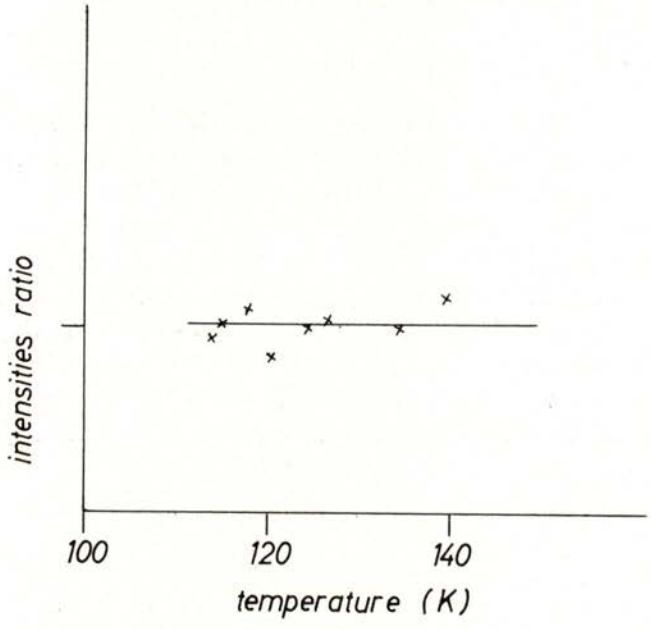

Fig. 2 b — Ratio between the intensities of the 27084 cm^{-1} and 26942 cm^{-1} zero-phonon lines at different temperatures.

The correlation together with the energy spacing between the two zero-phonon lines (142 cm^{-1}) suggest that they occur at the same centre and are originated from a common ground state. We have measured the strengths of the two zero-phonon lines at different temperatures, all above 77 K, and found their ratio to be constant (Fig. 2b).

Fig. 3 — Effects of uniaxial stress on the 26942 cm^{-1} and 27084 cm^{-1} zero-phonon lines. Spectra measured at 77 K for a stress of 1.6 GPa. The spikes show the theoretical results for an E to A_1 transition with the π spectra shown above and the σ below the horizontal line. In 3 a and 3 b (facing page) spectra shown by full and broken curves are measured with electric vector of light parallel (π) and perpendicular (σ) to the stress axis, respectively.

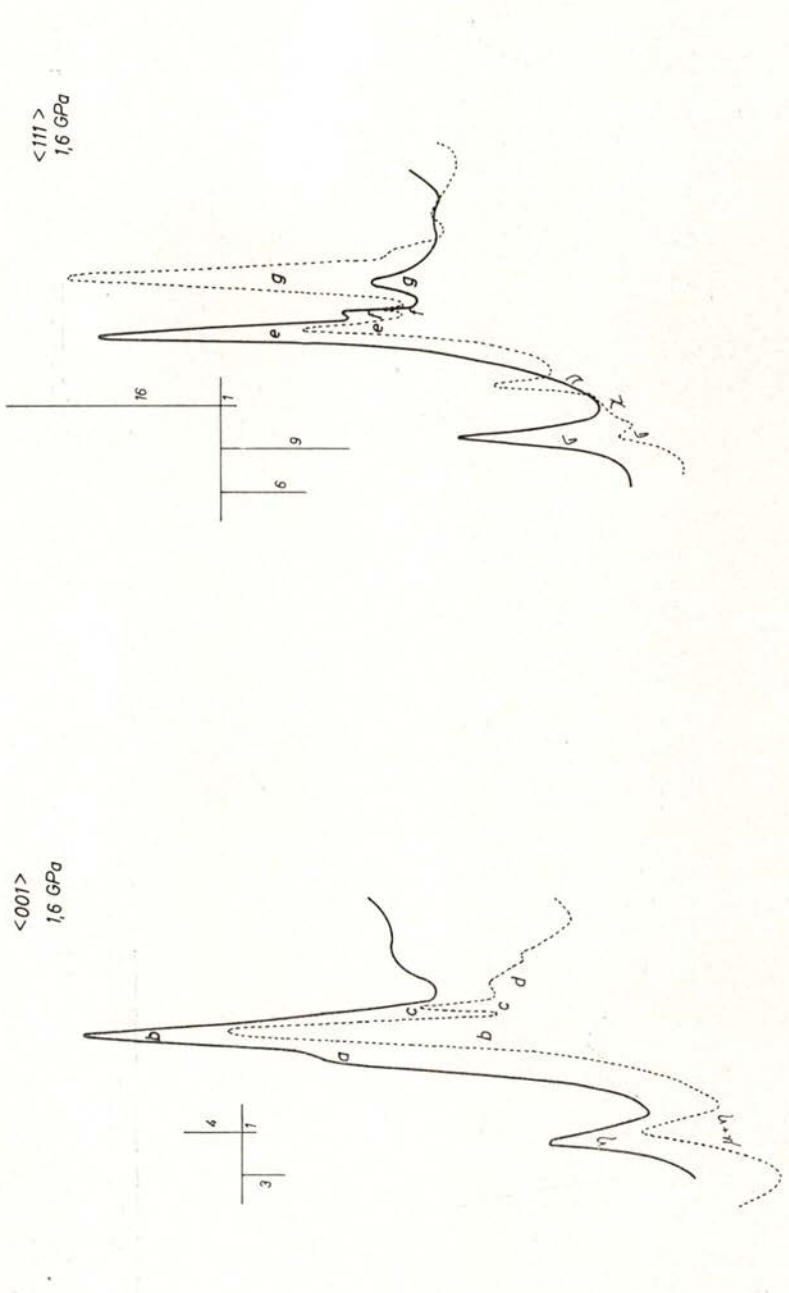

Fig. 3 a) and b) — Effects of uniaxial compression along <001> and <111> (for detailed caption see facing page).

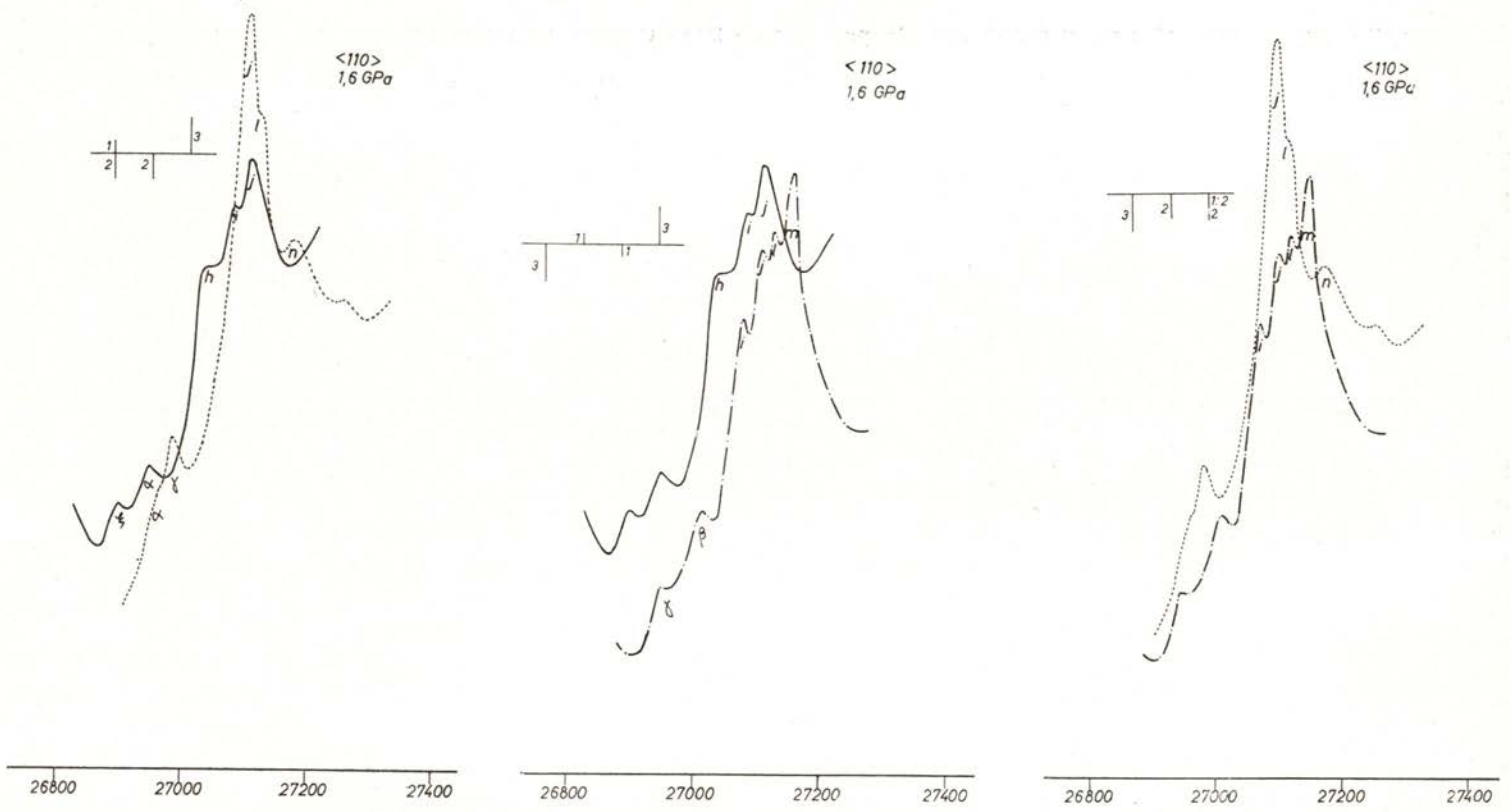

Fig. 3 c), d) and e) — Uniaxial compression along $<110>$. Full curves π; broken curves σ_{001}; chain curves $\sigma_{1\bar{1}0}$.

3.2 — *Uniaxial stress data*

Uniaxial stress of up to 2 GPa have been applied along <001>, <111> and <110> crystallographic directions; absorption measurements have been taken at 77 K. Typical spectra are given in Fig. 3. The energy of the stress split components as a function of applied stress is given in Fig. 4. We consider first the line at 26942 cm^{-1}. At higher stresses the intensities of the absorption components vary with stress. The energies of several of stress split components are seen to vary non-linearly with stress (Fig. 4). The intensities of many of the stress split components of the 27084 cm^{-1} line are also stress dependent.

3.3 — *Phenomenological interpretation of the data*

At low stress the 26942 cm^{-1} line splits in the way characteristic of an electric dipole transition between an E and an A_1 (or A_2) state at a trigonal centre (Kaplyanskii [4], [5]). The intensity variations are consistent with thermalisation among the components of the E state, identifying it as the ground state. This is confirmed by the satisfactory agreement between Kaplyanskii's first order perturbation theory and the experimental results for the stress split components, there being four arbitrary parameters in the theory (Table 1; Fig. 3).

The line at 27084 cm^{-1} in spite of being about 5 times stronger than the 26942 cm^{-1} line is not so easy to analise. Its stress splitting is inconsistent with any of the cases tabulated by Kaplyanskii [4], [5] and by Hughes and Runciman [6] and can only be understood if the transition occurs at a trigonal centre between two double degenerate levels (Davies and Nazaré [7]). Given the large number of predicted transitions and the thermalisation effects in the split ground state not all the stress split components are observed (Fig. 3, Table 2). This tentative assignment is supported by the fact that transitions at 26942 cm^{-1} and 27084 cm^{-1} correlate in strengh (Fig. 2; 3.1) and that the 26942 cm^{-1} zero-phonon transition occurs at a trigonal centre.

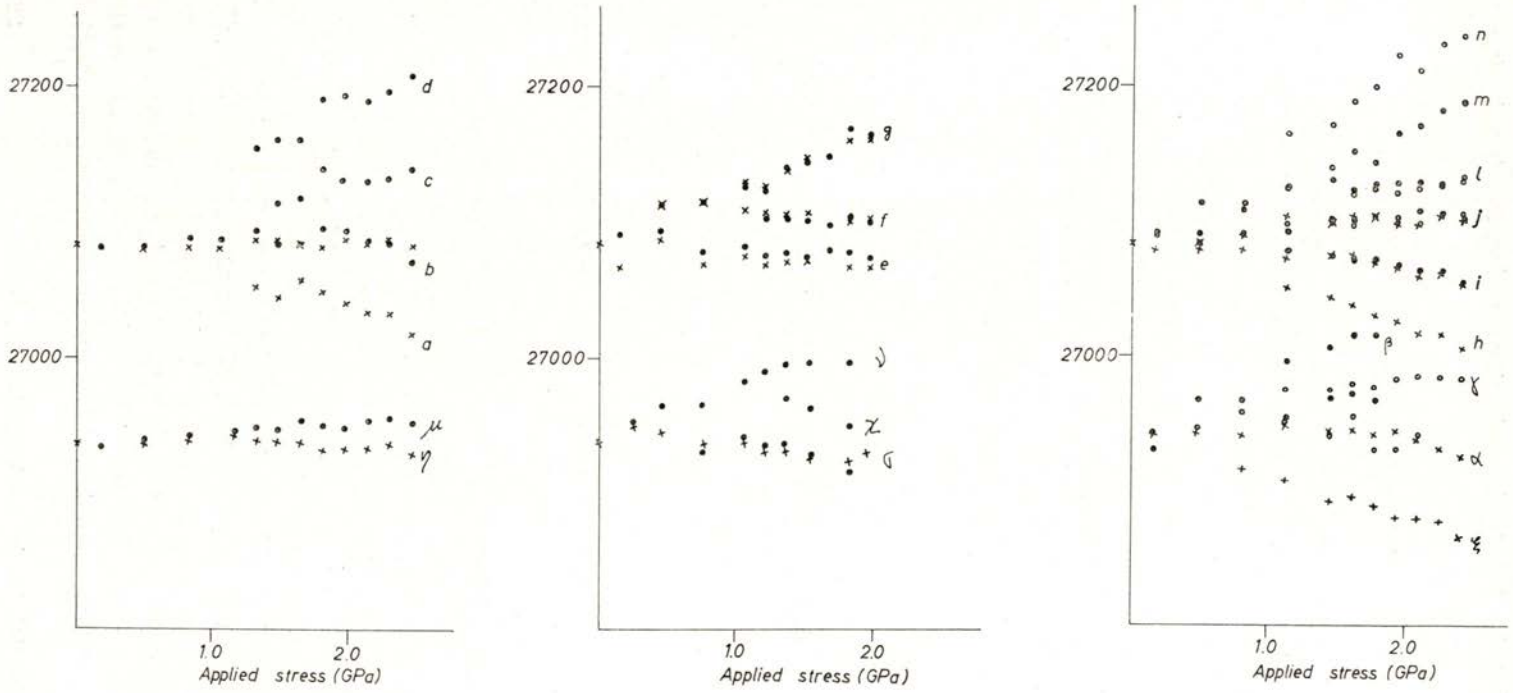

Fig. 4 — Energies of the stress split components of the 26942 cm^{-1} and 27084 cm^{-1} zero-phonon lines as functions of applied stress at 77 K. a) <001>, b) <111> and c) <110> compressions. Experimental data are shown by crosses for π polarization and by dots for σ polarization. Under <110> compression σ_{001} data are shown by open circles, and $\sigma_{1\bar{1}0}$ data by full circles.

TABLE 1 — Effect of uniaxial stress on the 26942 cm^{-1} line

Stress axis	Line	Initial state	Shift rate		
			Experiment	Theory (1)	Best fit (2)
<001>	η	Θ	0	$A_1 - 2/3\,B - 2\sqrt{2}/3\,C$	4
	μ	ε	8	$A_1 + 2/3\,B + 2\sqrt{2}/3\,C$	10
	α	Θ	2	$A_1 + 1/2\,A_2 - 1/3\,B + 2\sqrt{2}/3\,C$	6
	β	ε	40	$A_1 + 1/2\,A_2 + 1/3\,B - 2\sqrt{2}/3\,C$	35
<110>	γ	Θ	20	$A_1 - 1/2\,A_2 + B$	12
	ξ	ε	−30	$A_1 - 1/2\,A_2 - B$	−24
	ν	$\left\{ \begin{matrix} \Theta \\ \varepsilon \end{matrix} \right\}$	34	$A_1 + A_2$	34
<111>	χ	ε	17	$A_1 - 1/3\,A_2 + 8/9\,B - 4\sqrt{2}/9\,C$	19
	σ	Θ	−10	$A_1 - 1/3\,A_2 - 8/9\,B + 4\sqrt{2}/9\,C$	−22

(1) The differences between the perturbations to the energies of the ground and excited states are shown in terms of the stress parameters, A_1, A_2, B and C. Kaplyanskii's notation is obtained from the one used in this table through the transformations: $A_1 \rightarrow A_1$; $A_2 \rightarrow 2\,A_2$; $B \rightarrow 3\,(B+C)/4$; $C \rightarrow 3\,(B-C)/2\sqrt{2}$

(2) Stress parameters used (units $cm^{-1}\ GPa^{-1}$): $A_1 = 7.25$, $A_2 = 26.48$, $B = 17.67$, $C = -9.22$.

In view of the present data it is highly probable that the two zero-phonon absorption lines at 26942 cm^{-1} and 27084 cm^{-1} are electric dipole transitions occuring at the same trigonal centre from the same double degenerate ground state into an A_1 (or A_2) and E excited states respectively. In this case it is evident that under large stresses the intensities of the lines are stress dependent not only through termalisation but also through interaction of neighbour states. That interaction is also responsible for the non-linearity of the shift rates of some of the stress split components.

TABLE 2 — The effect of uniaxial stress on a E to E transition at a trigonal centre according to Davies and Nazaré [7].

Stress axis	Initial state	Final state	Shift rate (1)
<001>	Θ	Θ	$A'_1 + 2/3\, B_1 + 2\sqrt{2}/3\, C_1$
	Θ	ε	$A'_1 - 2/3\, B_2 - 2\sqrt{2}/3\, C_2$
	ε	Θ	$A'_1 + 2/3\, B_2 + 2\sqrt{2}/3\, C_2$
	ε	ε	$A'_1 - 2/3\, B_1 - 2\sqrt{2}/3\, C_1$
<111>	$\left\{ \begin{matrix} \Theta \\ \varepsilon \end{matrix} \right\}$	$\left\{ \begin{matrix} \Theta \\ \varepsilon \end{matrix} \right\}$	$A'_1 + A'_2$
	Θ	Θ	$A'_1 - 1/3\, A'_2 + 4/9\, B_1 - 4\sqrt{2}/9\, C_1$
	Θ	ε	$A'_1 - 1/3\, A'_2 - 4/9\, B_2 + 4\sqrt{2}/9\, C_2$
	ε	Θ	$A'_1 - 1/3\, A'_2 + 4/9\, B_2 - 4\sqrt{2}/9\, C_2$
	ε	ε	$A'_1 - 1/3\, A'_2 - 4/9\, B_1 + 4\sqrt{2}/9\, C_1$
<110>	Θ	Θ	$A'_1 + 1/2\, A'_2 + 1/3\, B_1 - 2\sqrt{2}/3\, C_1$
	Θ	ε	$A'_1 + 1/2\, A'_2 - 1/3\, B_2 + 2\sqrt{2}/3\, C_2$
	ε	ε	$A'_1 + 1/2\, A'_2 - 1/3\, B_1 + 2\sqrt{2}/3\, C_1$
	ε	Θ	$A'_1 + 1/2\, A'_2 + 1/3\, B_2 - 2\sqrt{2}/3\, C_2$
	Θ	Θ	$A'_1 - 1/2\, A'_2 - B_1$
	Θ	ε	$A'_1 - 1/2\, A'_2 + B_2$
	ε	ε	$A'_1 - 1/2\, A'_2 + B_1$
	ε	Θ	$A'_1 - 1/2\, A'_2 - B_2$

(1) The differences between the perturbations to the energies of the ground and excited states are shown in terms of the stress parameters A'_1, A'_2 B_1, B_2, C_1 and C_2. In terms of the basis set $|\Theta>$, $|\varepsilon>$ of an E electronic state the stress parameters are defined as:

$$A'_1 = <\Theta^e|C_{A_1}|\Theta^e> - <\Theta^g|C_{A_1}|\Theta^g>$$

$$A'_2 = <\Theta^e|C'_{A_1}|\Theta^e> - <\Theta^g|C'_{A_1}|\Theta^g>$$

$$B_{1,2} = <\Theta^e|C_{E_\Theta}|\Theta^e> \mp <\Theta^g|C_{E_\Theta}|\Theta^g>$$

$$C_{1,2} = <\Theta^e|C'_{E_\Theta}|\Theta^e> \mp <\Theta^g|C'_{E_\Theta}|\Theta^g>$$

The C_{A_1}, C'_{A_1}, C_{E_Θ} and C'_{E_Θ} are electronic operators transforming as A_1 and E_Θ; the superscripts g and e label the ground and excited state.

4 — SUMMARY AND SUGGESTIONS FOR FURTHER WORK

Uniaxial stress measurements have suggested that the transitions at 26942 cm^{-1} and 27084 cm^{-1} occur at a centre with trigonal symmetry, both from a common ground state. However, this is a tentative interpretation of the data, and it clearly requires further work namely on luminescence and uniaxial stress at liquid helium temperature. A detailed discussion of the vibronic system in Fig. 1 will be given later.

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