DECAY TIMES OF LUMINESCENCE FROM BROWN DIAMONDS

MARIA ISABEL B. JORGE, MARIA ESTELA PEREIRA, M. F. THOMAZ
Departamento e Centro de Física (INIC)
Universidade de Aveiro, 3800 Aveiro, Portugal

GORDON DAVIES, ALAN T. COLLINS
Wheatstone Physics Laboratory
King's College, Strand, London WC2R 2LS, U. K.

(Received 18 May 1983)

ABSTRACT — Brown diamonds form an appreciable fraction of all natural diamonds. This paper reports the first measurements of the decay times of luminescence from these diamonds. The red luminescence excited by visible light (~ 500 nm wavelength) has a decay time of 6 ns, almost independent of temperature over the range $80 < T < 600$ K. Yellow luminescence (caused by an emission band centred on 540 nm) has a decay time of 6 ns at low temperature, decreasing with increasing temperature as expected for a centre with a thermally activated nonradiative decay. Decay times are also reported for four zero-phonon lines observed in cathodoluminescence. The lines, at 515.8, 500.2, 395.5 and 491 nm have decay times at 80 K of 32.5, 40, 45 and 70 ns respectively.

We also show that the red photoluminescence band may consist, depending on the wavelength of the exciting light, of a series of overlapping vibronic bands which are very similar to each other. This implies the existence of a 'family' of closely related optical centres in these diamonds.

1 — INTRODUCTION

About 2 to 5 % of all gem-quality natural diamonds are brown in colour. Of these 1 to 50 % (depending on the geological source of the sample) emit yellow luminescence when excited by 365 nm Hg radiation (Collins and Mohammed 1982). Despite their common occurrence and the ease with which they may be selected, it is only recently that this class of diamonds has been subjected to spectroscopic studies (Collins and Mohammed 1982, Mohammed et al. 1982). It has been shown that the yellow luminescence arises partly from a vibronic band with its zero-phonon line at 455.5 nm (2.721 eV), and partly from a featureless underlying background (Collins and Mohammed 1982). The absorption spectra of these diamonds apparently always contain a broad absorption band peaking near 480 nm (2.6 eV). Absorption of light in this band produces luminescence in the red part of the spectrum.

The cathodoluminescence spectra of these diamonds are typically as shown in Fig. 1. The cathodoluminescence spectrum consists of a red band (very similar to the red photoluminescence band); luminescence in the yellow region (which is partly made up of the 455.5 nm (2.721 eV) band seen in photoluminescence, but with a strong underlying component); and luminescence peaking in the blue part of the spectrum near 430 nm (2.9 eV). Superimposed on this luminescence are many sharp zero-phonon lines, some of which are labelled A to J in figure 1. This complicated picture has been simplified slightly by recent studies of the effect of uniaxial stresses on the zero-phonon lines. It has been shown that the optical centres producing lines C, D and E at 467.9, 459.2 and 451.1 nm (2.649, 2.699 and 2.748 eV) respectively have rhombic I symmetry, and the centre producing the 2.721 eV line has monoclinic I symmetry; however, these four optical centres are only slightly modified versions of each other (Mohammed et al. 1982). Thus these four optical centres form a "family" of almost identical crystal defects. Similarly line H (386.9 nm, 3.204 eV) which occurs at a trigonal centre, line J (384.5 nm, 3.224 eV) which occurs at a monoclinic I centre, and line F (393.5 nm, 3.150 eV), which occurs at a centre with unknown symmetry, are all produced by a second "family" of very similar optical centres (Mohammed et al. 1982).

To date, luminescence decay times have not been reported for any of the optical transitions listed above. By luminescence decay time we mean the time taken for the luminescence to decay to 1/e of its original value, when the excitation source is switched off. The luminescence decay time is an extremely useful parameter, giving microscopic information about the optical transition. For example, it is directly related to the matrix elements of the luminescence transition when there are no competing de-excitation mechanisms. Non-radiative de-excitation within the optical centre by internal conversion may sometimes be detected from the temperature dependence of the decay time, as at the " N3 " centre in diamond (Thomaz and Davies 1978), while non-radiative de-excitation involving energy transfer from the optical centre to another crystal defect may be identified by the specimen dependence of the decay time, as at the " H3 " centre in diamond (Crossfield et al. 1974).

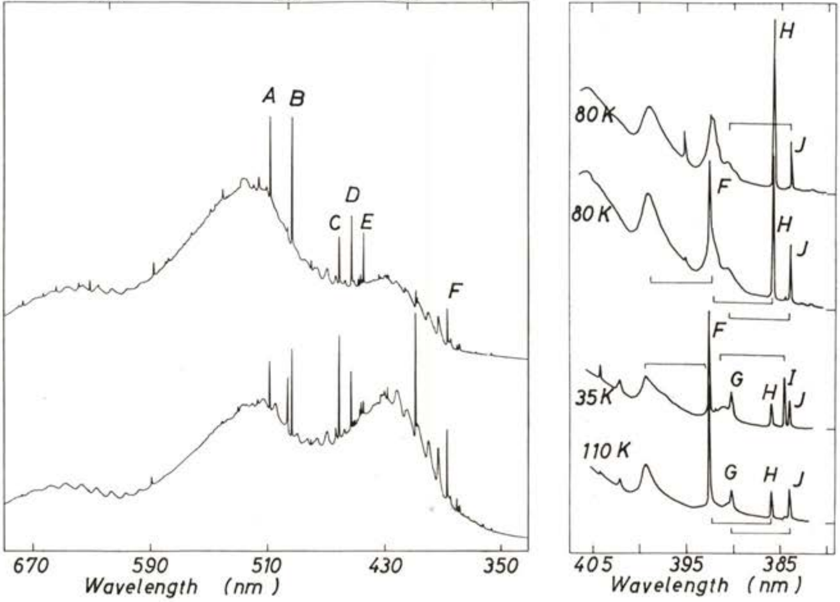


Fig. 1 — At left: Cathodoluminescence spectra of two yellow-photoluminescent brown diamonds, recorded at 77 K using an extended-red-response (RCA 31034A) photomultiplier. The spectra have not been corrected for the wavelength-dependent response of the photomultiplier and spectrometer. At right: Detailed spectra of the I, J, H, F, G lines in two specimens at 80 K and in the same specimen at 35 K and 110 K. The braces link zero-phonon lines and assigned one-phonon sidebands with quanta of 54 meV.

The purpose of this paper is to report the luminescence decay times of some of the transitions observed in the yellow-luminescing brown diamonds. We will also show that the red luminescence can be composed of one band or several overlapping bands, depending on the energy of the exciting radiation. This occurs in a way consistent with there being another "family" of very similar optical centres in these brown diamonds. The experimental data are listed in §3, and briefly discussed in §4. We begin by describing the experimental techniques.

2 — EXPERIMENTAL DETAILS

Photoluminescence was excited by a high pressure xenon arc filtered by a Bausch and Lomb high intensity grating monochromator. Photoluminescence decay time measurements were made using the single photon statistical technique (see, for example, Birch and Imhof 1977). The flashlamp source was a free-running discharge in air at normal pressure or in nitrogen at 2 atmospheres (Thomaz and Barreto 1971), operating at 7 kV at a frequency of ~ 10 kHz. The band of excitation wavelengths was selected using a filter or the Bausch and Lomb monochromator and focussed on to the diamond. The luminescence was collected from the diamond and focussed through a filter on to the photocathode of the photomultiplier. An electrical signal derived from the spark, and the output from the photomultiplier, were connected respectively to the start and stop inputs of a time-to-amplitude converter, the output of which was fed to a multichannel analyser (Fig. 2). Provided that the count rate from the photomultiplier was kept below 100 s^{-1} the data accumulated on the multichannel analyser correctly represented the build-up and decay of the luminescence from sample (Birch and Imhof 1977).

Three different sample mounting arrangements enabled the decay time to be measured with the sample at ~ 77 K, at a range of temperatures between 90 and 300 K, or at a range of temperatures between 300 and 700 K.

The cathodoluminescence equipment operated at 45 kV with beam currents of typically ~ 10 μA. The electron beam was focussed to a spot about 350 μm in diameter on to the diamond mounted at the end of a liquid nitrogen cold-finger. By applying pulses to parallel plates in the electron flight tube the beam could be deflected on or off the sample in about 1 ns.

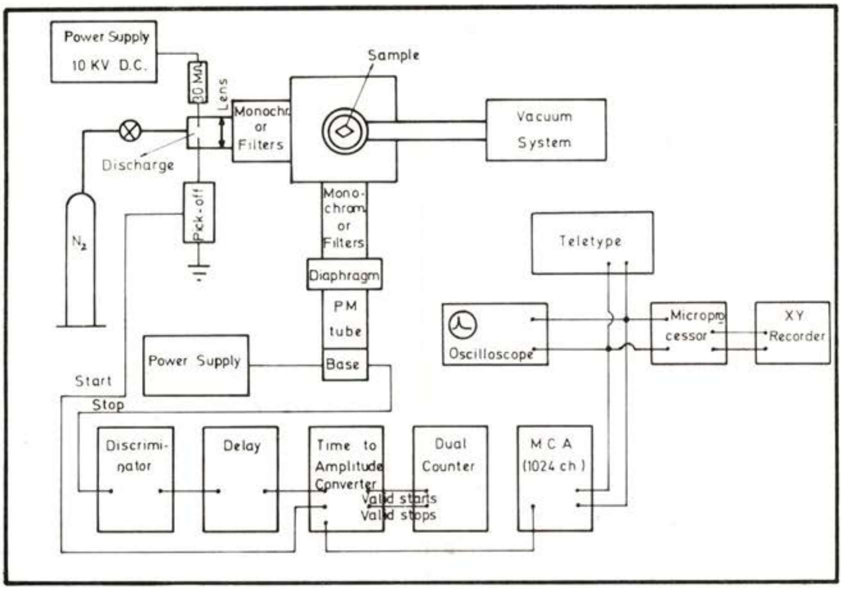


Fig. 2 — Single-photon system block diagram.

The luminescence from the sample was collected by a spherical mirror and focussed on to the entrance slit of a Spex 1500 monochromator. The photomultiplier used (I. T. T. type 4027) differed from a conventional tube in having a fine mesh grid structure immediately behind the photocathode. By applying a small bias potential to the so-called "gate" the photomultiplier could be turned on or off, depending on the polarity of the bias. For time resolved spectroscopy the photomultiplier was pulsed on for a short time by a Tektronix type 111 pulse generator which was triggered by the pulse generator deflecting the electron beam (Fig. 3). The time interval between the excitation of the sample and switching on the photomultiplier could be varied, enabling spectra to be recorded at different delays. The normal practice was to excite the sample for a period somewhat longer than the decay time of the luminescence system being measured, and to gate the photomultiplier on for a time period about half that of the decay time. Thus, for example, for a decay time of 20 ns the sample would be excited for 50 ns at a repetition rate of 30 kHz and the photomultiplier would be gated on for 10 ns. In such a case the delay between excitation and gating the photomultiplier on would be varied in the range 0 to 100 ns. Pulse lengths and delays were all determined by standard lengths of coaxial cable.

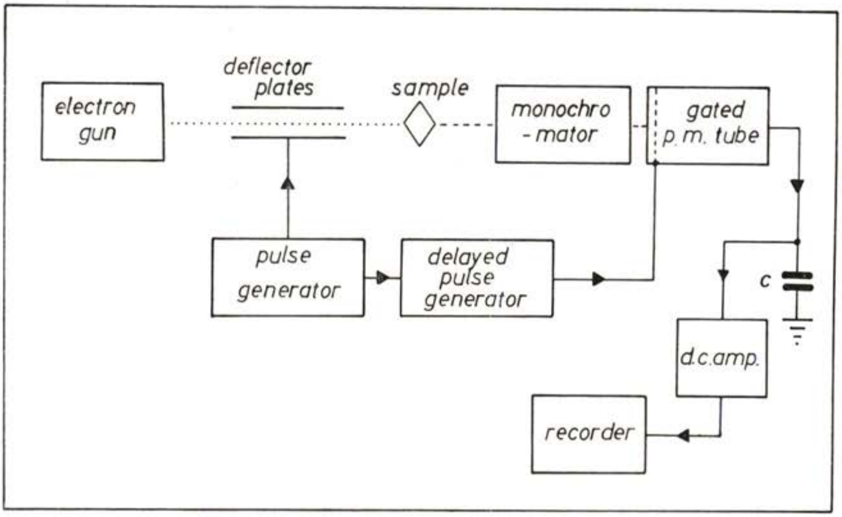


Fig. 3 — Time resolved spectroscopy system diagram.

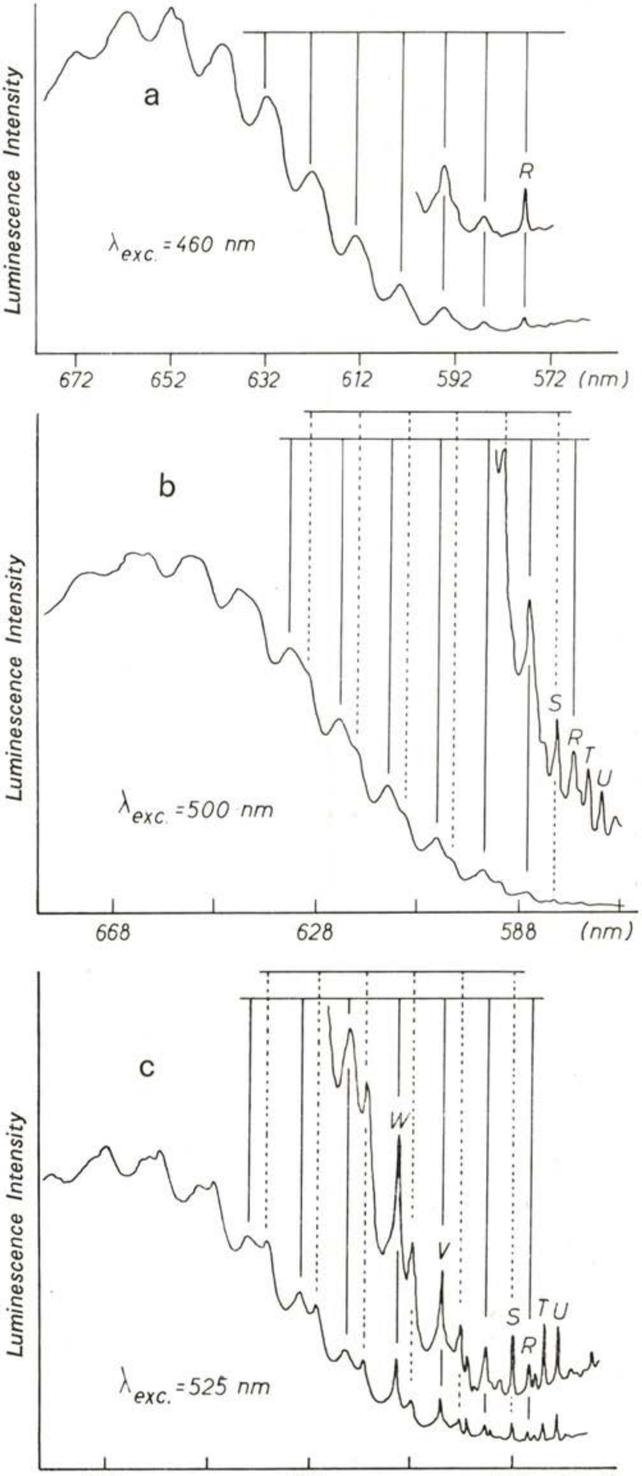
3 — EXPERIMENTAL DATA

3.1 — *Red luminescence band*

Exciting the diamonds with light of 460 nm (2.69 eV) produces luminescence as shown in Fig. 4a. This spectrum is similar to the

---

Fig. 4 — (facing page) — Photoluminescence spectra (uncorrected) of a brown diamond at 77 K using excitation light of: a) 460 nm; b) 500 nm; c) 525 nm


a
Luminescence Intensity
λexc.=460 nm
R
672
652
632
612
592
572
(nm)
b
Luminescence Intensity
λexc.=500 nm
V
S
R
T
U
668
628
588
(nm)
c
Luminescence Intensity
λexc.=525 nm
W
V
S
R
T
U
661
621
581
(nm)

original report of the red luminescence by Collins and Mohammed (1982) who used exciting light of 489 nm (2.53 eV). The energy spacing of the vibronic peaks in figure 4a corresponds to a phonon quantum of 31 meV. When exciting light of a longer wavelength is used, further features appear in the red spectral region (Fig. 4b, c). These features also form vibronic progressions with phonon energies of 31 meV, very similar to the simple spectrum obtained with excitation at 460 nm. The vibronic bands have their origins at the zero-phonon lines R (577.8 nm, 2.146 eV), S (581.0 nm, 2.134 eV), T (574.8 nm, 2.157 eV) and U (572.1 nm, 2.167 eV).

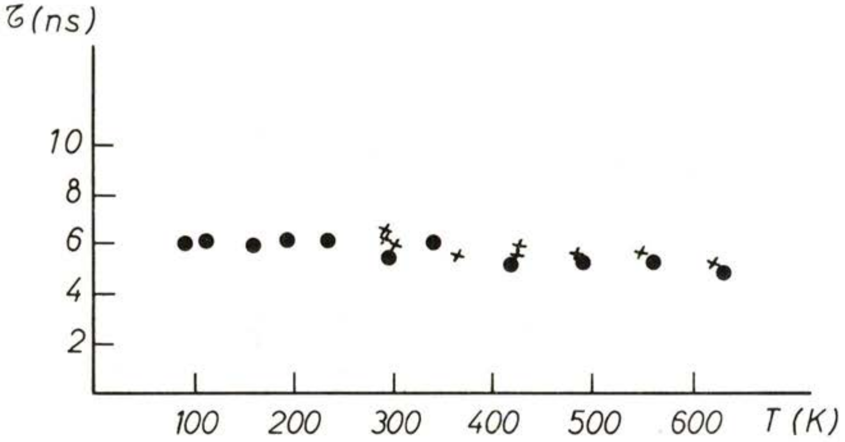


Fig. 5 — Decay times of the red photoluminescence as a function of temperature (• refer to one brown diamond; x refer to another).

Photoluminescence decay time measurements have been made with exciting light of 480 ± 20 nm, (2.58 ± 0.1 eV) chosen to excite predominantly the simple vibronic band with the zero-phonon line R. The luminescence decreased, after spark excitation, with an accurately exponential time dependence. The decay time is 6 ns at room temperature, and changes by less than 1 ns in the temperature range 80 to 600 K (Fig. 5). The same result was obtained when we used exciting light of 500 ± 10 nm

(2.48 ± 0.05 eV) and between 470 and 530 nm (Corning 5.61 and 3.71 filters on the excitation). The decay time is consequently independent of the wavelength of the exciting light over the wavelength range 460 to 530 nm. The luminescence was detected through a Corning 2.61 filter (cut-off at ~ 600 nm), in all cases.

Luminescence decay times have also been measured for the red luminescence band using cathodoluminescence, with the samples at liquid nitrogen temperature. The cathodoluminescence decay is nonexponential initially with a decay time of about 10 ns. However, about 10 ns after the cessation of excitation, the luminescence decay slows to an approximate decay time of 25 ns.

3.2 — *Yellow luminescence band*

When the yellow luminescence is excited by relatively long-wavelength light (e.g. 425 ± 10 nm, 2.92 ± 0.07 eV) the spectral distribution of the luminescence has the temperature dependence of Fig. 6. The luminescence mainly consists of one

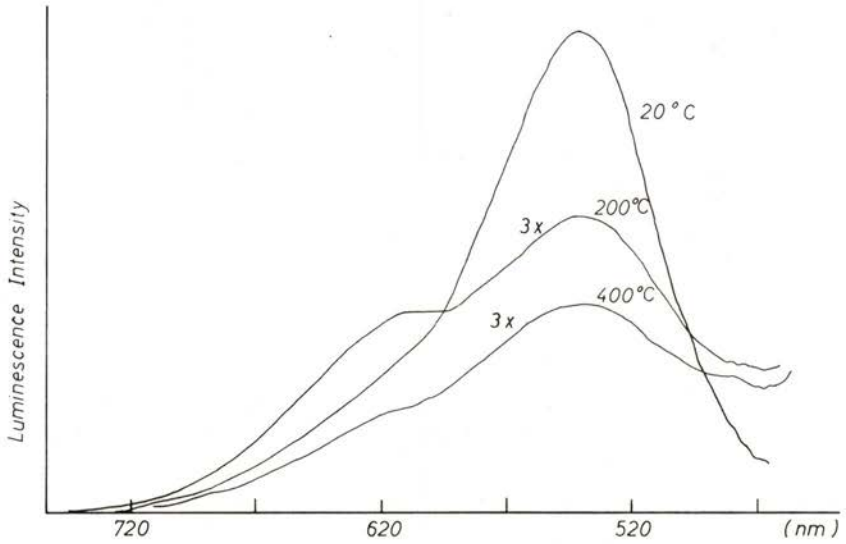


Fig. 6 — Photoluminescence spectra for one brown diamond at three different temperatures and $\lambda_{\mathrm{exc}} = 425$ nm

band centred on 540 nm (2.30 eV), and the intensity of this band decreases with increasing temperature. When shorter wavelength exciting light is used (e.g. at 325 nm, 3.81 eV) the 540 nm band is seen together with a band near 460 nm, 2.70 eV (Fig. 7). The 460 nm band increases in *absolute* intensity as the temperature increases.

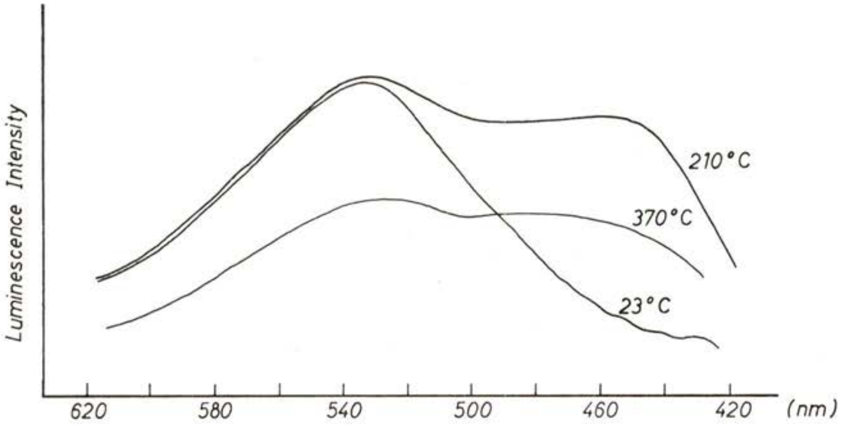


Fig. 7 — Photoluminescence spectra for one brown diamond at three different temperatures and using $\lambda_{exc} = 325$ nm

With 400 ± 20 nm (3.10 ± 0.16 eV) exciting light and a Corning 3.70 filter (cut-off at ~ 500 nm) on the emission side one single exponential decay is obtained with a decay time of 5.8 ± 0.2 ns at room temperature: this presumably is the decay time of the 2.721 eV system. Excitation at 400 nm creates the yellow luminescence most efficiently and the red luminescence is absent.

When shorter wavelength excitation is used (with the exciting light filtered by Chance 0X7 and 0B10 filters to pass light of 330-420 nm) and the luminescence is detected through a Corning 3.70 filter (cut-off at ~ 500 nm) non-exponential decay curves are obtained. These curves were fitted numerically to the sum of two exponentials. One has a decay time of 5.8 ns at room temperature, decreasing with increasing temperature above 350 K

(Fig. 8): this is presumably the decay time of the 2.721 eV system. The second decay time is longer and shows no significant variation with temperature. This component is a weak contributor to the luminescence, giving approximately 15 % of the emission immediately after excitation, and so its decay time is very uncertain (18 ± 4 ns).

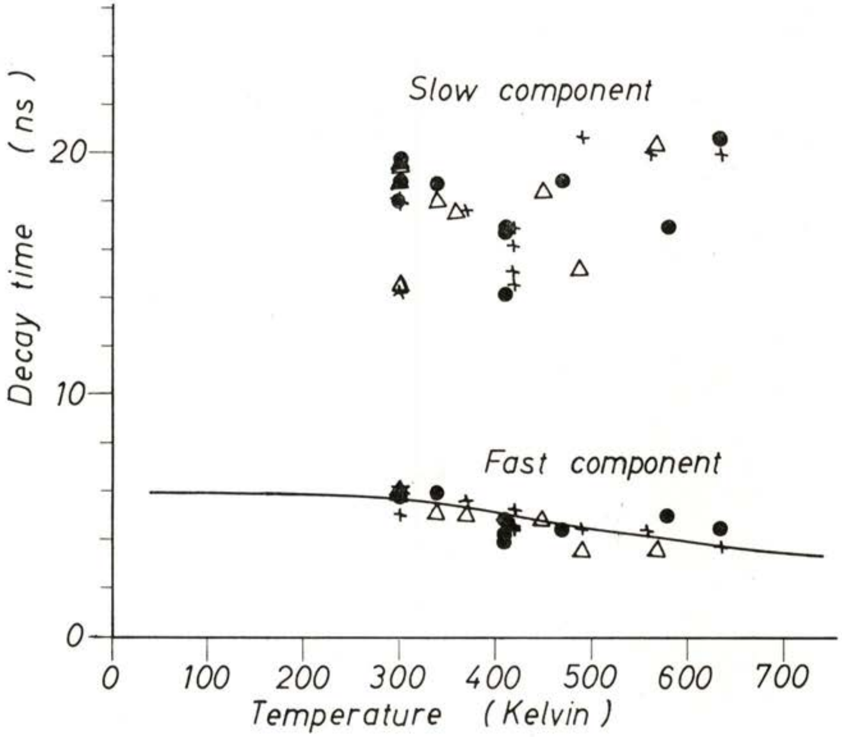


Fig. 8 — Decay times of yellow photoluminescence as a function of temperature. (•, Δ and x refer to three different brown diamonds). The curve drawn through the points of the faster component obeys the equation of section 4.

A third much longer-lived component is also observed using the same excitation conditions, confirming the suggestion (Collins and Mohammed 1982) that the yellow luminescence band is complex (several zero-phonon lines are observed over the band as the S1 system, the 440.2 nm, 489 nm, 496.6 nm, 518 nm, 523.2 nm, 524.2 nm and N3). The intensity of this slow component increases as the specimen temperature increases but is always less than 3 % of the emission immediately after excitation. It corresponds presumably to the 460 nm band whose absolute intensity increases with temperature as shown in Fig. 7.

Measurements have also been made of the decay times of some of the many sharp lines observed in the cathodoluminescence of these brown diamonds (§1). The decay times for lines A (2.403 eV, 515.8 nm), B (2.478 eV, 500.2 nm), F (3.150 eV, 393.5 nm) and another zero-phonon line at 491 nm (2.526 eV) as measured at liquid nitrogen temperature are 32.5, 40, 45 and 70 ns respectively (with an uncertainty of about ± 5 %) as shown in Figs. 9 and 10.

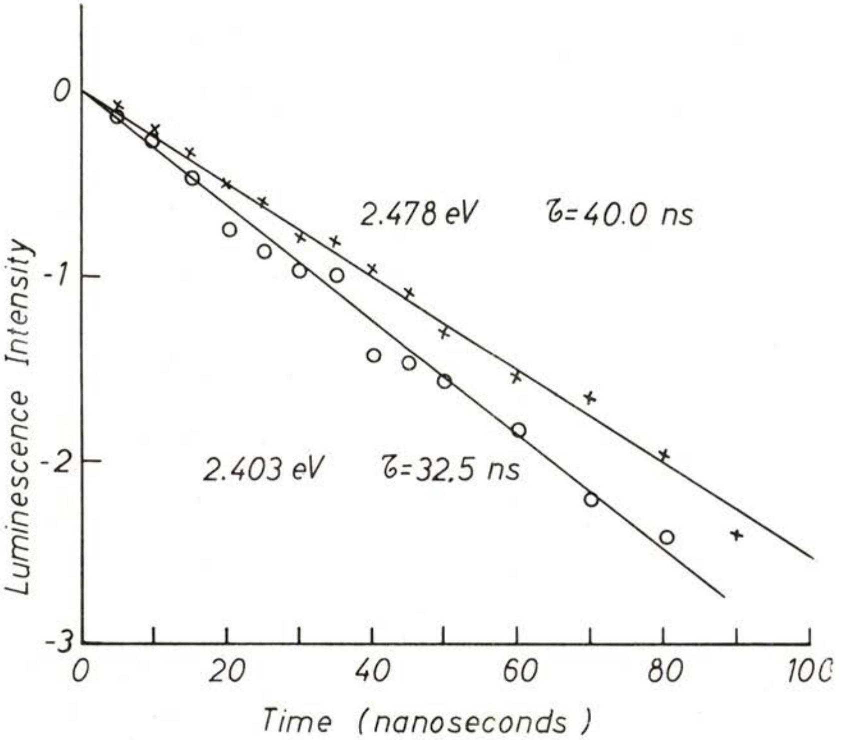


Fig. 9 — Cathodoluminescence decay curves of A line (2.403 eV) and B line (2.478 eV) at liquid nitrogen temperature.

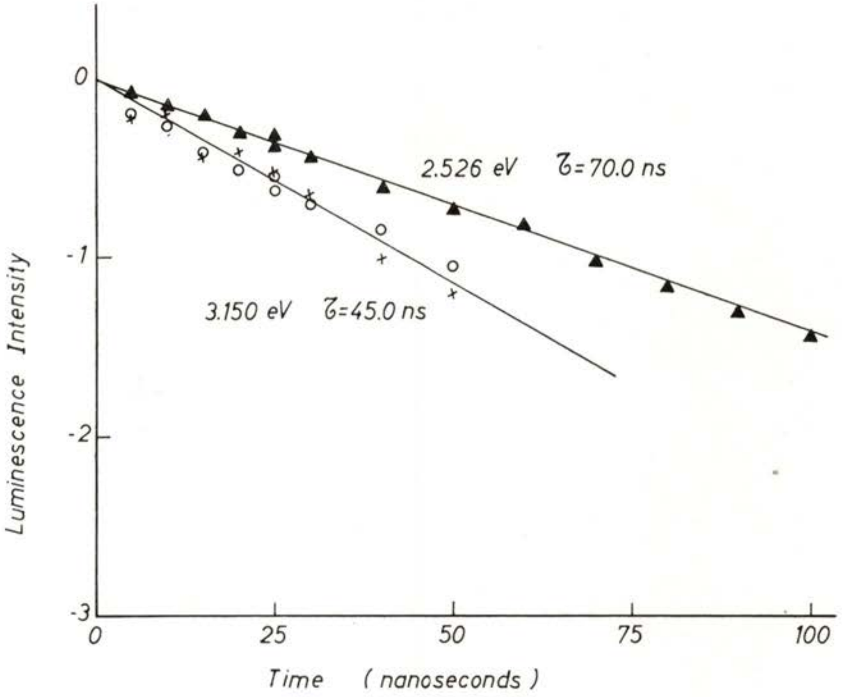


Fig. 10 — Cathodoluminescence decay curves of F line (3.150 eV) and the 491 nm line (2.526 eV) at liquid nitrogen temperature. (Symbols ○ and x refer to the same brown diamond and ▲ refers to a different diamond).

4 — DISCUSSION

The red luminescence band, excited by 460 nm (2.7 eV) light appears to consist of a single vibronic band with its zero-phonon line at 2.146 eV (R of Fig. 4a). The vibronic progression involves phonons of 31 meV (well away from any critical point in the phonon dispersion curves of diamond (Zdetsis 1979)). The Huang-Rhys factor of the band, at low temperatures, is of the order of 10. (We are currently investigating the electron-phonon coupling of this band in more detail). When the excitation light is changed to 525 nm (2.362 eV) many other transitions are excited (Fig. 4c), with similar phonon energies and Huang-Rhys factors. In particular vibronic bands with zero-phonon lines W (2.051 eV) and V (2.082 eV) are excited (§3.1). As these changes occur, the luminescence decay times are little changed (§3.1). Evidently the red spectral region contains many similar vibronic bands, derived from another "family" of similar optical centres in these diamonds. Closely related optical centres are common in diamond – in addition to those occurring in brown diamond (§1) there are also several similar radiation damage centres (de Sa and Davies 1977).

In Fig. 8 we showed that the decay time of the photoluminescence band centred on 540 nm (zero-phonon energy 2.721 eV) decreases with increasing temperature. This decrease, and the loss of luminescence intensity with increasing temperature (Figs. 6 and 7), are consistent with a thermally activated non-radiative decay, internally at the optical centre, to another energy level. This process may be described by the well-known single vibrational coordinate model (Freed and Jortner 1970):

$$\tau^{-1} - \tau_0^{-1} = C\,(kT^*)^{-1/2}\,\coth(\hbar\omega/2kT)\,\exp(-\Delta E/kT^*)$$

The line on Fig. 8 shows a fit of this equation to the experimental data with the parameters $\hbar\omega = 34$ meV, $C = 2.0$ ns^{-1} meV$^{1/2}$, and $\Delta E = 127$ meV. T* is the effective temperature defined by

$$kT^* = (\hbar\omega/2)\,\coth(\hbar\omega/2kT)$$

and τ_0, the decay time at 0 K, was assumed to be 6.0 ns. We note the similarity of the value of $\hbar\omega$ with the quantum observed in the luminescence spectrum.

In §3.2 we reported the decay times of four zero-phonon lines observed in cathodoluminescence in the brown diamonds. The values obtained are several tens of nanoseconds, typical for electric dipole optical transitions in diamond (Crossfield et al. 1974, Thomaz and Davies 1978). The decay times for these zero-phonon lines have not been reported before, except for a measurement of the 491 nm (2.526 eV) line by Crossfield (1981). He reported that the decay was not exponential, in contrast to the result reported here (§3.2). However, the conditions used by Crossfield were inappropriate to determine the decay time of this line. In his diamonds the 491 nm line was a very minor feature superimposed on the blue "band A" donor-acceptor pair recombination. The latter system has a fast decay time (~ 8 ns) and by exciting his samples for 20 μs and looking at the luminescence after a delay of 500 ns

Crossfield was able to obtain a spectrum in which the 491 nm system was the dominant emission. For longer delays (up to 100 μs) the intensity of the 491 nm system decayed in a nonexponential fashion. The behaviour at such long delays is probably determined by other processes in the diamond, rather than by the lifetime of the centre itself. In contrast our measurements have been made on diamonds in which the 491 nm luminescence was the dominant emission and the exponential decay with a time constant of 70 ns is characteristic of the centre itself. Collins and Woods (1982) have shown that the 491 nm emission is associated with a defect which has decorated dislocations in the diamonds.

5 — SUMMARY

Brown diamonds with yellow photoluminescence (under 365 nm Hg excitation) form an appreciable fraction of total natural diamond production. In this paper we have presented the preliminary results of a systematic investigation of the luminescence transitions observed in this class of diamonds. The photoluminescence in broad outline has the form of bands centred at 550 nm (yellow luminescence) and at 650 nm (red luminescence).

The decay time for the red luminescence band is 6.0 ± 0.2 ns at room temperature and does not vary significantly as the temperature is changed in the range 80 K – 600 K. The decay time is also independent of the exciting wavelength, even though different vibronic bands are then excited (§3.1).

The decay curves for the yellow luminescence band can be resolved into a fast component and a slower component. The fast component is shown to be temperature dependent, becoming faster as the temperature is increased. The fast decay time constant (5.8 ± 0.2 ns) is assigned to the 455.5 nm, 2.721 eV luminescence system (§3.2).

We have also measured the decay times of some of the many sharp zero-phonon lines observed in the cathodoluminescence spectra of the brown diamonds, obtaining values of the order of tens of nanoseconds (§3.2) as expected for electric dipole transitions in diamond.

Further work is in progress on the vibronic properties of these bands and on the temperature dependence of the decay times.

This work was partly subsidized by JNICT (Junta Nacional de Investigação Científica e Tecnológica). DIALAP and Sociedade Portuguesa de Empreendimentos are acknowledged also for financial support. Mr. J. M. Januario helped in the experiments.

REFERENCES

BIRCH, D. J. S. and IMHOF, R. E. 1977, *J. Phys. E: Scientific Instruments,* **10**, 1044-1049.

COLLINS, A. T. and MOHAMMED, K. 1982, *J. Phys. C: Solid State Phys.,* **15**, 147-158.

COLLINS, A. T. and WOODS, G. S. 1982, *Philosophical Magazine B,* **45**, 385-397.

CROSSFIELD, M. D. 1981, PhD. Thesis, University of London, King's College.

CROSSFIELD, M. D., DAVIES, G., COLLINS, A. T. and LIGHTOWLERS, E. C. 1974, *J. Phys. C: Solid State Phys.,* **7**, 1909-1917.

DE SA, E. S. and DAVIES, G. 1977, *Proc. R. Soc. Lond.* **A357**, 231-251.

FREED, K. F. and JORTNER, J. 1970, *J. Chem. Phys.* **52**, 6272-6291.

MOHAMMED, K., DAVIES, GORDON and COLLINS, ALAN T. 1982, *J. Phys. C: Solid State Phys.,* **15**, 2789-2800.

THOMAZ, M. F. and BARRETO, V. J. 1971, *Rev. Fis., Quim. e Engenharia* — vol. III, Serie A, 7-19.

THOMAZ, M. F. and DAVIES, G. 1978, *Proc. R. Soc. Lond.* **A362**, 405-419.

ZDETSIS, A. D. 1979, *Chem. Phys.* **40**, 345-347.