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Abstract—Observations of the transient behaviour of electroluminescence in sublimation flakes have shown that quenching of the delayed electroluminescence component by the carriers themselves becomes important at high currents. The results show quenching is of the same order as observed for carrier quenching of optically produced triplet excitons. No quenching was observed in thick crystals though carrier densities of the same order are present. This is presumably due to the difference in recombination zone width which may be larger in these thick crystals.

1. Introduction

Electroluminescence has been the subject of many investigations,[1,2] however in general the prime interest has centred upon the final exciton states produced. In aromatic hydrocarbon crystals such as anthracene, electron-hole recombination produces both singlet and triplet excitons.[3] These excitons decay either radiatively or non-radiatively to the ground state, through monomolecular or bi-molecular processes. Reactions of either singlet or triplet excitons are easily separated for there is a vast difference in their respective lifetimes, about 10^{-8} seconds for singlets[4] and about 10^{-3} seconds for triplet excitons.[5] Thus electroluminescence in anthracene consists of two components, one fast component due to the radiative decay of singlet excitons produced directly by carrier recombination, and a second delayed component due to the radiative decay of singlet

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excitons produced by bimolecular triplet–triplet annihilation.[3] Recent experiments have also shown that carrier–exciton interactions are not negligible in organic crystals, and in particular it has been observed that delayed fluorescence was quenched when charge carriers were injected into the crystal.[6] This quenching of delayed fluorescence was seemingly even observed with a very high triplet exciton densities where a simple triplet–carrier interaction could not be important. Electroluminescence studies offer an obvious alternate probe for such carrier–exciton interactions, for under such conditions it is evident that both carriers and triplet excitons must be present at one and the same time. For this reason we have studied the steady state and pulsed characteristics of anthracene electroluminescence to give further insight into these carrier–exciton quenching processes, particularly when high triplet densities are present. Pulsed experiments offer a simple technique for separation of delayed and prompt electroluminescence if a voltage source is available which will give a flat voltage pulse with either fast rise or decay characteristics. Such a pulse amplifier has been used for many experiments in our laboratories, and in view of its simplicity and versatility we give a description of its general circuitry. With this voltage source we have studied electroluminescence in both thick and thin crystal samples (2 mm–0.050 mm) so that a very broad range of carrier densities and hence triplet densities could be obtained. This has allowed us to monitor carrier–triplet quenching over a range of triplet densities where either monomolecular (low triplet density) or bimolecular triplet decay (high triplet density) is the dominant triplet relaxation process.

2. Experimental

For these experiments high quality sublimation flakes and melt grown crystals were used,[7] triplet lifetimes $\approx$20–25 msec. The sublimation flakes were between 50–200 μ thick whereas the melt grown samples were between 1–2 mm thick. Sodium-potassium amalgam was always used as the cathode, but either an anthracene positive ion solution or silver paste was used as the anode.[1] Contact areas were between 0.5–1 cm². These contact combinations both give rise to electroluminescence, but it has been found that an

anthracene cation anode saturates at crystal currents greater than 10^{-5} amps, and hence it was not used for high current experiments. The electroluminescence emanating from these crystals was detected by a 6256B EMI photomultiplier and either recorded directly, or stored in a time averaging computer when the signal level was low. Various levels of bias voltage were applied from a dc regulated voltage supply for the transient measurements, the driving voltage being given by a second high voltage supply connected to the high
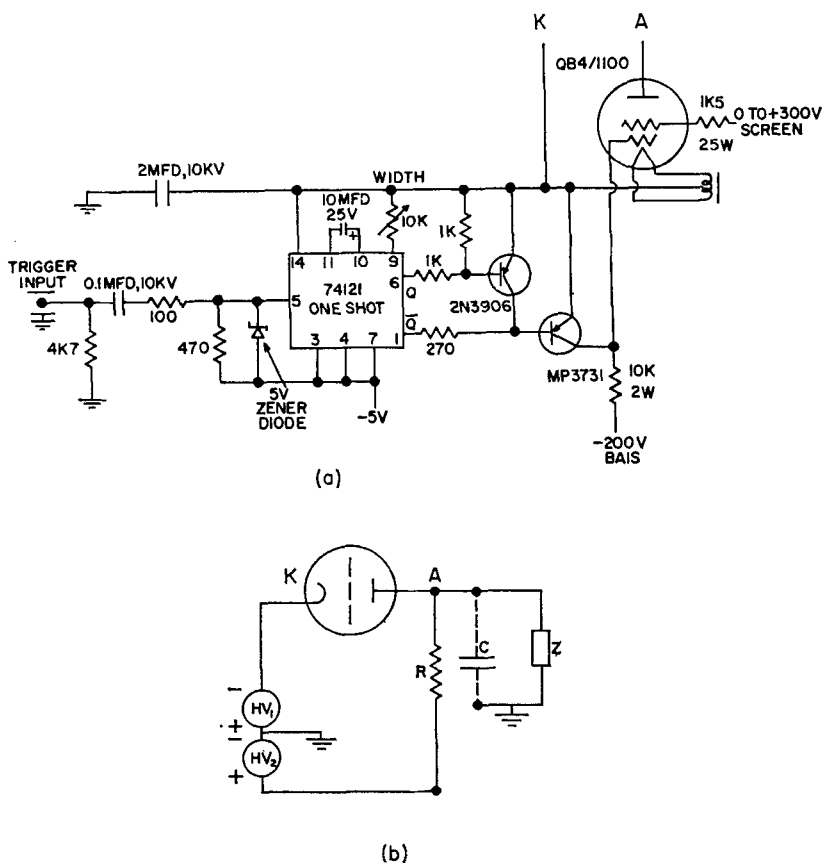

Figure 1. (a) General circuit of the pulse amplifier. (b) Configuration of pulse amplifier used providing reverse bias voltage and fast decay and rise time characteristics for the driving voltage. C is the sample.

voltage pulse amplifier. These voltage supplies are V_1 and V_2 respectively in Fig. 1. Figure 1 describes the general electronic circuitry used in this high voltage pulse amplifier.

A) PULSER CIRCUIT DESCRIPTION

The heart of this pulsing circuit is a HV-HF tetrode, Philips QB4/1100. Although other tetrodes may be chosen, this tube has been found satisfactory for voltages of up to 7 kV with anode current pulses of several amps, though lower limiting values are given by the manufacturer. The voltage applied to the screen grid of the QB4/1100 is variable between 0 and 300 V, allowing easy adjustment for different operating conditions. The voltage on the control grid is either " 0 " or – 200 V, and is determined by the trigger circuit. These two voltages correspond to the conducting and nonconducting state of the tetrode. Thus a trigger circuit is required which will drop the bias voltage of the control grid to zero for a length of time equal to that of the required voltage pulse. By this means a 74121 (TTL logic) one shot integrated circuit is used to generate a pulse with a width of 20 to 120 msec from a 10 V positive trigger. The 5 V power supply for the 74121 has its positive side connected to the filament of the tetrode. Thus the $\overline{Q}$ output of the one shot, which would normally go to " 0 ", now goes to – 5 V and is used to drive the MP 3731, which switches the control grid directly to the filament, resulting in zero bias and the tetrode turns on. The MP 3731 should be selected for low leakage current. It is important to note that all circuits used most must be capable of floating up to the highest voltages required.

Several commercial fast pulse generators are available which may be used to directly drive the grid if their pulse width is satisfactory. No matter how this pulser is driven, the final dc high voltage pulse is not symmetric with respect to its voltage rise and decay times. Depending upon the crystal connections either fast rise or fast decay can be chosen, and the arrangement of Fig. 1b is particularly convenient for such situations. The short time constant of the voltage pulse is characterized by a slewing rate of I/C where I is the current through the conducting tube (about 1 amp) and C the corresponding capacitance (approximately 100 pf), and is thus in the order of

10 kV/μsec. The long time constant is given by RC which, with a typical R of 100 KΩ, is 10 μsec.

The pulsed experiments reported were in general performed with a fast decay voltage characteristic, however similar results were found from fast voltage rise applications.

B) RESULTS

The steady state electroluminescence intensity dependence upon crystal current was measured for both melt grown and sublimation flakes. The results for melt grown crystals were the same as reported earlier, namely throughout the current range the electroluminescence showed an ~1.1 power dependence upon crystal current.[1] For sublimation flakes the electroluminescence intensity showed a linear relationship with high crystal currents, as shown in Fig. 2, though for low currents, ~10^{-7} amps and lower, a superlinear dependence became apparent.

Experiments were performed in which both the rise and decay characteristics of the electroluminescence transient were monitored. When two injecting contacts were used, the total transient was symmetric at room temperature within experimental accuracy. With a sodium potassium amalgam and silver paste contact combination the transient was not symmetric, but this difference was due only to a change in the rise time.[1] The decay transient was independent of contact combination when the on time for the voltage pulse was sufficient to reproduce steady state delayed electroluminescence conditions. For these reasons, as the majority of experiments were performed with forced injection contact combinations, results were compared only from the electroluminescence decay.

Results for thick crystals, 1–2 mm, showed that for increasing crystal currents of up to 10^{-5} amps, the ratio of delayed :: prompt electroluminescence increased to a maximum value of 0.55. The magnitude of the crystal current at which this maximum value for the ratio was obtained depended upon the crystal thickness, for example it was attained with currents of about 10^{-6} amps for crystals 1 mm thick. This increasing ratio is observed because at high crystal currents both electroluminescence components increased linearly with current, but for low currents, 10^{-8} amps, the
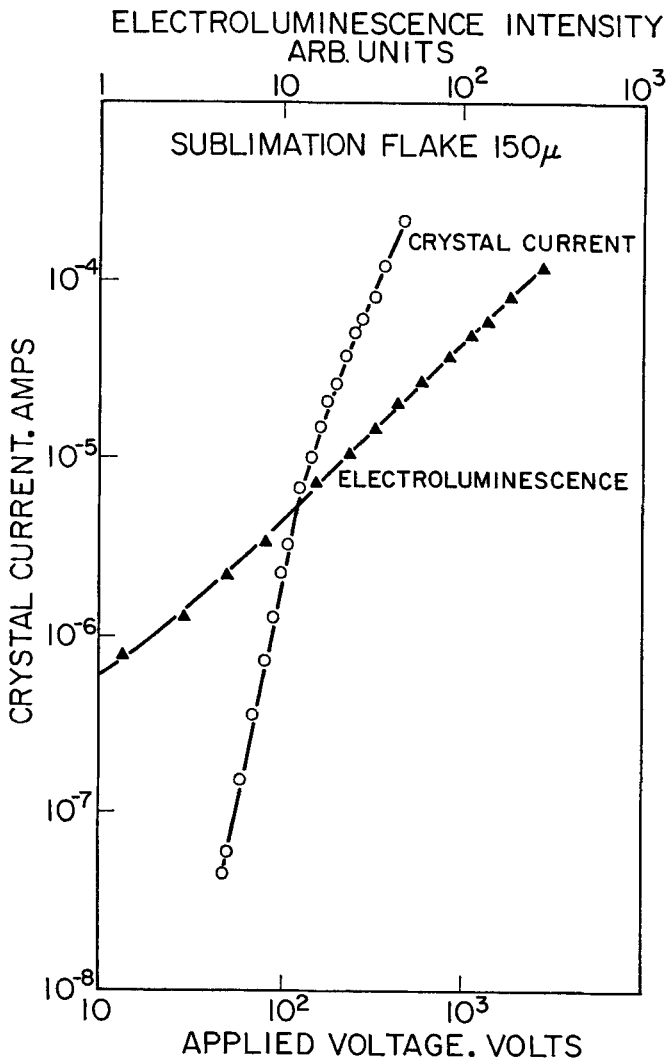
Figure 2.   Variation of (i) the crystal current with applied voltage and (ii) electroluminescence intensity with crystal current for an anthracene sublimation flake.

TABLE 1   Typical Results Obtained from Electroluminescence Transients for Different Crystals with Various Forward and Reverse Bias Voltages

Crystal thickness	Applied voltage	Bias voltage	Crystal current	Ratio slow :: fast electro- luminescence
	V	V	Amps	
	240	900V	1.4×10^{-8}	0.26
	300	900V	4.0×10^{-8}	0.50
1.0 mm	430	900V	1.5×10^{-7}	0.48
	550	900V	3.7×10^{-7}	0.50
	760	900V	1.5×10^{-6}	0.52
	150	100–400	1×10^{-6}	0.65
	210	100–400	5×10^{-6}	0.38
90μ	290	100–400	4×10^{-5}	0.30
	390	100–400	1×10^{-4}	0.22
	520	100–400	4×10^{-4}	0.19
	680	100–400	1×10^{-3}	0.11
	140	100–400	1×10^{-6}	0.62
	170	100–400	5×10^{-5}	0.50
150μ	200	100–400	1×10^{-5}	0.31
	270	100–400	5×10^{-5}	0.24
	345	100–400	1×10^{-4}	0.14

delayed component increases more rapidly. Results for a 1 mm thick crystal are shown in Table 1 and this pattern of results was always followed. When the crystal current was increased further, to greater than 10^{-6} amps, the ratio of slow : : fast electroluminescence decreased again. Figure 3 shows the change of slow and fast electrolumin-escence components with increasing current for a sublimation flake and Fig. 4 the variation of slow : : fast ratio for a similar crystal. For each crystal a series of experiments was performed with the same forward bias voltage but with different reverse bias voltages. The results were found to be independent of the reverse bias, showing that recombination of thermally detrapped carriers did not contri-bute significantly to the magnitude of the delayed electroluminescence at any crystal current. The results for several thin crystals are also shown in Table 1, and the small ratio of delayed : : prompt electro-luminescence at high crystal currents is very obvious. Results from thin flakes also indicated that this delayed : : prompt ratio became small again with very low crystal currents, but the experimental
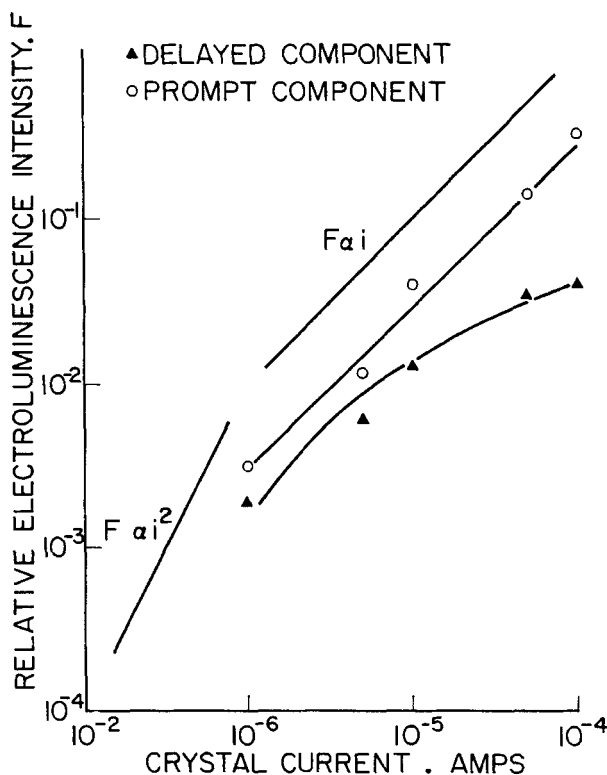
Figure 3.   Variation of the relative intensities of prompt and delayed (slow) electroluminescence with crystal current.   Lines denoting a linear and square dependence of intensity or crystal current are added for reference.

error in this current region is reasonably large due to the combination of thin crystal and weak electroluminescence.

3. Discussion

When two carriers recombine, the resulting charge transfer exciton will have an overall spin of either 0 or 1, i.e. singlet or triplet character. These charge transfer excitons then decay either through the singlet manifold or triplet manifold; the former gives rise to prompt electroluminescence, time scale 10^{-8} sec, and the latter, slow electroluminescence through triplet–triplet annihilation time scale $\sim 10^{-3}$ sec. Thus the final bi-exciton process involved in producing delayed electroluminescence is the same as that producing delayed fluor-
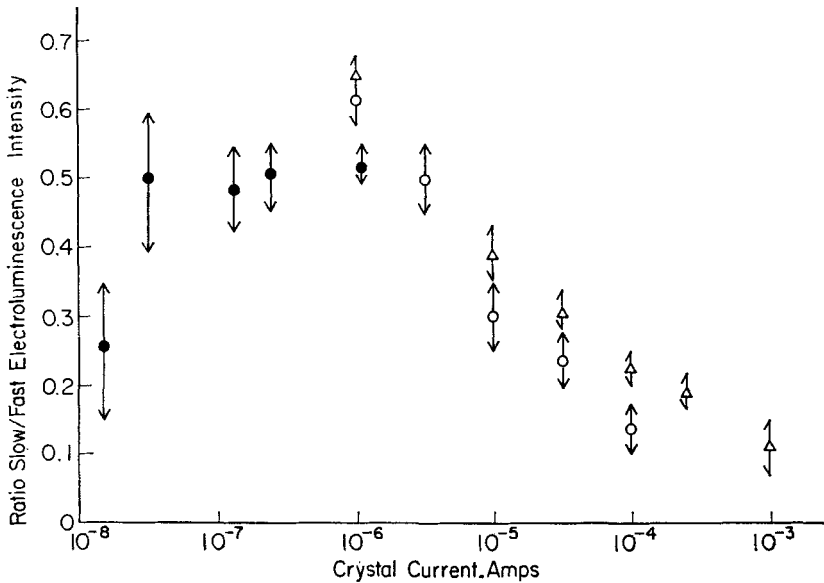
Figure 4.   Ratio of the slow:: fast electroluminescence intensity observed at different crystal currents for thick crystals ●, and sublimation flakes ○ △

escence.   This can be shown to be the case, for with low currents the decay rate of delayed electroluminescence is the same as that for delayed fluorescence with low triplet densities.   Both are controlled by the monomolecular triplet decay constant.   A similar behaviour of slow electroluminescence and delayed fluorescence with respect to the triplet exciton density is also observed; that is with low currents (low triplet density) the slow electroluminescence intensity shows approximately a square dependence on crystal current and at high crystal currents (high triplet densities) a linear intensity dependence on crystal current.   This behaviour can be seen in Fig. 3 where for comparison lines denoting a linear and square dependences are shown. Since the triplet density in electroluminescence experiments is a function of the carrier recombination zone width as well as the crystal current, then if thin crystals are used it is possible to physically constrain the recombination zone giving rise to high triplet densities even with low crystal currents.   Quenching of delayed fluorescence by injected carriers has recently been reported and this phenomenon must cause the relatively decreased intensity of the delayed com-

ponent of electroluminescence with increasing crystal current. This quenching for sublimation flakes is seen in Fig. 3. Assuming that in the absence of quenching slow electroluminescence is linearly proportional to the crystal current, then from Fig. 3 it can be seen that the magnitude of the quenching is also linearly dependent on crystal current, that is free carrier density[7] (Figs. 4 and 5). These results
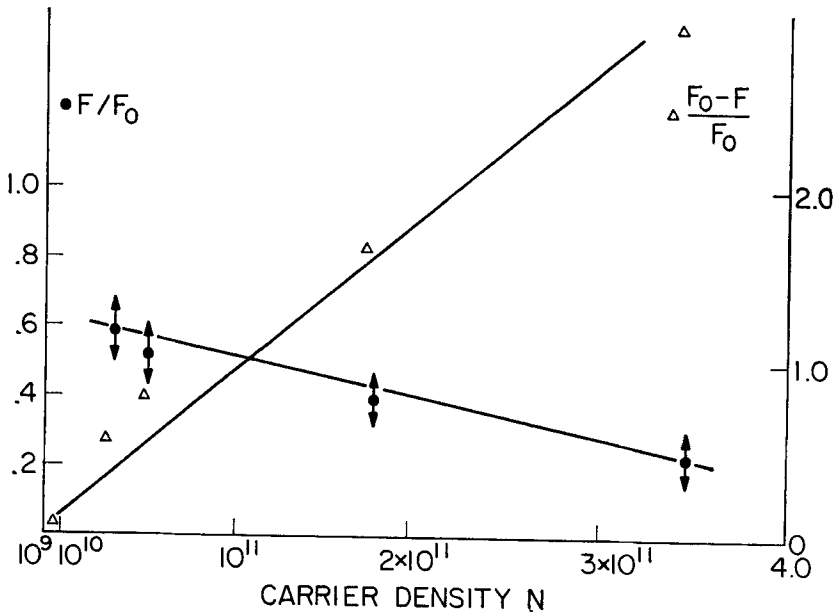

Figure 5. Variation of the quenching of delayed electroluminescence with injected carrier density for a sublimation flake.

can be shown to be in agreement with earlier high density triplet quenching reports[6] as follows: the triplet density is controlled by the equation

$$dT/dt = G - \beta T - \gamma T^2$$

where G is the triplet generation rate and is proportional to the crystal current, T is the triplet concentration, β the triplet monomolecular decay rate and γ the bimolecular triplet–triplet annihilation rate constant. The term giving rise to delayed fluorescence or delayed electroluminescence is γT^2. Thus the critical triplet concentration where monomolecular and bimolecular triplet exciton

decay are equally probable is given by $T_c = \beta/\gamma$. With $\beta \approx 10^2$ sec^5 and $\gamma \approx 10^{-11}$ cm^3 sec^{-1},[7] T_c is $\approx 10^{13}$ cm^{-3}. Assuming that each carrier recombination event produce se triplet exciton (actually spin statistics say only 3 in 4 recombinations produce triplet excitons), then the number of triplet excitons generated per cm^2 with a current of $\sim 10^{-7}$ amps cm^{-2} is $\sim 10^{14}$ cm^2 sec^{-1}. Since the triplet lifetime is 10^{-2} sec, the number of triplet excitons per cm^2 is $\sim 10^{12}$ cm^{-2}. In order to produce a critical concentration of 10^{13} cm^3, the recombination zone must be less than $10^{12}/10^{13}$, i.e. 1 mm thick. This is obviously the case for sublimation flakes where the thickness is typically $50-200 \mu$. Table 2 shows the fluorescence quenching, carrier density and triplet densities obtained from the results shown in Figs. 3 and 4, the numerical values being determined from this simple analysis. These results show approximately the same degree of quenching of triplet–triplet annihilation with carrier densities of $\sim 10^{11}$ cm^{-3} and triplet densities of $\sim 10^{14}$ cm^{-3} as was observed when triplet excitons were generated optically. It is interesting to note that even with very high triplet densities where β is no longer important in determining triplet concentrations, delayed electroluminescence quenching by carriers still occurs.[6]

Although delayed electroluminescence quenching was observed for sublimation flakes, it was not observed in thick crystals where we had either the same carrier density or the same crystal currents. Nevertheless the ratio of slow::prompt electroluminescence ob-

TABLE 2   Calculated Triplet Exciton and Carrier Densities Present in a Sublimation Flake together with the Calculated Slow Electroluminescence Quenching Assuming a Linear Dependence of Slow Electroluminescence on Crystal Current if No Quenching Occurred

Crystal current amps i	Slow electroluminescence intensity		Normalized electro- luminescence quenching $Q = F/F_0$	Carrier density cm^{-3} N	Triplet density cm^{-3} T
	Predicted F	Observed F_0 arb units			
1×10^{-6}	2×10^{-3}	2×10^{-3}	1.0	7×10^9	4.6×10^{12}
5×10^{-6}	6×10^{-3}	1×10^{-2}	0.6	3×10^{10}	2.3×10^{13}
1×10^{-5}	1.03×10^{-2}	2×10^{-2}	0.5	5×10^{10}	4.6×10^{13}
5×10^{-5}	3.5×10^{-2}	1×10^{-1}	0.35	1.9×10^{11}	2.3×10^{14}
1×10^{-4}	4×10^{-2}	2×10^{-1}	0.20	2.9×10^{11}	4.6×10^{14}

served for these thick crystals was that predicted from a considera-
tion of simple spin statistics for electron hole recombination, pro-
vided that bimolecular triplet recombination is the dominant means
of triplet decay. This means that for thick crystals the recombina-
tion zone is sufficiently large that exciton diffusion from the region
into an area influenced by charge carriers is small.

In conclusion it has been observed that quenching of delayed
electroluminescence by the recombining charge carriers themselves
occurs in situations where the carrier recombination zone is small.
The magnitude of this recombination zone can be controlled simply
by the physical characteristics of the crystal. Thus such carrier–
exciton interactions will reduce the maximum electroluminescence
efficiency of organic materials such as anthracene, and will be parti-
cularly important where thin film devices are considered. However
only the electroluminescence component produced by triplet–triplet
exciton annihilation was affected. The prompt electroluminescence
intensity was always linearly proportional to the crystal current.

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