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Electroluminescence in Tetracene Crystals†

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dc and pulsed electroluminescence (EL) in tetracene crystals have been studied at room temperature. The crystals are provided with Na/K alloy electron injecting contact and Au semitransparent layer as a hole injecting contact.

dc EL intensity shows a superlinear relationship with crystal current.

EL decay indicates that the electroluminescence in tetracene consists of two components: one prompt and a second delayed component.

The results can be understood if the delayed component depends upon crystal current and upon some characteristics of the active traps in the crystal.

The spectral distribution of the electroluminescence as compared to photoluminescence spectrum reveals the intensive long wavelength emission. It is presumably due to trapped excitons.

I INTRODUCTION

Electroluminescence (EL) has been the subject of many investigations in the case of anthracene.[1–9] The experiments have made use of double injection[1] of charge carriers and subsequent recombination as a result of which various excited states could be created: free singlet excitons,[2,6,9] triplet excitons[2,7–9] and charge transfer excitons.[10–12] Recently, the delayed electroluminescence has intensively been investigated.[8,9] This type of EL is due to the radiative decay of singlet excitons produced by bimolecular triplet-triplet annihilation. Since the singlet exciton fission[13] is an efficient channel for triplet generation in tetracene crystal, one can expect that the delayed EL behaviour should be different from that observed in the case of anthracene. For this reason we have studied the steady state and pulsed characteristics of tetracene recombination electroluminescence.

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The electroluminescence intensity is obviously a function of the total number of electron-hole pairs injected, spatial distribution of the recombination events and, the quantum yield of fluorescence. The fluorescence quantum yield in tetracene crystal is known to be very low (2×10^{-3} as compared to 0.95 for anthracene).[14] Consequently, at similar voltage-current conditions the total EL efficiency in tetracene[15] is much lower than that in anthracene. In addition, because the triplet exciton lifetime in tetracene crystal is relatively short ($\sim 10^{-5}$ s)[16] a very sensitive technique should be used for detection of the electroluminescence decay.

For this purpose a single photon counting technique[17,18] combined with a short pulse excitation of the recombination radiation was developed in our laboratory.

This has allowed us to study the electroluminescence decay time as a function of crystal current. The results of this study together with those related to steady state conditions and spectral distribution indicate that the delayed electroluminescence is governed by the following processes:

1) triplet–triplet and triplet–charge carrier interaction,[19]

2) movement of the quasi-Fermi level among charge carrier trapping levels; in the case when the quasi-Fermi level moves towards conduction and/or valence band more recombination events take place by the free-shallow trapped carrier interaction, decreasing the probability of the direct formation of triplet excitons,

3) recombination of thermally detrapped carriers.

2 EXPERIMENTAL

Vapour grown single crystals of tetracene were used. The crystals originated from two different laboratories designated I,† II,‡ III.† Crystal thicknesses were

$$d_1 = 16.5\ \mu\text{m (I)},$$

$$d_2 = 118\ \mu\text{m (II)}$$

and

$$d_3 = 19.5\ \mu\text{m (III)}.$$

Sodium potassium alloy was always used as the cathode and a semitransparent evaporated gold layer as the anode.

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Effective contact areas were 0.04 cm^2. It was established[22] that gold forms an ohmic contact for hole injection into sublimation grown tetracene crystals. Ohmic electron injection contacts are formed by sodium and barium.[22] A Na/K alloy forms an (liquid) ohmic contact for electron injection into anthracene at room temperature.[4] As the energetic conditions at the contact are more favorable for tetracene crystals it is expected that Na/K alloy can also be utilized to form an electron injecting contact to tetracene.

Figure 1 shows double injecting current-voltage characteristics $j(U)$ for the three crystals. The applied field was always perpendicular to the (ab) crystal plane. There is no evidence of saturation even for currents higher than 10^{-4} A/cm^{-2}. A detectable electroluminescence was emitted from the crystals for applied voltages above ~50 V (III), ~150 V (I) and ~300 V (II).

The electroluminescence emission was collected from the gold film covered side of the crystals with a lens and imaged onto the input slits of a

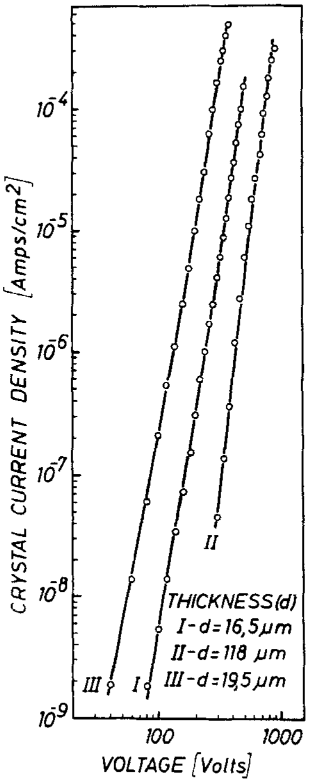

FIGURE 1 Current-voltage relationships for three different tetracene crystals provided with the electron injecting contact Na/K and counter electrode of the hole injecting contact Au.

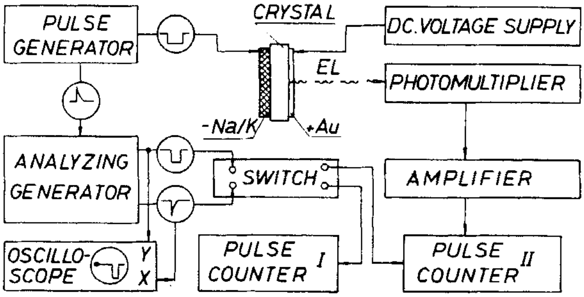

FIGURE 2 Block diagram of the apparatus used to study the electroluminescence decay in tetracene crystals.

Zeiss SPM-1 monochromator or directly onto the photocatode of an EMI model 6256 S photomultiplier operated at −1300 V within a single photon counting apparatus. To achieve adequate counting rates it was necessary to increase the bandpass of the monochromator to ~15 nm for the short wavelength region of the emission spectrum (~500 nm) and to ~20 nm for the long wavelength region (~610 nm) of the spectrum.

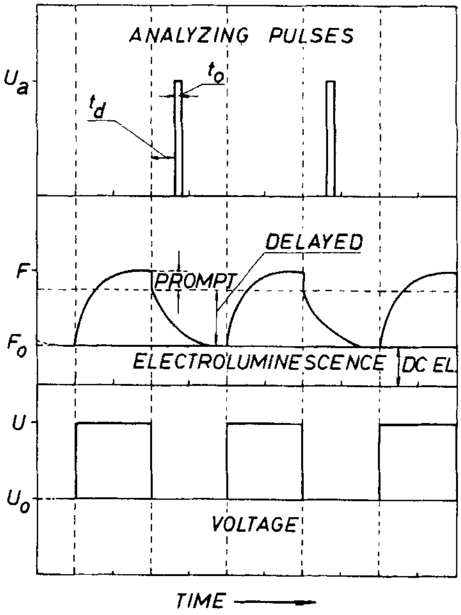

FIGURE 3 Illustration of the analyzing procedure of the electroluminescence relaxation. Reading from bottom to top are the bias voltage U_0, the voltage pulses ($U - U_0$), the relaxation curve of electroluminescence (F) referring to the steady-state level F_0, the analyzing pulses with regulated duration time t_0 and delay time t_d.

Pulsed experiments were made by a combination of a single photon counting technique and a short pulse excitation of the electroluminescence. A block diagram of the apparatus is shown in Figure 2 and the relaxation curve of the electroluminescence (F) in Figure 3. Concurrently with the voltage pulse (amplitude: $U - U_0 = 90$ V; width 75 μs), the analyzing generator was started giving two types of pulses. The peak-type pulses were accumulated in the pulse counter I and the rectangular-type pulses (analyzing pulses) switched the pulse counter II on for the period $t_0 = 2$ μs with the regulated delay time 0.5 $\mu\text{s} < t_d < 150$ μs. This made possible the pulse counter II to count the electroluminescence photons at different times of the EL-relaxation. For the delay times comparable with the electroluminescence decay time, approximately one photon count was recorded for 100 analyzing pulses. Various levels of bias voltage (U_0) were applied from a dc regulated voltage supply to get different steady-state current conditions for the pulsed electroluminescence.

3 RESULTS AND DISCUSSION

A Steady-State Electroluminescence-Current Characteristics

The room-temperature EL-j relationships observed for the crystals provided with two injecting contacts are shown in Figure 4. The over-all electroluminescence intensity (F_{TOT}) appears to be superlinear with the crystal current. The low current slopes are given in the figure. At high crystal currents, similar to the situation with high excitation photoluminescence experiments,[20,24,25] the triplet exciton densities produced in the fission process are sufficiently high to give rise to triplet–triplet fusion increasing the quantum efficiency of the emission from the crystal. However, at high crystal currents a slight decrease in the slope can be seen for all of the crystals.

A possible mechanism, with which our results might be explained, would require that the delayed electroluminescence contributes to the total EL and the contribution varies from crystal to crystal and with the current flowing through the crystal as well.

From the electroluminescence kinetics the expression for the steady state total EL intensity (F_{TOT}) as a function of current density (j) can be derived and written in the form

$$F_{\mathrm{TOT}} = \frac{\eta\tau}{e}(A - \alpha_1)j + \frac{\eta\gamma_{\mathrm{TS}}}{Le^2}\tau_{\mathrm{eff}}^2(2A - \alpha_1)^2 j^2, \qquad (1)$$

where η is the quantum efficiency of the crystal fluorescence, γ_{TS} is the rate constant for the triplet–triplet annihilation as a result of which a singlet

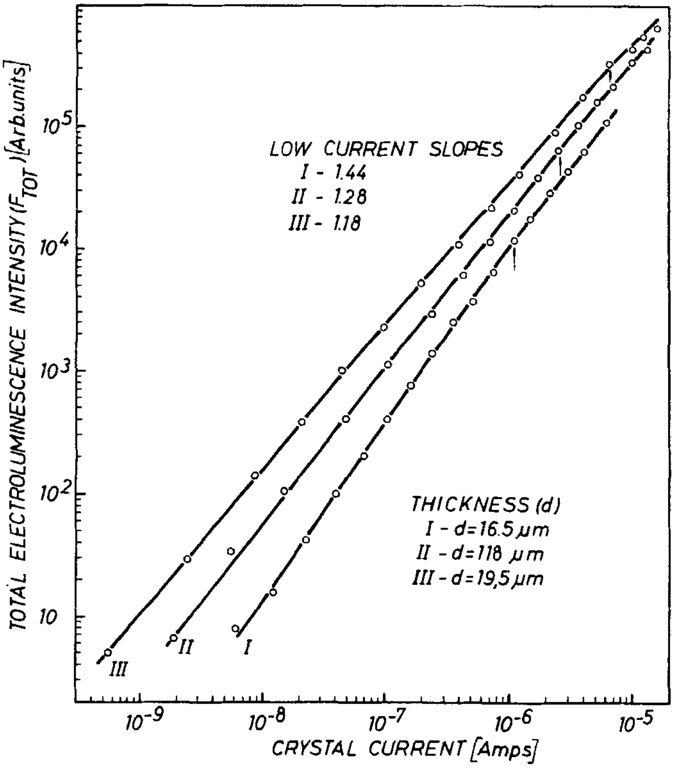

FIGURE 4 Intensity of the total electroluminescence as a function of the double injection current. The arrows mark the points where a change in the slope takes place.

exciton is created, L = the width of the recombination zone, e = electronic charge, $A(j)$ = const† < 1, and α_1 is the probability of triplet exciton creation; τ and τ_{eff} stand for the effective lifetime of the singlet and triplet excitons, respectively.

We shall assume that the dominant decay process for singlets is the fission[20] into two triplets and τ remains constant for all conditions under

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† The constant A stands for the sum of the probabilities of singlet and triplet exciton creation. It is, in principle, less than unity because in some cases recombination leads to vibrationally excited ground states which can decay into the ground state by the radiationless transition, without passing through electronically excited singlet or triplet states. As for $\lambda_{\mathrm{ex}} \gtrsim 400$ nm the fluorescence efficiency of tetracene does not practically depend on wavelength of excitation light,[35] the probability of this transition is independent of the vibrational energy up to ~3 eV which corresponds to the first conduction band of the crystal.

Thus, it is concluded that A is independent of what is the energy of the trapped carrier undergoing recombination. Consequently, as mentioned above, A is not a function of the current density j.

consideration. However, τ_{eff} can be modulated as a result of triplet–triplet (γ_{TOT}) and triplet charge carrier (k_{TD}) interaction.

If we denote the first-order rate constant for the triplet decay β_0 and the total charge concentration by N, then

$$\tau_{\mathrm{eff}}^{-1} = \beta_0 + k_{\mathrm{TD}} N + \gamma_{\mathrm{TOT}} T. \qquad (2)$$

From Eqs. 1 and 2 it is seen that the total EL is not a linear function of the current density and, in general, $F_{\mathrm{TOT}} \sim j^n$, where $1 \leq n < 2$. The value of the power n is determined by the current dependence of L, τ_{eff} and α_1.

It has been shown[9] that under conditions where two injecting contacts are used the recombination width (L) in anthracene crystals does not change for current densities of 10^{-8}–10^{-5} A/cm^2.

The curves in Figure 4 correspond to these conditions up to $\sim 10^{-6}$ A. Thus it is assumed that the main reason determining n in this region is the current dependence of τ_{eff} and α_1.

It is possible that at higher crystal currents the recombination volume increases[9] and the slight decrease in the slope of the log EL-log j relationship can be attributed to this increase.

In addition, at higher current densities the concentration of triplet excitons (T) becomes sufficiently large as to influence the effective triplet lifetime Eq. 2 and to cause further decrease in the value of n.

In order to explain variations of n from crystal to crystal it may be assumed that the probability of triplet exciton creation (α_1) depends on whether the recombining hole and electron are free or one of these carriers is trapped.

Energy conservation requires α_1 to be high when the recombination event takes place on a deeply trapped carrier. Consider traps with the energetic depth greater than E_D which is given by the difference between the conduction band and singlet exciton energy. We assume E_D to be the demarcation energy depth; the carriers sitting in traps of depth $E \geq E_D$ recombine with $\alpha_1 \cong 1$. If $E_F(x) < E < E_D$ ($E_F(x)$ is the local quasi-Fermi level), then

$$\alpha_1(x) = \tfrac{3}{4} + \tfrac{1}{4}\exp\{-[E_D - E_F(x)]/kT_c\}, \qquad (3)$$

where the first term results from the triplet multiplicity[2] and kT_c is the trap parameter characterizing the trap distribution in the crystal (see e.g. Reference 1). For $E_F(x) \geq E_D$, $\alpha_1 \cong 1$ for all trapped carriers.

In fact, a difference in α_1 should be expected for various crystals with different kT_c.

It must be pointed out that $\alpha_1(x)$ is an indirect function of j and the total concentration of traps (H). This is because for any x the quasi-Fermi level is a decreasing function of the current density[21,22] and an increasing function of H.[21] Consequently, $\alpha_1(x)$ also is a decreasing function of current density and according to Eq. 1 causes the power n to change in the opposite direction to that resulting from the current dependence of L and τ_{eff}.

This argumentation implies that due to the movement of the quasi-Fermi level towards conduction and/or valence band, more recombination events take place on shallow-trapped charge carriers,[†] reducing the probability of the direct formation of triplet excitons (Eq. 3).

In order to see the influence of traps we measured EL-j dependence for pentacene-doped tetracene crystals. An example of the results obtained is shown in Figure 5. The magnitude of the specific trapping levels created by pentacene molecules in tetracene crystals are important when electron hole recombination will occur on such sites. The depth of these traps can be estimated as the difference in electron affinities of tetracene and pentacene for electrons, $\Delta A_g = 1.2 - 0.8 = 0.4$ eV[‡] and as the difference in respective ionization energies for holes, $\Delta I_g = 5.3 - 5.1 = 0.2$ eV.[‡] These values are smaller than the demarcation energy depth for tetracene crystal ($E_D = 3.1 - 2.4 = 0.7$ eV) but according to Eq. 3, should influence the probability

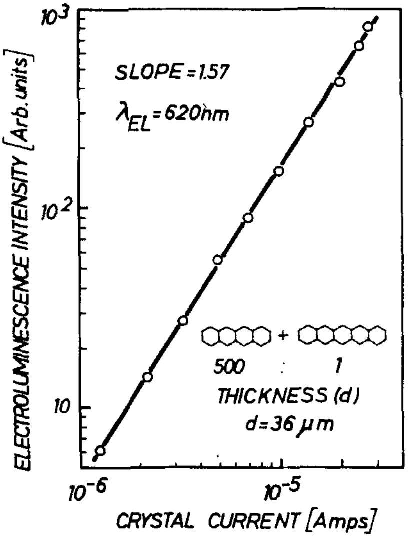

FIGURE 5 Intensity of the pentacene guest electroluminescence as a function of the double injection current in a pentacene-doped tetracene crystal.

[†] Here, trap depth is considered as a factor influencing the result of recombination and not the concentration of free carriers. Therefore, it is related to the demarcation energy (E_D) and shallow has the particular meaning denoting traps with $E_F(x) < E \ll E_D$.

[‡] These data were taken from tabulated values given in Ref. 30.

of yielding a triplet exciton. This will lead to a relative increase in delayed EL. In particular, as a result of heterofusion[25] the guest delayed EL will contribute to the total EL. This contribution which is proportional to the concentration of guest triplets indicates the pentacene traps are considerably involved in creation of triplet excitons. Indeed an increase in the power of the EL–j relationship for the O—O emission of pentacene molecules incorporated in tetracene crystal lattice (~620 nm)[31] is evident from Figure 5. A superlinear dependence between EL and the crystal current was also observed for pentacene-doped anthracene crystals.[36]

In order to observe the delayed EL directly, pulsed electroluminescence characteristics were studied.

B Pulsed Electroluminescence Characteristics

Figure 6 shows the decay curves of the electroluminescence measured for different crystal currents at room temperature when two injecting contacts were used. For each decay a linear part of the curve can be distinguished and decay time evaluated. The values obtained in this way are shown in Table I.

If changes in τ_{eff} account for these values, they should agree with those calculated from the expression Eq. 2. Let us consider the higher limit for

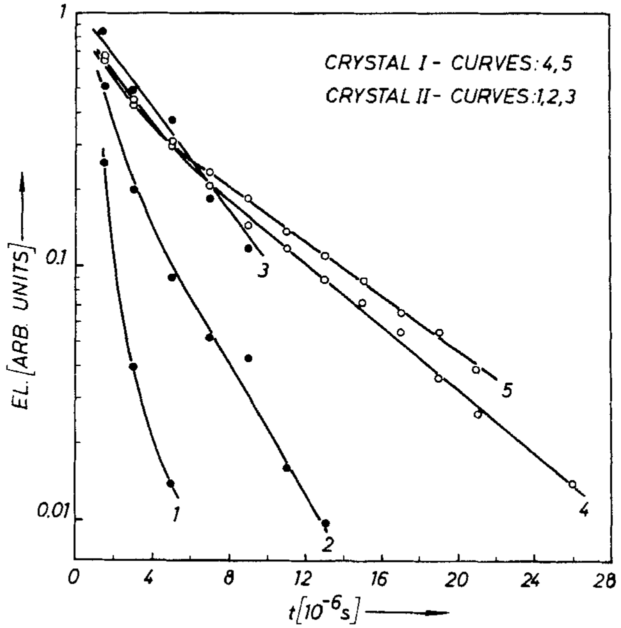

FIGURE 6 The electroluminescence decay for two tetracene crystals under different steady-state current conditions, the decay time decreases with increasing crystal current (see Table I).

TABLE I

Curve/crystal	1/II	2/II	3/II	4/I	5/I
j[A cm^{-2}]	6.3×10^{-5}	2.3×10^{-5}	7.0×10^{-7}	2.8×10^{-5}	6.1×10^{-6}
τ_D [10^{-6} s]	~4.0	6.0	8.8	14.0	20.0
$\tau_{\mathrm{eff}}(N)$ [10^{-6} s]	9.3	10.4	13.7	0.40	0.53

$\tau_{\mathrm{eff}} = \tau_{\mathrm{eff}}(N)$ which is determined only by triplet-charge carrier interaction with the lower limit of the charge concentration given by

$$N = \frac{3}{2}\frac{\varepsilon_0 \varepsilon}{ed^2} U, \tag{4}$$

where U stands for the voltage applied to the crystal. We can, now, calculate

$$\tau_{\mathrm{eff}}(N) = \tau_0[1 + k_{\mathrm{TD}} N \tau_0]^{-1}. \tag{5}$$

For the purpose of the present discussion we will use $\tau_0 = 3.5 \times 10^{-5}$ s[16] and $k_{\mathrm{TD}} = 5 \times 10^{-9}$ cm^3 s^{-1} (Ref. 19). Table I shows $\tau_{\mathrm{eff}}(N)$ obtained from Eqs. 4 and 5 and the results shown in Figure 1.

It is seen that in the case of crystal II $\tau_{\mathrm{eff}}(N)$ is relatively close to the measured decay time and after taking into account the third term in Eq. 2 or a greater value of N one can expect much better agreement. This is not the case for the crystal I.

We can conclude that the electroluminescence decay in the crystal II is attributed to the effective triplet exciton lifetime and in the crystal I to the charge carrier trapping time. This would agree with the variation in slopes of steady-state log EL-log j characteristics for various crystals. The long trapping indicates the effective traps to be deeper in average as compared to the short-trapping time case. This means that the triplet production and thus the delayed EL in the crystal I is relatively more efficient than in the crystal II.

A higher value of the power in EL-j dependence observed for the crystal I appears quite consistent with above predictions (see Figure 4).

These conclusions agree well with those resulted from our study of magnetic field effects on tetracene electroluminescence.[23]

If the delayed component due to the triplet–triplet annihilation is present in tetracene crystal EL the magnetic field decrease in the triplet-charge carrier interaction rate constant[13,32] should be demonstrated by the increase in the delayed EL. This is opposite to the low-field decrease of prompt EL due to the increase in the rate of molecular singlet fission.[13,33]

Thus, in tetracene, the algebraic sign of the magnetic field effect for low fields (below ~500 Gs) depends on the contribution of the delayed EL. It means that it is possible to distinguish the crystals with large and low delayed components of EL by examining the magnetic field dependence of the total EL. This is shown in Ref. 23 for the crystals I and II. It appears that, in contradiction to the crystal II, the dominant proportion of the electroluminescence in the crystal I is the delayed EL due to the triplet–triplet annihilation process.

Let us now consider the apparently paradoxical problem, relatively large ($\sim$7.7) slope of $\log j - \log U$ dependence for the crystal II (Figure 2) and relatively small ones ($\sim$5.5 and $\sim$6.5) for the crystals III and I, respectively. This slope that is expected to characterize the trap parameter (kT_c) should be larger for the crystals I and III than that for the crystal II.

This paradox can be resolved by involving the triplet exciton-trapped charge carrier interaction as an additional process detrapping charge carriers in the crystal.

At sufficiently high triplet concentrations exciton release of carriers will be comparable with thermal detrapping and the power of j–U relationship

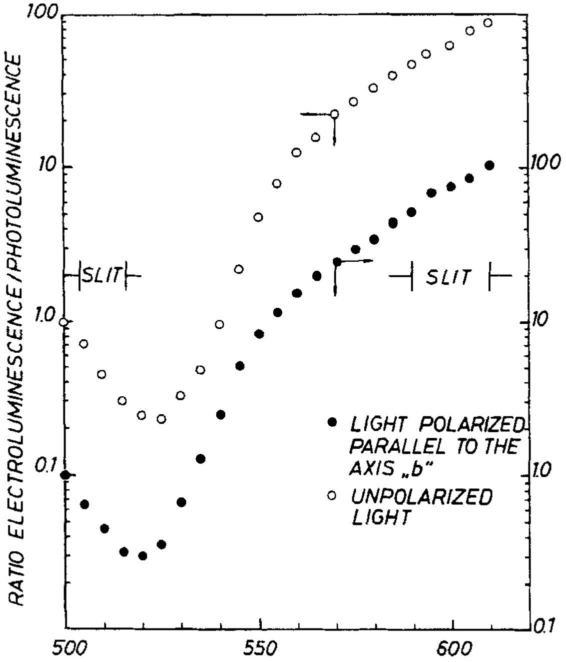

FIGURE 7 A comparison of the electro- and photoluminescence spectra in the tetracene crystal II; the front observed photoluminescence was excited by the light with λ = 366 nm falling on the gold covered surface of the crystal. The filled circles were obtained when both types of emissions were observed through a polarizer oriented parallel to the axis "b" of the crystal.

become smaller (see Reference 1 where it has been shown for the limiting case of high exciton concentration with one injecting contact). If the triplet concentration is low, thermal detrapping dominates and the current will be the same as in the absence of excitons. Furthermore, the magnetic field effect on double injected current in the presence of the effective triplet exciton detrapping must be observed.

Indeed in the case of the crystal I and III we have found ~1–3 % decrease in the current, applying the magnetic field of $B = 6$ kGs oriented along the high-field resonance direction (c.f. Ref. 13, 32, 34). This effect could not, in the limit of error (0.2 %), be detected in the case of the crystal II. There is, however, no simple correlation between the slopes given in Figures 1 and 4. This is because the crystal region responsible for the exciton-enhanced current is rather a complicated function of the crystal thickness.

C Electroluminescence Spectral Characteristics

The electroluminescence spectrum appears to be different from that of photoluminescence. A comparison of these two kind of spectra taken at room temperature with the same crystal (II) is shown in Figure 7.

The minima in the ratio of electroluminescence/photoluminescence are found to be at ~518 nm in the case of emissions observed with a polarizer parallel to the axis b of the crystal and at ~525 nm in the case of unpolarized emissions. A possible explanation in the long-wavelength region ($\lambda \gtrsim 560$ nm) is the assumption that in addition to free singlet excitons other emitting species are produced more efficiently in the recombination processes than under excitation by light.

This species can be a molecular pair in sandwich configuration[26] a genuine excimer[27,28] or a trapped singlet exciton.[29] Such a supposition seems to be supported by the conclusion that free-trapped carrier recombination is the important recombination mechanism.

Assuming the crystal defects to trap the injected charge carriers it can be said that the most recombination events occur at the lattice sites showing a certain distribution of molecular distances and orientations different from those in an ideal crystal.

Thus the formation probability of any of the above mentioned species is in this case much higher than in the case of optical excitation of the crystal.

The difference between electroluminescence and photoluminescence spectra in the short-wavelength region can be ascribed to the spatial distribution of recombining charge carriers which will be analyzed in the forthcoming paper.

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