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The Variation of the Carrier Recombination Region with Carrier Density in Anthracene Crystals†

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Abstract—The time dependence of slow electroluminescence has been used as an experimental probe for studying the physical characteristics of the recombination region in anthracene. Under conditions where two injecting contacts are used, and neither carrier is trapped to a large extent, the recombination zone is found to occupy approximately 0.3 of the crystal volume for current densities of 10^{-5}–10^{-8} amps cm^{-2}. When forced hole injection is used, the recombination volume at low currents decreases, particularly at low temperatures. This decrease in recombination volume is discussed in terms of carrier trapping and filament formation.

1. Introduction

If electrons are injected into one side of a crystal and holes into the other side, and the carriers are allowed to drift into the crystal by an applied electric field, then there will necessarily be some recombinations between electrons and holes. If the recombination probability is very small, most of the carriers will drift through the crystal without recombining and they will then decay near the other contact, where the decay mechanisms are influenced by the contact-crystal interface. If the recombination probability is fairly large, most of the carriers will recombine within the bulk of the crystal. For molecular crystals such carrier recombinations produce highly excited neutral exciton states which then participate in a wide variety of relaxation mechanisms. A number of experiments have been performed with anthracene crystals, which have made use of

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double injection[1] of carriers and subsequent recombination as a means of populating excited states, such as singlet,[2] triplet[3] and charge transfer exciton[4] states. Multiexciton interactions are also possible if the exciton densities produced following carrier recombination are sufficiently high. The densities of these excitons is obviously a function of both the total number of electron-hole pairs injected, and the spatial distribution of the recombination events.

The region in which most of the carriers recombine is called the recombination region. The width of this region, perhaps much smaller than the actual crystal thickness, is a complex function, depending upon crystal characteristics such as carrier mobility, recombination rate constant, trap parameters[5] etc. There are two main reasons why the magnitude of the width of this recombination region is important. First, in order to calculate exciton densities following carrier recombination, it is necessary to know the recombination rate density, which is a function of both the number of carrier injected, i.e. the current, and the volume in which these carriers recombine. Secondly, the width of the recombination region can be calculated from double injection[5] theories, and a comparison with experimental results then offers a practical test of the injection theory. An obvious technique to measure the width of the recombination region, one would think, would be to observe the spatial distribution of electroluminescence, that is the light emission produced following carrier recombination. Electroluminescence from an anthracene crystal is readily visible, indeed, anthracene has even been proposed for use as a LED.[6] Unfortunately due to the high refractive index of the crystal, a substantial fraction of the light emitted undergoes many reflections inside the crystal, and the region of emission cannot be defined.[7] However anthracene electroluminescence is produced by two district processes. Carrier recombination produces either an excited singlet exciton which unimolecularly radiatively decays almost immediately ($\sim 10^{-9}$ sec) or a triplet exciton which only produces light following bimolecular annihilation with a second triplet exciton, the light emitted having time characteristics of $\sim 10^{-3}$ sec. Since triplet–triplet annihilation,[8] is a quadratic process the electroluminescence produced in this manner offers a second experimental probe to measure the recombination region width. This is because for all nonlinear processes,

the total rate integrated over the crystal volume, depends on the distribution of this rate over the crystal.

We have used this quadratic triplet–triplet annihilation process to measure the width of the recombination region for different anthracene crystals as a function of the crystal current. We have also studied tbe change in recombination width which occurs between double injection and forced injection electrode systems. Forced injection occurs where individually poorly injecting contacts become efficient injecting contacts when opposed to counterion injecting contacts,[2] and electroluminescene results.

2. Theoretical Considerations

The triplet exciton concentration within an anthracene crystal is given by

$$\mathrm{d}n/\mathrm{d}t = g - \beta n - \gamma n^2 \tag{1}$$

where n is the triplet density, g the triplet generation rate and, β and γ the monomolecular and bimolecular triplet decay rate constants respectively.[8] Introducing the normalized parameters

$$\hat{g} = \frac{\gamma}{\beta^2} g, \quad \hat{n} = \frac{\gamma}{\beta} n, \quad \hat{t} = \beta t \tag{2}$$

Equation (1) becomes

$$\mathrm{d}\hat{n}/\mathrm{d}\hat{t} = \hat{g} - \hat{n} - \hat{n}^2 \tag{3}$$

The solution of this equation is obviously simplified if $\hat{n} \gg 1$ or $\hat{n} \ll 1$ but for our experimental situation it can be shown $\hat{n} \simeq 1$, and hence both $\hat{n}$ and $\hat{n}^2$ have to be considered. When triplet production is stopped, $\hat{g} = 0$, the time decay of the triplet density is then given by

$$\hat{n}(\hat{t}) = \frac{\exp[-(\hat{t}+\hat{t}_0)]}{1-\exp[-(\hat{t}+\hat{t}_0)]} \tag{4}$$

where

$$\hat{t}_0 = ln\frac{1+\hat{n}_0}{\hat{n}_0} = ln\frac{\frac{1}{2}+\sqrt{\hat{g}_0+\frac{1}{4}}}{-\frac{1}{2}+\sqrt{\hat{g}_0+\frac{1}{4}}} \tag{5}$$

and $\hat{n}_0$ and $\hat{g}_0$ are the triplet density and generation rate respectively the instant the triplet generation ceases. The delayed electroluminescence is produced by triplet–triplet annihilation and thus its

intensity is proportional to $\hat{n}^2$. The measured electroluminescence signal F is thus given by

$$F = \alpha \int \hat{n}^2 \, \mathrm{d}V \tag{6}$$

where the integration is performed over the whole crystal volume V, and α is a constant including the annihilation rate constant, geometric factors etc. We will assume that the generation rate $\hat{g}_0$ is homogeneous within the recombination region, Volume V_r, and is zero outside this region. In reality g_0 is a complex function of various crystal parameters. But for these experiments on anthracene where carrier mobilities are approximately equal and carrier trapping was nominal, a constant value for g_0 is a good first approximation. Then by inserting Eq. (4) into Eq. (6)

$$F(\hat{t}) = \alpha V_t \hat{n}^2 = \alpha V_r \frac{\exp[-2(\hat{t}+\hat{t}_0)]}{\{1-\exp[-(\hat{t}+\hat{t}_0)]\}^2} \tag{7}$$

By comparing the experimentally measured $\log F(\hat{t})$ curve with the calculated curve

$$\log \hat{n}^2 = 2 \log \frac{\exp[-\hat{t}]}{1-\exp[-\hat{t}]} \tag{8}$$

t_0 and $\hat{n}_0$ can be determined and hence with Eq. (5) the magnitude of $\hat{g}_0$ is obtained. The recombination volume V_r then follows from Eq. (7) for $\hat{t} = 0$, that is

$$V_r = \frac{F_0}{\alpha \hat{n}_0^2} \tag{9}$$

α cannot be experimentally determined with sufficient accuracy, unfortunately and only relative values for V_r are obtained.

A second method for calculating V_r exists due to the fact that the probability of a recombining electron-hole pair with overall triplet character to yield a triplet exciton is close to unity: that is there are no other significant paths for decay. From spin statistics, the ratio of electron-hole pairs with overall triplet characture to those with overall singlet character is 3:1 and thus the probability of a recombining electron-hole pair to yield a triplet exciton is $\frac{3}{4}\eta$ where η is the overall probability of electron-hole recombination. When a

current J is flowing through the crystal and recombining in the volume V_r, the triplet generation rate $\hat{g}_0$ is given by

$$\hat{g}_0 = \frac{\gamma}{\beta^2} g_0 = \frac{\gamma 3\eta J}{\beta^2 4 V_r}$$

and from this

$$\frac{V_r}{\eta} = \frac{3\gamma J}{4\beta^2 \hat{g}_0} \tag{10}$$

Since the values for γ, β and J are either directly observed or may be determined in a secondary experiment, a reliable value for $V_r\eta^{-1}$ may be determined from Eq. (10).

3. Experimental Results

We will concentrate our attention to the results obtained from one crystal with different contact combinations and at different temperatures, but measurements with other crystals showed similar results. Figure 1 shows the decay curves of the delayed electroluminescence at room temperature when two injecting contacts were used.[2] The decay curves for different currents are superimposed on the theoretical curve given by Eq. (8). For each current, the decay was measured over about 2 decades and good agreement with the theoretical curve was obtained. The triplet lifetime β^{-1} of this crystal determined in a separate experiment was 22.5 msec, and for γ the literature value of $2 \times 10^{-11}\,\mathrm{cm^3\,sec^{-1}}$ was used.[9] The calculated volumes of the recombination region, using Eqs. (9) and (10) are shown in Fig. 2 as a function of the crystal current.

The results for V_r and V_r/η for the same crystal, but with electroluminescence produced from a forced injection contact combination[2] are shown for room temperature in Fig. 3 and for about $-10\,^\circ\mathrm{C}$ in Fig. 4. At low crystal currents, the electroluminescence decay becomes almost perfectly exponential and thus predicted values for $\hat{n}_0^2$ and $\hat{g}_0$ are less accurate in this region [as can be seen in Fig. 1].

4. Discussion and Conclusions

To discuss the concept of the recombination region, let us first consider the case of double injection into a trap-free insulator with

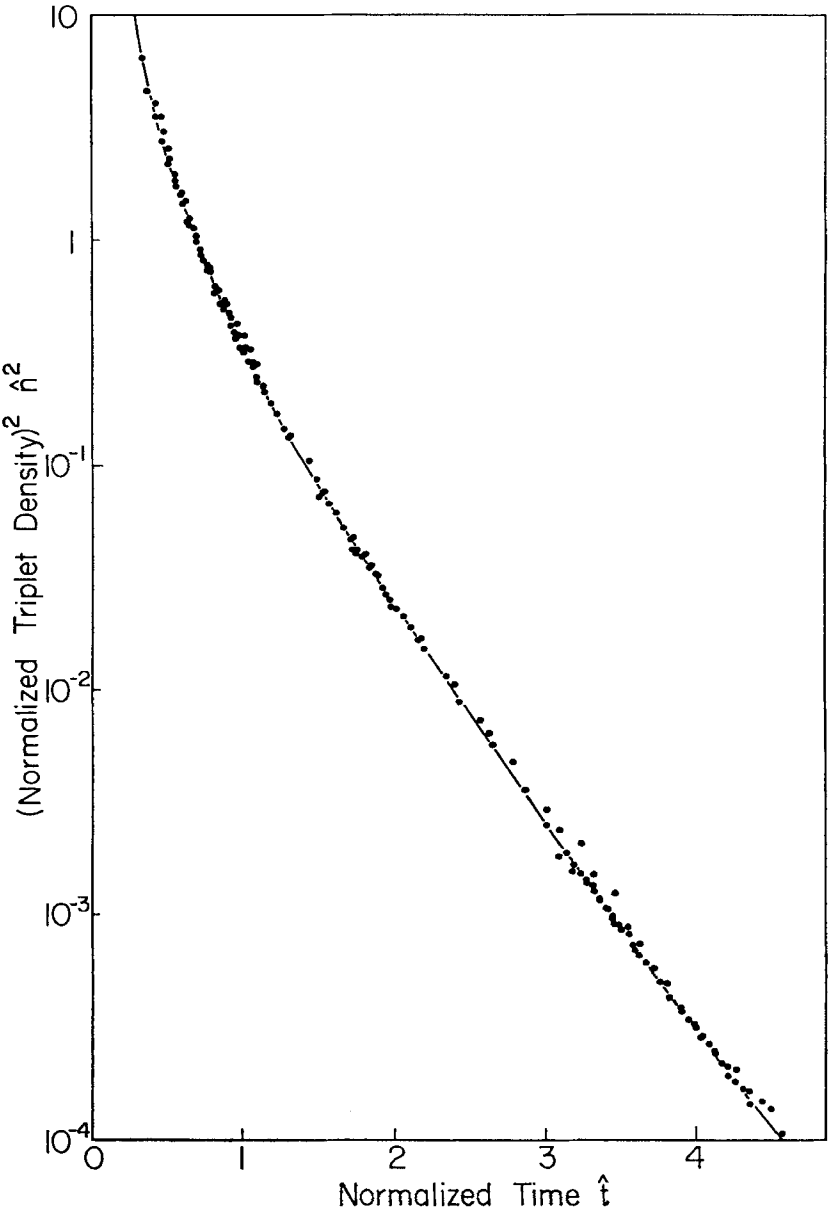

Figure 1. Theoretical decay curve (solid line) and experimental results (.) obtained for the electroluminescence decay with different crystal currents.

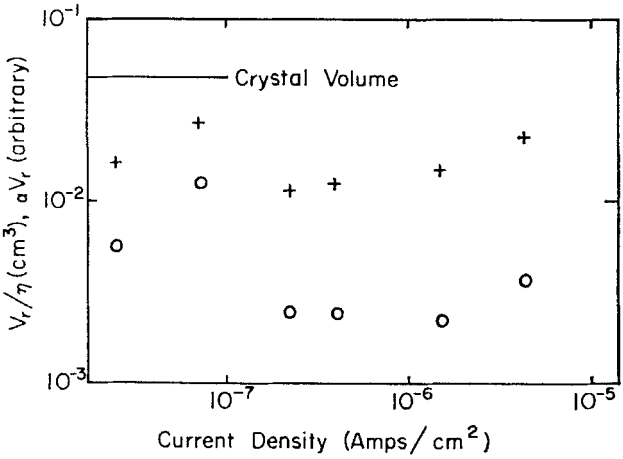

Figure 2. Current dependence of the absolute and relative volume of the recombination region, V_r/η (+) and αV_r (○) respectively. The measurements were made at room temperature with two injecting contacts.

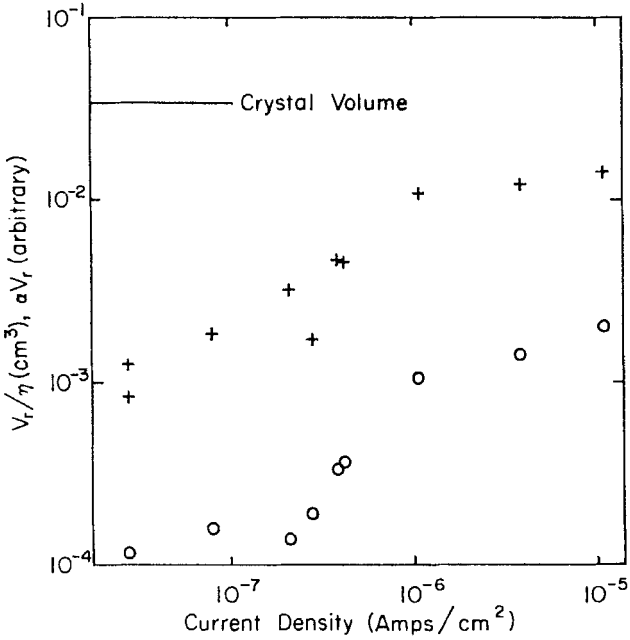

Figure 3. Current dependence of the absolute and relative volume of the recombination region V_r/η (+) and αV_r (○) respectively. The measurements were made at room temperature on the same crystal as in Fig. 2 but with forced injection contacts.

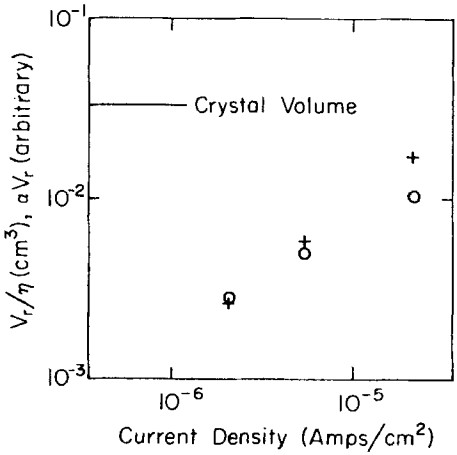

Figure 4. Current dependence of the absolute and relative volume of the recombination region V_r/η ($\bigcirc$) and αV_r ($+$) respectively, at $-10\,^{\circ}$C. These results were obtained with the same crystal as in Figs. 2 and 3 with a forced injection electrode system.

bimolecular recombination. This case has been treated first by Parmenter and Ruppel[10] and later by Rosenberg and Lampert.[11] The solutions are characterized by the values of $\nu_n = 2e\mu_n/\epsilon c$ and $\nu_p = 2e\mu_p/\epsilon c$, where e is the electronic charge, μ_n and μ_p the electron and hole mobilities respectively, ϵ the dielectric constant and c the bimolecular recombination rate constant. The electron current J_n and the recombination rate r are related by the continuity equation $\mathrm{d}J_n/\mathrm{d}X = er$. For $\nu_n \approx \nu_p$ $\nu_p \ll 1$ (large c, small μ) the carriers recombine as soon as they meet, resulting in a small recombination region inside the crystal. For $\nu_n \approx \nu_p \gg 1$, most of the carriers will cross the crystal without recombining and the carriers recombine mostly at the contacts, resulting in two small separate recombination regions. The intermediate case occurs for $\nu_n \simeq \nu_p \simeq 1$, where the recombination region is expanded throughout the crystal. When we introduce either trapping, or very different electron and hole mobilities, the two cases $\nu_n \gg 1$, $\nu_p \gg 1$ and $\nu_n \ll 1$, $\nu_p \ll 1$ become alike. This is because for both cases in general, either the hole or electron current will dominate and there will be only one small recombination region close by one of the two contacts.

For anthracene, where the Langevin formula[12] for the re-

combination rate constant $c = e(\mu_n + \mu_p)/\epsilon$ is expected to hold, and where the electron and hole mobilities are of the same order, $\nu_n \simeq \nu_p \simeq 1$, and therefore in the trap-free case the recombination region is large. Indeed an approximate calculation by Helfrich shows, that the recombination region equals about the crystal thickness.[3] From Fig. 2, which shows the recombination region volume under double injection and at room temperature, calculated from Eqs. (9) and (10), it can be seen that the measured absolute volume V_r/η and the relative value for V_r are both approximately constant over the complete current range studied. The ratio of αV_r and V_r/η give a relative value for the recombination probability. Because η does not substantially change and because the high currents injected are close to the trap-free limit,[2] the assumption that η is close to unity is satisfactory. With $\eta = 1$ the volume of the recombination region becomes about 1/3 of the crystal volume. This magnitude of the recombination region is expected for high crystal currents where trapping is negligible; but that this volume remains constant with lower crystal currents when trapping is considerable, indicates that the densities of hole and electron traps are about equal.

When silverpaste is used instead of a hole injecting contact, electroluminescence is produced due to forced hole injection.[2] Fig. 3 shows the corresponding calculated recombination volumes at room temperature. At high currents we again find a volume for the recombination region of about 1/3 of the crystal volume assuming $\eta = 1$. η remains constant as shown by the constant ratio of αV_r and V_r/η. At small currents the recombination volume V_r decreases. Because this decrease was not observed for double injection contact combinations on the same crystal, this decrease is related to the characteristics of hole injecting silverpaste contact. When the crystal is cooled to $-10\,^{\circ}\mathrm{C}$, the crystal current decreases by a factor of about five, indicating carrier trapping becomes more important, and it can be seen from Fig. 4 that the volume of the recombination region becomes much smaller than the crystal volume except with the highest crystal currents. It is possible that this temperature decrease is again due to characteristics of the silverpaste contact, but it is more likely that this is an effect simply due to increased trapping, so that over almost the entire crystal thickness the electron current dominates and the recombination region becomes confined near one

of the contacts. We favour this latter explanation for the temperature decrease of V_r, because, first the same changes in V_r are observed at room temperature with crystals showing more trapping, and, secondly it is generally observed that for our crystals hole traps become important at temperatures below $-10\,^{\circ}\mathrm{C}$.[13] In order to explain quantitatively the observed behaviour of the recombination region, a thorough analysis of the carrier distribution is necessary. Although it has been shown that this is possible, it involves an intense study of the crystal, including trap parameters etc. One could then study the validity of the assumption of Eq. (7), i.e. that the triplet generation rate $\hat{g}$ is constant within the recombination region, and finally Eq. (6) could be solved explicitly. The assumption of a constant generation rate is valid for a large recombination regions, but is less satisfactory for a small recombination regions.

We can now discuss the room temperature decrease in the recombination region volume with decreasing crystal current for forced injection contacts in terms of contact phenomena. First if this decrease was due to insufficient injection from the silverpaste contact, this defficiency would also give rise to a decreased recombination probability η. This is because some of the electrons would reach the anode before recombining and would not be able to produce a free triplet. This is not observed. A second explanation, namely the formation of filaments is probable, because sometimes with forced injection the electroluminescence intensity is not homogeneous throughout the crystal but intense spots also appear. Similarly the crystal current sometimes becomes noisy, a high frequency ac component being superimposed upon the dc component.[14] Electroluminescence emission is seen to mirror the current characteristics in all cases.

Thus whereas in the analysis considered earlier, we have assumed the problem to be of a planar nature, perpendicular to the applied field, this would no longer be correct if filaments were present. These filaments would constitute direct channels wound from one contact to another and would support most of the current. The filament itself would be the region where most of the delayed electroluminescence would be produced. As shown theoretically by Ridley[15] and experimentally with silicon and other crystals, the formation of filaments is always associated with a negative, current

controlled resistance.[16] A model for the forced injection has been proposed,[2] but filament formation was not considered. Nevertheless, independent of the exact model for injection, the occurrence of a negative resistance cannot be ruled out in anthracene. For low crystal fields, silverpaste acts only as a blocking contact, and thus only an electron current is observed. The transition from this regime to the one where silverpaste injects holes may well show a negative resistance, because when hole injection occurs, silverpaste is able to deliver currents of up to 1 mamp/cm^2 without saturation effects. The crystal could then be divided into regions of high and low current densities, and the regions with high current densities (the filament) could become larger as the crystal current increased. The experimental current-voltage curves do not show a negative resistance, but only a very steep increase at the breakthrough voltage. However as has been noted, often the electroluminescence intensity distribution is not homogenous with silverpaste contacts. Then for example in Fig. 3, at a current of about 10^{-6} amp/cm^2 the filaments could become so large as to fill the whole crystal volume for higher currents and the current distribution becomes homogenous. Experimentally it is not possible to determine whether filament formation is indeed present, however such a change in the carrier distribution does not alter the general observation of decreasing recombination volume with decreasing current.

5. Summary

Delayed electroluminescence is produced by the mutual annihilation of two triplet excitons. As a quadratic process, the triplet decay rate associated is a function of the local density of triplet excitons. Therefore we have used the time decay of slow electroluminescence as an experimental probe for the physical size of the carrier recombination region. The experimental decay curve was compared directly to the theoretical decay curve. The total number of injected carriers was calculated from the total crystal current, and the recombination region volume was obtained from the magnitude of the equivalent triplet density determined from theoretical decay curves. Results showed that when two injecting contacts are used, the recombination region occupies approximately one third of the

crystal volume for injected current densities of $10^{-8} - 10^{-5}$ amp/cm^{-2}. When electroluminescence is produced by forced injection, the recombination regions for high crystal currents, 10^{-5} amp/cm^{-2}, is also about 0.3 of the crystal volume, but the region becomes smaller for lower current densities even at room temperature. The origin of this decrease in recombination volume with low crystal currents is associated with the injection mechanism, and may be due to the formation of filaments. Such filaments are often observed with very high crystal currents. At lower temperature, carrier trapping becomes important.

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