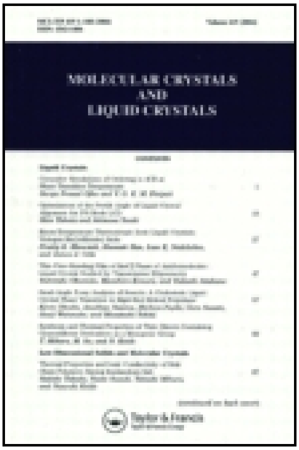

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Recombination Radiation and Fluorescence in Doped Anthracene Crystals‡

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Abstract—In anthracene crystals doped with tetracene the spectrum of the radiative recombination of electrons and holes has been studied at different currents through the crystal. The spectrum is compared with the steady state fluorescence and the delayed fluorescence.

With electrochemical electrodes it is possible to inject holes as well as electrons into anthracene crystals.[1-3] This two-carrier current is limited by space-charge and recombination of the carriers. In anthracene the recombination is partially radiative and emission of the characteristic fluorescence is observed. This phenomenon has been attributed by Helfrich and Schneider[4] to recombination of electrons and holes via the first excited singlet state.

The experiments reported here are an extension of previous investigations of recombination and energy transfer in doped anthracene crystals.[5,6]

Zone-refined anthracene with a certain molefraction, C_T, of tetracene was used. The crystals were grown in a Bridgman furnace.

In such a mixture it is to be expected that the emission corresponds to the fluorescence of both partners as a result of energy transfer from host (anthracene) to guest (tetracene). It has been shown[7] that if such a crystal is excited by an external light source,

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the quantum yield for the fluorescence of tetracene, I_T, is related to that of anthracene, I_A, by the equation $I_T/I_A = K \cdot C_T$, where K does not depend on the intensity of the excitation and is approximately 10^5. This expression shows that for $C_T = 10^{-5}$ the fluorescence of both partners should be of the same magnitude.

Two series of experiments were performed. In the first the recombination radiation emitted along the b-axis of the crystal (i.e. perpendicular to the current) was focused on the entrance slit of a Jarrell-Ash 0.25 m grating monochromator and the output was measured as a function of current with a photomultiplier. Using filters instead of the monochromator the emission as a function of current was measured at different fixed wavelengths. In the second series of experiments the fluorescence of the same crystal was investigated with the crystal in the same position. The only change is that one electrode is removed and the crystal is excited in this position with UV from a 125 watt mercury lamp or with light from a 900 watt Xenon lamp. With this geometry the influence of the internal absorption is identical in both cases. The spectrum of the fluorescence has been recorded with the crystal illuminated (steady state fluorescence) and after the exciting light was removed (delayed fluorescence).

The experimental results for a anthracene crystal doped with tetracene 1 ppm are presented in Fig. 1. For the recombination radiation there are recordings of the emission spectra at two currents with the crystal at room temperature (Fig. 1(a)). The two spectra consist of five bands, three of them corresponding to tetracene and two to anthracene. For comparison the steady state fluorescence and the delayed fluorescence of the same crystal is displayed in Fig. 1(b) and 1(c) respectively.

The steady state fluorescence differs significantly from the recombination spectra with regard to the efficiency of tetracene which appears to be considerably higher for the recombination. However the intensity of the spectrum of the delayed fluorescence (2.5 msec after the excitation has been turned off) shows approximately the same distribution as the recombination radiation at low currents.

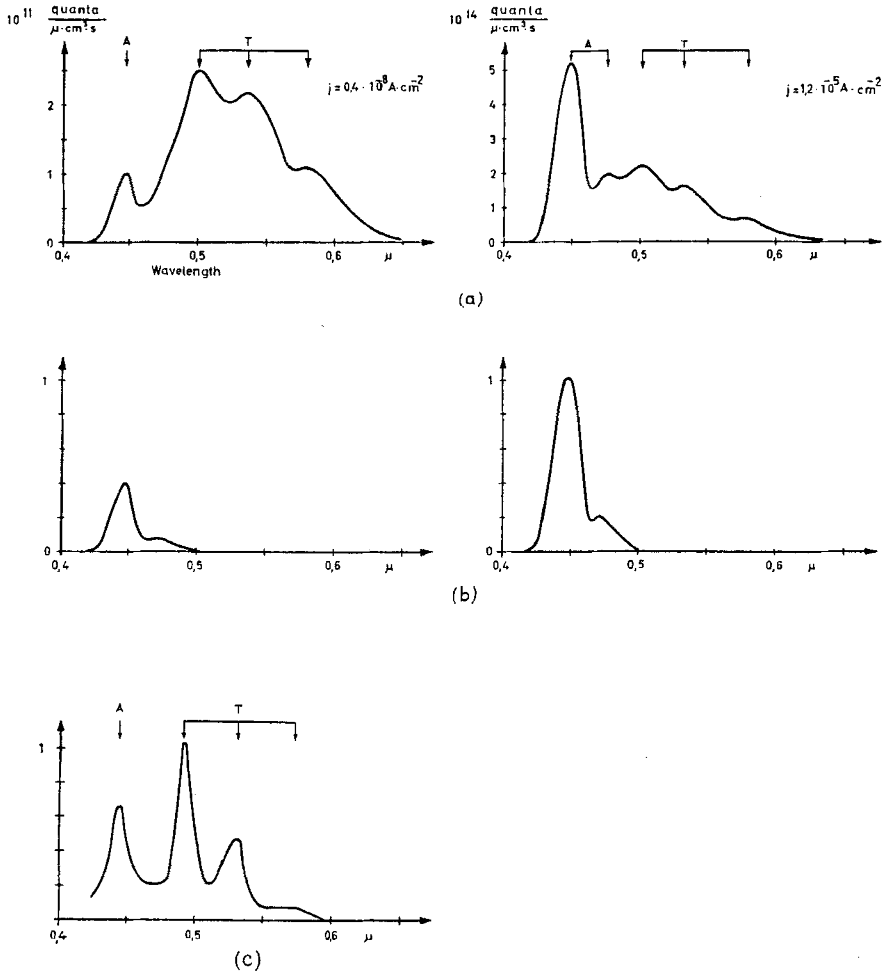

Figure 1. Spectra of (a) radiative recombination, (b) steady state fluorescence and (c) delayed fluorescence in the same crystal, anthracene doped with tetracene 1 ppm. A: anthracene, T: tetracene.

In contrast to the steady state fluorescence which does not change with excitation level the recombination radiation spectrum depends on the current. Therefore the emission as a function of the average carrier density ($\propto j \cdot V^{-1}$) has been measured at different fixed wavelengths. The results for $\lambda = 4340$ Å (o), representative for anthracene, and for $\lambda = 5480$ Å (+), representative for tetracene, are shown in Fig. 2. The emission, L, in the anthracene region of the spectrum increases as $L_A \propto (j \cdot V^{-1})^{1.8}$. This power law holds over five decades. In the tetracene region a smaller slope of about $L_T \propto (j \cdot V^{-1})^{1.3}$ is observed except at small currents where the slope is the same for both. The same general behaviour has been observed in other anthracene crystals with different doping levels and at different fixed wavelengths.

The spectral dependence of the radiative recombination and its current dependence can be explained as follows: it is known that tetracene in anthracene acts for electrons as a deep trap[8] with a capture cross section of about 10^{-17} cm^2. For holes tetracene acts as a shallow trap[8] of depth 0.43 eV with a cross section of 10^{-15} cm^2. Therefore at low injection rate the recombination of electrons occurs predominantly with holes localised on tetracene molecules. The recombination leaves tetracene in a excited molecular state which decays to the ground state by emission of the guest fluorescence. With higher currents a smaller fraction of the injected holes are trapped and the bimolecular recombination in anthracene predominates. A similar behaviour has been observed also in pyrene-doped anthracene crystals.

It has been observed that the relative intensity of the bands changes slightly with current, especially in the spectral region of tetracene. Our experiments suggest, that this is caused by a background contribution present in this region of the spectrum, due to other traps from yet unidentified impurities. Even in undoped single crystals the recombination radiation in anthracene has a tail going out to longer wavelengths than the fluorescence.

Turning to the delayed fluorescence, its decay is shown in Fig. 3 for three different wavelengths. The decay of both anthracene and tetracene show multiple timeconstants. The broken line in

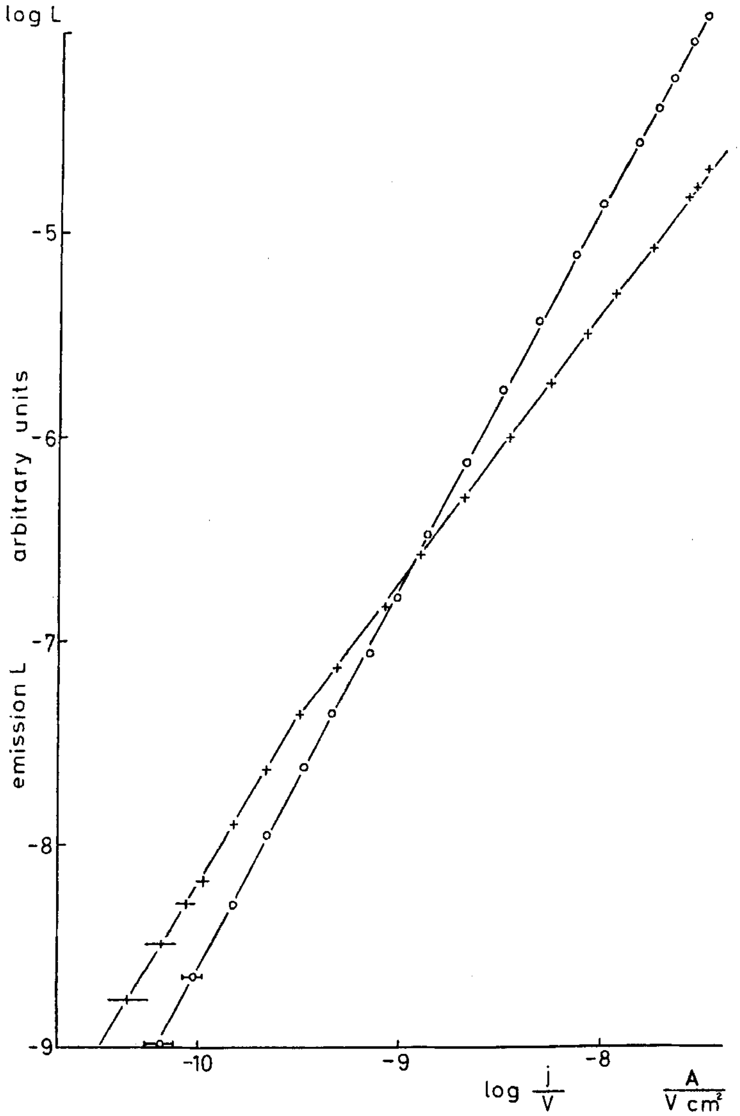

Figure 2. Intensity of the recombination radiation vs. log ($j \cdot V^{-1}$) for the same crystal as in Fig. 1. $\lambda = 4340$ Å (o) anthracene, $\lambda = 5480$ Å (+) tetracene.

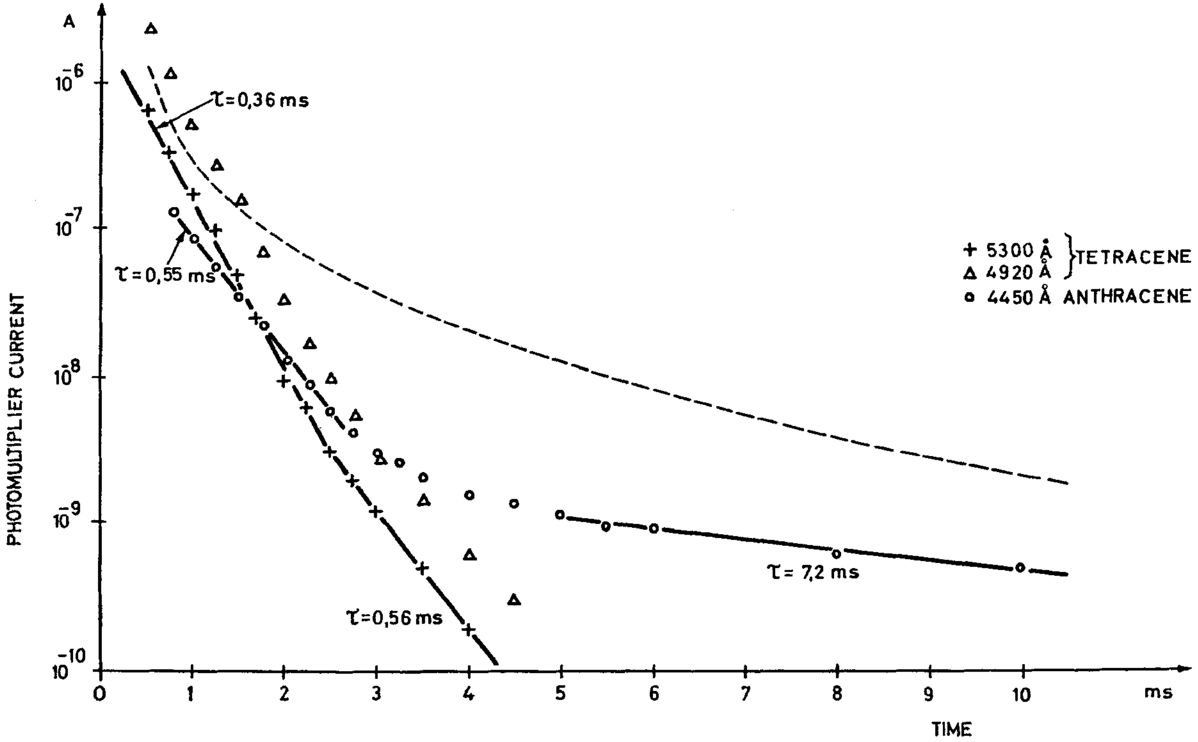

Figure 3. Time decay of the delayed fluorescence at different wavelengths (same crystal as in Fig. 1).

Fig. 3 indicates the curve which is expected if the anthracene triplet population were controlled by triplet-triplet annihilation and decay to the ground state. In order to fit the measurements at short times the annihilation of anthracene triplets with tetracene triplets must be considered. If the annihilation of two triplets of different nature really exists in this system it could possibly also contribute to the spectral distribution of the recombination radiation in doped anthracene crystals.

One conclusion which can be drawn from these experiments is that for certain cases the investigation at different wavelengths of the recombination radiation and the delayed fluorescence at short times are far more sensitive to impurities than is the measurement of the triplet lifetime of anthracene only or the current-voltage dependence.

REFERENCES

1. Helfrich, W. and Schneider, W. G., *Phys. Rev. Letters* **14**, 229 (1965).
2. Mehl, W., *Int., Luminescence Symposium*, Munich (1965).
3. Granacher, I., Organic Crystal Symposium, Chicago (1965).
4. Helfrich, W. and Schneider, W. G., *J. Chem. Phys.* **44**, 2902 (1966).
5. Zschokke-Grynacher, I., Schwob, H. P. and Baldinger, E., *Solid State Comm.* **5**, 825 (1967).
6. Schwob, H. P. and Zschokke-Grynacher, I., 4th Molecular Crystal Symposium, Enschede, 1968, p. 136 (unpublished)
7. Benz, K. W. and Wolf, H. C., *Z. f. Naturforschung* **19a**, 181 (1964).
8. Hoesterey, D. C. and Letson, G. M., *J. Phys. Chem. Solids* **24**, 1609 (1963).