laxation time, these do not have wavelike character. Finally, we remark that kinetic-energy effects arising from overlap terms in E^2 for several fluxoids are not likely to exceed the ones discussed here, since the coefficients of $\dot{r}_1^2$ will contain rapidly diminishing Bessel functions of the distance between the lines.

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RECOMBINATION RADIATION IN ANTHRACENE CRYSTALS*

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In this note we report the observation of fluorescence due to recombination of electrons and holes in anthracene single crystals. High concentrations of carriers were obtained by using injecting electrodes. The crystals used were 1 to 5 mm in thickness and 1 cm in diameter. They were melt-grown from chromatographed and repeatedly zone-refined material. Glass tubes cemented to the crystal surface contained the liquid electrodes. The contact areas were 0.2 cm^2, and the direction of current was perpendicular to the *ab* plane.

It is known that steady-state space-charge-limited (SCL) hole currents can be injected into anthracene.[1-3] Most of the space charge is trapped, the traps being distributed more or less exponentially in depth. In previous work a concentrated solution of $KI + I_2$ in water[4] was often used for hole injection. We found that this electrode was Ohmic only up to 3×10^{-8} A. We could obtain a saturation current of 3×10^{-6} A and higher by use of a solution of positive anthracene ions (prepared by adding $AlCl_3$ to a solution of anthracene in nitromethane[5]). Aqueous Na_2SO_4 solution served as the opposite noninjecting electrode.

Injection of electrons into anthracene has hitherto not been observed. Using a solution of negative anthracene ions (prepared by interacting metallic sodium with a solution of anthracene in tetrahydrofuran[6]), we could inject steady-state electron currents up to 10^{-5} A without observing saturation effects. The following observations indicated that these currents were SCL: (1) At low voltages the dependence of current on voltage is greater than a second power, as is generally found with SCL hole currents. (2) These low currents can be increased by light, the wavelength dependence of the response being completely analogous to that of SCL hole currents.[7,8] Besides a response in the singlet absorption region, we observed four triplet absorption maxima and two weak maxima in the near infrared. (3) At high voltages the current is proportional to the square of the voltage and much larger than the SCL hole current measured on the same crystal. Apparently the trap-filled limit is reached. Using Child's law, electron mobilities of 0.36 and 0.44 cm^2 V^{-1} sec^{-1} ($\perp ab$ plane, taking $\epsilon = 3.4$) for two different crystals were calculated.[9]

Two-carrier SCL currents were obtained when the electron-injecting electrode was combined with a hole-injecting electrode. At low voltages these currents were considerably larger than those with only one injecting electrode. At high voltages the currents were much larger than the SCL hole currents but only by a factor of three larger than the SCL electron currents. The flow of doubly injected current is accompanied by the emission of blue light, observed from the side of the crystal between the opaque electrodes. No light could be seen with only one injecting contact. The emitted light was analyzed with a monochromator and shown to be the fluorescence spectrum of anthracene modified on the short-wavelength

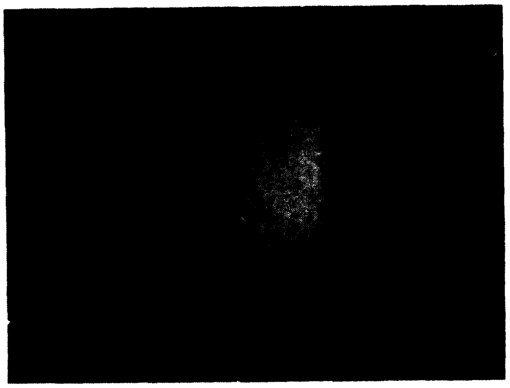

FIG. 1. Enlarged photograph of the recombination radiation from a 5-mm-thick crystal, viewed normal to the horizontal current path through a polished side of the crystal. The region of maximum brightness (=luminous zone) on the right-hand side is in front of the positive electrode.

side by reabsorption in the crystal. The whole volume of the crystal, including the outer parts which did not carry current, assumed a characteristic glow. In a 5-mm-thick crystal, however, a very bright zone could be discerned in front of the hole-injecting electrode and reaching 2 mm into the crystal, as shown in Fig. 1. Figure 2 shows the dependence of current and emitted light intensity on the applied voltage for the 5-mm-thick crystal. The intensity-current dependence is linear for $i > 10^{-10}$ A. At small currents, $i < 10^{-10}$ A, the light intensity drops much faster than the current when the voltage is lowered. A similar behavior was found with the two other crystals studied.

The existence of a luminous zone clearly indicates that the light observed is generated in the crystal and not at an electrode surface. The limited width of the zone and its position close to the positive electrode suggest that an SCL electron current flows through the crystal to meet a hole current in front of the positive electrode.[10] The electrons will recombine with holes in the crystal and not reach the positive electrode so long as the latter remains Ohmic. Therefore, a linear dependence of light intensity on current is to be expected. This interpretation is supported by the result of a preliminary measurement of the light output. At high currents, where intensity $\propto$ current, one blue-light quantum seems to be emitted for roughly every electron injected. The rapid drop of the intensity at small currents where the linear relationship no longer holds may be due to radiationless recombination with trapped carriers becoming predominant in this region.

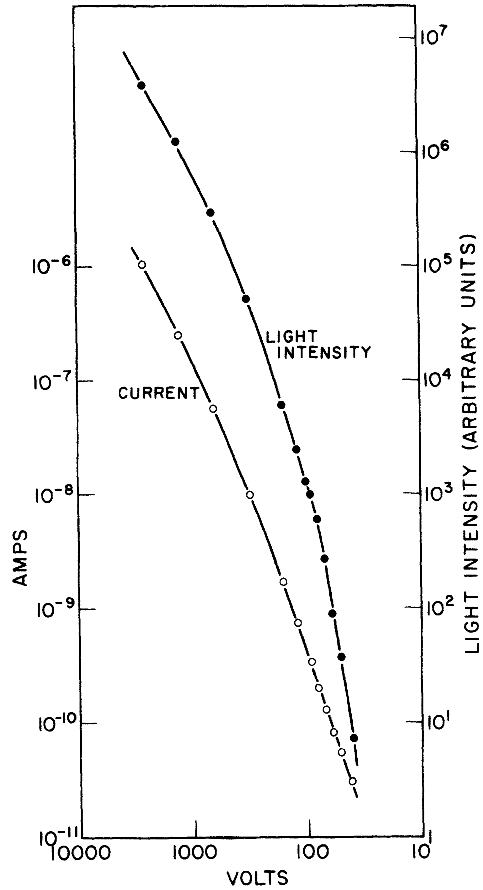

FIG. 2. Dependence of current and light intensity on applied voltage.

Although both singlet and triplet excitons may be expected to be generated by carrier recombination, only blue light due to singlet excitons was observed. As is known from studies of the delayed fluorescence of anthracene, triplet excitons decay by a monomolecular radiationless process at low concentrations, while a bimolecular recombination, resulting in a singlet exciton, prevails at high concentrations. Calculations based on experiments which were performed on crystals of the same origin[11] indicate that at currents below 10^{-6} A monomolecular decay should predominate, leading to a square dependence of singlet generation on current. Therefore the observation of a linear dependence of light intensity on current down to 10^{-10} A suggests that the singlet excitons observed in our experiments are probably formed directly by carrier recombination. These questions are being investigated further.

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[9]This agrees with the value 0.4 $\text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}$ found by R. G. Kepler [Phys. Rev. 119, 1226 (1960); Organic Semiconductors, edited by J. J. Brophy and J. W. Buttrey (The MacMillan Company, New York, 1962)].

[10]Using the width of the luminous zone we can give a rough estimate of the hole-electron recombination cross section. With only electron injection the electron concentration n in the crystal is $n=2\epsilon\epsilon_0 V/e_0 d^2$, where d = crystal thickness. We assume that this concentration is not seriously modified by simultaneous hole injection. Before recombination occurs a hole will travel an average distance λ from the positive electrode into the crystal. Neglecting trapping effects and assuming a homogeneous field, we can write

$$\lambda=\frac{\mu_h V}{n v_{\text{th}} s d}=\frac{\mu_h e_0 d}{2\epsilon\epsilon_0 v_{\text{th}} s}.$$

Using $\mu_h = 1\ \text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}$, $v_{\text{th}}=10^5\ \text{cm sec}^{-1}$, $\epsilon=3.4$, and equating λ with the width of the luminous zone (2 mm in a 5-mm-thick crystal), we obtain the cross section $s=1\times10^{-11}\ \text{cm}^2$. This agrees exactly with the cross section of the sphere on which the Coulomb potential around an elementary charge in the crystal is equal to kT (at room temperature).

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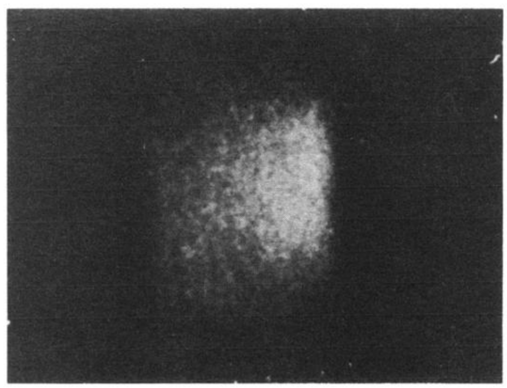

FIG. 1. Enlarged photograph of the recombination radiation from a 5-mm-thick crystal, viewed normal to the horizontal current path through a polished side of the crystal. The region of maximum brightness (=luminous zone) on the right-hand side is in front of the positive electrode.