TABLE IV. AB, donor-acceptor combinations that give rise to the three pair-spectrum types.

Type I	Type II	Type III
Sub. A–Sub. A	Sub. A–Sub. B	Sub. A–Int. A
Int. A–Int. A	Int. A–Int. B	Sub. B–Int. B
Sub. B–Sub. B	Sub. A–Int. B	
Int. B–Int. B	Sub. B–Int. A	

erally do not correspond to stable pairs, so no $N(r)$ values are listed for these (exciton-donor or exciton-acceptor interaction becomes larger than the pair complex interaction at close distance). The relationships between shell number m and pair separation r are

$$\text{Type I:}\quad r=(2m)^{1/2}a_0,$$
$$\text{Type II:}\quad r=(8m-5)^{1/2}a_0/4,$$
$$\text{Type III:}\quad r=(2m+1)^{1/2}a_0.$$

In a zinc-blende lattice, for a compound AB, the donor-acceptor combinations that give rise to the three types of spectra are listed in Table IV.

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Diffusion of Triplet Excitons in Anthracene Crystals

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Diffusion of triplet excitons in anthracene crystals has been detected by time-dependent studies of the delayed blue fluorescence under varying spatial distribution of the exciting red light. The delayed fluorescence which results from triplet-triplet annihilation was used as a passive probe for detecting the triplets. The observed changes in the time dependence of the delayed fluorescence can be interpreted uniquely as due to triplet-exciton migration, and can be described by a diffusion equation. A diffusion constant of 2×10^{-4} cm^2 sec^{-1} was obtained for triplet diffusion in the ab plane of anthracene crystals at room temperature.

INTRODUCTION

THE exciton, an excited state of a crystal which transports electronic excitation energy without transport of charge, has been studied extensively both theoretically and experimentally.[1,2] The concept of the exciton has led to the understanding, at least in principle, of the optical properties of numerous nonmetallic crystals. The experimental status of the energy-transport properties of the exciton, however, is not clear-cut.[1,2] Until recently the study of exciton motion was confined to systems in which the exciton diffusion length was less than the wavelength of light and, consequently, values of diffusion length have been inferred indirectly.[1,2]

Recently, two of the present authors[3] reported a diffusion length of about 10 μ for metastable triplet excitons in anthracene. In these steady-state experiments the exciton was used as its own detector by observing the delayed blue fluorescence resulting from the triplet-triplet annihilation process. It has been established that two triplets which get sufficiently close annihilate each other, creating a blue-fluorescing singlet exciton, and that the resulting delayed fluorescence per unit volume of crystal is proportional to the square of the triplet-exciton concentration.[4–7] As the excitons spread out due to diffusion, the total delayed fluorescence intensity decreases. The actual experiment was carried out by irradiating the anthracene crystal with red light from a continuous helium-neon laser with a Ronchi ruling (a grating with alternating opaque and transparent strips) between the laser and the crystal. With sufficiently fine gratings the intensity of the blue emission did decrease, proving the presence of excitons within shadow regions of the crystal. It was assumed that the spreading of excitons into the shadow regions was due to diffusion. The alternative interpretation, that the presence of excitons within the shadow regions was due to direct generation of excitons by diffracted and scattered photons rather than diffusion, could not be ruled out completely.

In the present work on anthracene crystals, results of time-dependent experiments are presented in which the relatively slow spreading of triplet excitons can be dis-

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tinguished from direct effects of diffraction and scattering of photons. The time dependence of buildup and decay of blue emission in response to step pulses of red light from a chopped laser beam was measured with different Ronchi rulings between the laser and the crystal. In these experiments spurious effects of diffraction or scattering can produce only a decrease in the changes in the delayed fluorescence buildup and decay curves caused by diffusion. It is believed that these measurements can be uniquely interpreted on the basis of exciton diffusion.

The present results can be brought into agreement with the predictions of the time-dependent diffusion equation, on the assumption that a fraction of the exciting photon intensity incident on the crystal through the ruling openings is diffracted and scattered into the geometrical shadow regions. A value of the order of 2×10^{-4} cm^2 sec^{-1} is obtained for the triplet-exciton diffusion constant in the *ab* plane of anthracene. This value is consistent with the estimated diffusion length of 10 μ reported previously (the triplet lifetime for those crystals was about 2×10^{-3} sec) from the steady-state experiments.[3]

Kepler and Switendick[8] recently reported effects of triplet-exciton diffusion to the surface in thin anthracene crystals as well as in thick crystals where excitons were generated near the crystal surface. Assuming that a complete triplet-exciton quenching takes place at the crystal surface, they obtained diffusion constants that are at least one order of magnitude higher than that reported here. We are unable to offer a satisfactory explanation for this apparent discrepancy.

THEORETICAL

The rate of generation of triplet-exciton concentration $n(\mathbf{r},t)$ at a point $\mathbf{r}$ in the crystal is assumed to be governed by the differential equation

$$\partial n(\mathbf{r},t)/\partial t=\alpha i(\mathbf{r},t)-\beta n(\mathbf{r},t)-\gamma' n^2(\mathbf{r},t)+D\nabla^2 n(\mathbf{r},t)\,, \quad (1)$$

where α is the singlet-triplet absorption coefficient for the incident photon flux density $i(\mathbf{r},t)$, β the monomolecular decay rate constant (or the reciprocal of lifetime τ), D the triplet-exciton diffusion constant, and γ' the over-all bimolecular-annihilation-rate constant.

The total emitted photon flux (number of photons per second) will have the temporal dependence given by

$$\Phi(t)=\tfrac{1}{2}\gamma\int_V n^2(\mathbf{r},t)dv\,, \quad (2)$$

where the integral is taken over the volume of the crystal. Here $\gamma=f\gamma'$, where f is the fraction of triplet-triplet annihilations which leads to the observed delayed singlet fluorescence. The factor f is probably smaller than one, since, in principle, processes other than those leading to fluorescing singlet excitons could also result from the triplet pair annihilation.[6,7]

The present experiments were done at low exciton concentrations, that is in the region where $\gamma' n^2 \ll \beta n$. Furthermore, with the same chopper arrangement for the different geometries $g(\mathbf{r})$ of the incident light, the source term in (1) was restricted to the form

$$i(\mathbf{r},t)=i_0 g(\mathbf{r})f(t)\,, \quad (3)$$

where i_0 is a constant, $f(t)=1$ during the chopper's *on* half cycle of interval $T_0 \gg \tau$ (τ being the triplet lifetime) and $f(t)=0$ during the *off* half cycle.

Assuming that no net exciton current leaves the volume V of the crystal, it can be easily shown that the total number of triplet excitons in the crystal

$$N^j(t)=\int_V n_j(\mathbf{r},t)dv=N_s w_j(t)\,,$$

has a functional dependence $w_j(t)$ which is independent of the spatial geometry $g(\mathbf{r})$ of the incident photon flux. The index j refers either to the buildup ($j=b$) or decay ($j=d$) half cycle, and N_s is the steady-state population. For the present initial conditions $N_s=N^b(\infty)=N^d(0)$.

Similarly, the quantity

$$V_e{}^j(t)\equiv\frac{\left(\int_V n_j(\mathbf{r},t)dv\right)^2}{\int_V n_j{}^2(\mathbf{r},t)dv}\,,$$

an effective volume occupied by the excitons, can be written in the form

$$V_e{}^j(t)=V_{es}v_j(t)\,,$$

where V_{es} is the final (or initial) steady-state effective volume for buildup (or decay). $V_{es}=V_e{}^b(\infty)=V_e{}^d(0)$. Furthermore, in the absence of the diffusion term in Eq. (1), $v_j(t)\equiv1$; that is, the effective volume occupied by the excitons is independent of time.

From Eq. (2), the delayed blue photon flux, normalized to the steady-state value $\Phi_s=\gamma N_s{}^2/2V_{es}$, can be written as

$$\Phi_N{}^j(t)\equiv\Phi^j(t)/\Phi_s=w_j{}^2(t)/v_j(t)\,. \quad (4)$$

In the absence of diffusion, Eq. (4) simply reduces to $\Phi_N{}^j(t)=w_j{}^2(t)$; that is, the normalized delayed fluorescence has a functional form independent of the geometry of the exciting red light (or of the geometry of the exciton distribution at the start of the decay). Differences in the temporal dependence of $\Phi_N{}^j(t)$ with changes of spatial geometry of the exciting light can only be attributed to triplet diffusion. Smearing of the geometrical pattern due to spurious effects such as diffraction or scattering can only lead to a decrease of the observable diffusion effects.

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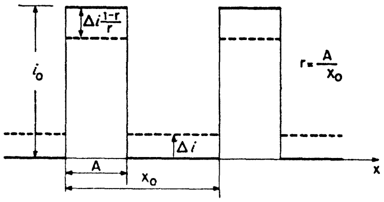

FIG. 1. Exciting-light intensity distribution. Solid line: the ideal geometrical shadow of the ruling. Dashed line: assumed intensity distribution with stray light intensity Δi in the shadow regions.

For the interpretation of the present experiments with Ronchi rulings, a simplified one-dimensional geometrical pattern was adopted for the exciting-light intensity distribution within crystal planes normal to the beam (dotted line Fig. 1). In practice, however, the rulings set up complicated Fresnel diffraction patterns in the crystal, which were further complicated by light scattering from the illuminated regions by crystal surface and bulk imperfections. It was assumed that a certain amount of constant stray light intensity Δi was present in the geometrical shadow regions of the rulings with conservation of the total incident flux.

With this assumption for the light-intensity distribution within the crystal for a ruling of period x_0 and window to period ratio r (Fig. 1), and if at $t=0$ the ruling is suddenly illuminated with a beam of uniform constant intensity i_0, then from (1) (with $\gamma' n^2 \ll \beta n$) and (2) the buildup of the delayed fluorescence, normalized to the steady-state value at $t=\infty$, is given by

$$\Phi_N{}^b(t) \equiv \frac{\Phi^b(t)}{\Phi_s} = \frac{1}{N(a)}\Big\{[1-\exp(-\beta t)]^2 + S_r \sum_{l=1}^{\infty} A_l \times [1-\exp\{-(1+l^2a^2)\beta t\}]^2\Big\}, \quad (5)$$

where the parameter

$$a \equiv 2\pi(D\tau)^{1/2}/x_0 = (2)^{1/2}\pi L/x_0, \quad (6)$$

scales the diffusion length L to ruling period, and

$$A_l \equiv \frac{2}{r^2\pi^2}\,\frac{\sin^2(l\pi r)}{l^2(1+l^2a^2)^2}, \quad l=1,2,3\cdots.$$

The "stray light" factor

$$S_r \equiv \left(1-\frac{1}{r}\frac{\Delta i}{i_0}\right)^2,$$

has the maximum value 1 for the ideal geometrical shadow configuration ($\Delta i=0$, solid line in Fig. 1). The function

$$N(a) = 1 + S_r \sum_{l=1}^{\infty} A_l \quad (7)$$

is proportional to the steady-state delayed fluorescence intensity with the rulings.

Similarly, the decay of the delayed fluorescence, normalized to the steady-state condition at $t=0$, is given by

$$\Phi_N{}^d(t) = \frac{1}{N(a)}\Big\{\exp(-2\beta t) + S_r \sum_{l=1}^{\infty} A_l \exp[-2(1+l^2a^2)\beta t]\Big\}, \quad (8)$$

where all the symbols have the same significance as before.

The normalized buildup expression (5) can be converted to the form

$$F(t) \equiv \frac{1}{N(a)}\Big\{\exp(-\beta t) + S_r \sum_{l=1}^{\infty} A_l \exp[-(1+l^2a^2)\beta t]\Big\} = \sum_{n=1}^{\infty} \frac{1}{2^n}[1-\Phi_N{}^b(2^n t)], \quad (9)$$

which shows the contribution of diffusion as a sum of exponential terms.

Experiments were done with rulings with $r=\frac{1}{2}$ (window equal to opaque strip) and with $r=\frac{1}{4}$ (window $\frac{1}{3}$ of opaque strip). For these rulings, expressions (7), (5), and (8) were computed with a convergence of 10^{-4} or better. For the a values of interest this required taking at most 10 terms in the expansions. Figure 2 compares the buildup and decay curves for a $r=\frac{1}{2}$ typical ruling ($a=1.0$) with the normal exponential response of the crystal under uniform illumination. For $a=0$ (and $a=\infty$), expressions (5) and (8) reduce simply to

$$[\Phi_N{}^b(t)]_{\text{uniform}} = (1-e^{-\beta t})^2,$$
$$[\Phi_N{}^d(t)]_{\text{uniform}} = e^{-2\beta t}.$$

Figure 3 shows the calculated time dependence of the quantities

$$\Delta\Phi_N(t) \equiv \Phi_N(t) - [\Phi_N(t)]_{\text{uniform}}, \quad (10)$$

that is, the differences caused by diffusion between the normalized delayed emissions from a crystal illuminated with and without a ruling. For the $r=\frac{1}{2}$ case, the highest

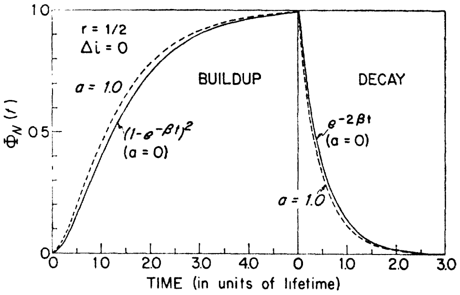

FIG. 2. Comparison of the theoretical normalized delayed fluorescence from a crystal illuminated through a ruling with $a=1.0$ and under uniform illumination ($a=0$).

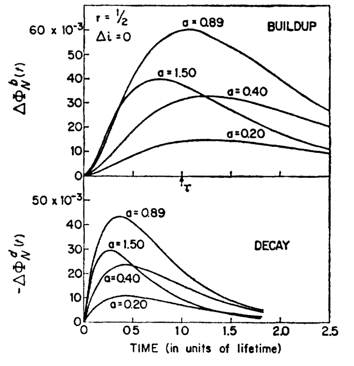

FIG. 3. Theoretical differences due to diffusion in the normalized buildup and decay of delayed fluorescence. The maximum effect occurs at shorter times for rulings of bigger parameter a. $\Delta i=0$ and $r=\frac{1}{2}$.

calculated difference occurs for a ruling with $a\approx 0.89$. This curve has a maximum at $t\approx 1.06\tau$ ($\Delta\Phi_N{}^b=0.060$) and at $t\approx 0.36\tau$ ($-\Delta\Phi_N{}^d=0.043$) for buildup and decay, respectively. The small effect of triplet diffusion is more easily detectable in the buildup of the delayed fluorescence. Departure of the factor S_r from 1, by inclusion of an amount Δi of stray light intensity in the geometrical shadow regions, reduces further the observable diffusion effects.

EXPERIMENTAL

The measurements were made at room temperature. The crystals were either melt grown in our laboratory from highly purified natural anthracene[9] or were obtained commercially.[10] Crystals about 2 mm thick were used to avoid possible effects due to exciton diffusion to the surface,[8] and to have adequate intensities of emitted light. Crystal perfection was essential and, unless the crystal surfaces had high-quality *ab* cleavage planes, the samples were polished to minimize the scattering of the incident light at the crystal surfaces.

The experimental setup is shown in Fig. 4. The 6328-Å light from a helium-neon laser, set up for fundamental mode operation at 10 mW output, was focussed onto a chopper blade and rendered parallel again with a second lens. The half-revolution time of the chopper was adjusted to be $T_0>5\tau$, according to the lifetime of the sample under study. This assured sufficiently accurate normalization of the delayed fluorescence as well as complete decay before starting a new cycle. The rise time of the pulses was better than 5×10^{-4} sec. The intensity of the beam was attenuated with a pair of Glan prisms, the second of which was kept fixed to preserve the direction of polarization. Spurious blue light was eliminated with a Corning (C.S. 2–62) cut-off filter. The cross section of the beam was expanded to about 1 cm diam via the lenses L_3 and L_4, in order to illuminate a sufficiently large area of the sample to average out local variations.

The crystal was placed on a platform at a distance of 1 mm above the Ronchi ruling lines with the beam falling onto the *ab* plane. In this way, rulings could be interchanged without disturbing the crystal.

To avert difficulties due to the strong double refraction of anthracene,[11] the crystals were oriented to cause extinction of light upon passage through a polaroid above the crystal with its transmission axis perpendicular to the electric vector of the laser beam. Most of the experiments were done with the **E** vector parallel to the *a* axis.

Very low levels of exciting light were used to satisfy the condition $\gamma' n^2 \ll \beta n$ in Eq. (1). The uniform incident intensity was reduced till, under steady-state conditions, the emitted blue photon flux was proportional to the square of the incident flux. Furthermore, it was ascertained that an excitation level had been reached such that a further reduction of the incident intensity did not affect the experimentally observed time dependence of the normalized buildup and decay curves. Departure from the region $\gamma' n^2 \ll \beta n$ can drastically change the exponential behavior of the blue emission. Delayed fluorescence is then no longer a passive probe for detecting triplets, and the bimolecular annihilation process controls partially the triplet population.

The blue emission from the crystal was observed with a photomultiplier (RCA 6199 with S-11 photocathode) through a blue-transmitting red-absorbing filter stack (Corning filters C.S. 5–57, 5–56, plus 4–72). The photomultiplier output was fed into a computer of average transients (Mnemetron Division of Technical Measurements Corporation CAT Model 400) via an operational amplifier (Tektronix Type 0). Successive chopping cycles were accumulated in CAT's memory. The accumulated content of the memory channels was recorded with a printer. The CAT was essential for enhancing the signal-to-noise ratio, so that the small changes in the normalized buildup and decay curves of delayed fluorescence could be detected.

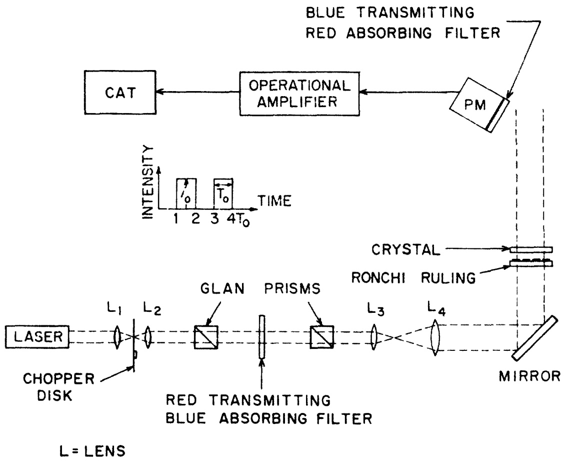

FIG. 4. Experimental setup.

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RESULTS

Figure 5 shows some of the experimental differences between the delayed emissions with several $r=\frac{1}{2}$ Ronchi rulings and with uniform illumination through a blank glass obtained for a crystal grown in our laboratory (crystal I). For this sample, the triplet lifetime, as measured under uniform illumination, was $\tau=24.0$ msec. With the available $r=\frac{1}{2}$ rulings, the maximum diffusion effect was observed with the ruling period $x_0=169.3\ \mu$ (150 lines/in.). The crystal was excited with the beam incident onto the *ab* plane, with the **E** vector and ruling lines (diffusion in the *b* direction) parallel to the *a* axis. The time resolution used on the CAT was $\frac{5}{8}$ msec/channel. Similar results for the diffusion in the *b* direction were obtained for a commercial crystal[10] of lifetime $\tau=8.5$ msec (crystal II), but the maximum observed effect occurred for the $(r=\frac{1}{2})$ ruling period $x_0=101.6\ \mu$ (250 lines/in.), indicating a shorter diffusion length. A time resolution of $\frac{1}{4}$ msec/channel was used to obtain the data in this sample of shorter lifetime.

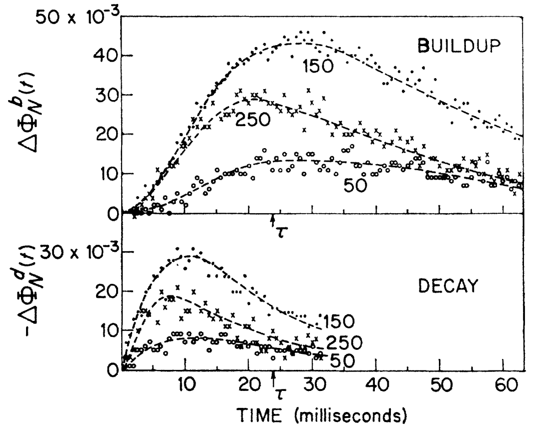

FIG. 5. Measured differences between the normalized delayed fluorescences for crystal I illuminated through some $r=\frac{1}{2}$ rulings and through a blank glass (uniform illumination). $\tau=24.0$ msec. Rulings labeled in lines/in. Lines through the experimental points are schematic.

All observed values $\Delta\Phi_N$ were smaller than the differences predicted by Eqs. (5), (8), and (10) for the ideal case of $\Delta i=0$. For each sample a percentage of stray light $\Delta i/i_0$ in the opaque regions was assumed, and values of the parameter a were determined for the best fit of the experimental differences in the buildup and decay curves. A reasonable fit for $r=\frac{1}{2}$ and $r=\frac{1}{4}$ rulings was obtained taking $\Delta i/i_0 \approx 8\%$ and $\Delta i/i_0 \approx 5.5\%$ for crystals I and II, respectively. From Eq. (6) the diffusion length was obtained from the ruling period by

$$L=x_0 a/(2)^{1/2}\pi.$$

Figure 6 shows some of the fitted curves for crystal I. The agreement between the function $F(t)$ [Eq. (9)] and experimental buildup points recalculated with the same expression is shown in Fig. 7 for this crystal. It is seen, furthermore, that the blank (uniform illumination) data agree reasonably with the assumed pure exponential behavior in the absence of the diffusion effect. The ratios of the steady-state fluorescence intensities for different rulings also corresponded to the predictions of

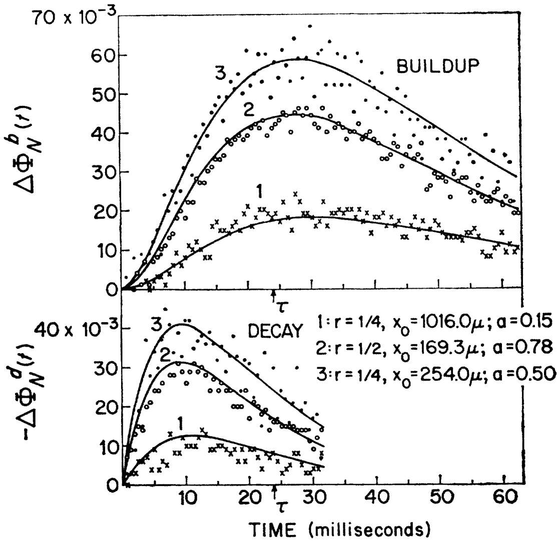

FIG. 6. Fit of some of the experimental differences in the normalized delayed fluorescence for crystal I (points) with the curves predicted by Eqs. (5), (8), and (10) with the indicated values of parameter a, and assuming $\Delta i/i_0=8\%$.

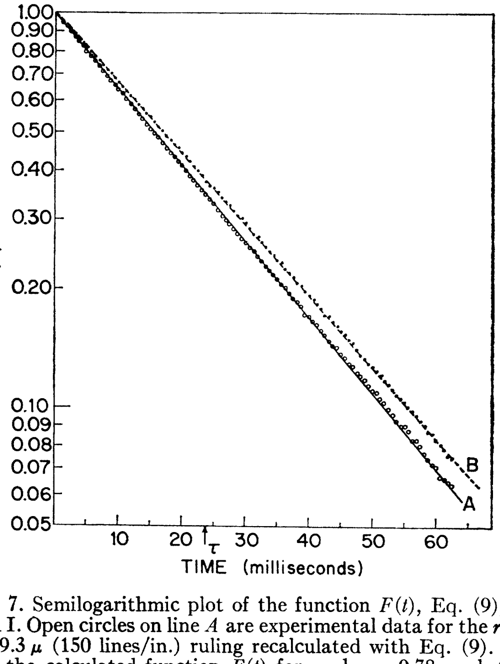

FIG. 7. Semilogarithmic plot of the function $F(t)$, Eq. (9), for crystal I. Open circles on line A are experimental data for the $r=\frac{1}{2}$, $x_0=169.3\ \mu$ (150 lines/in.) ruling recalculated with Eq. (9). The line is the calculated function $F(t)$ for $r=\frac{1}{2}$, $a=0.78$, and $\Delta i/i_0=8\%$. The contribution of the different exponentials cannot be separated on the time scale of the present experiments. Points on sketched line B are data of normalized buildup under uniform illumination assumed to be of the form $(1-e^{-\beta t})^2$, and recalculated to show the exponential behavior with $\tau=24.0$ msec.

TABLE I. Values of the parameter a obtained by fitting the experimental differences in the delayed fluorescence with the predictions of Eqs. (5), (8), and (10) with the percentages of stray light $\Delta i/i_0$ as shown for each crystal. Diffusion length obtained by $L=(1/\sqrt{2}\pi)x_0a$ for each ruling.

Ruling (lines/in.)	r	x_0 (μ)	a	L (μ)
		Crystal I		
		$\Delta i/i_0=8\%$		
25	$\frac{1}{4}$	1016.0	0.15	34.3
50	$\frac{1}{2}$	508.0	0.23	26.3
50	$\frac{1}{4}$	508.0	0.25	28.6
100	$\frac{1}{2}$	254.0	0.45	25.7
100	$\frac{1}{4}$	254.0	0.50	28.6
150	$\frac{1}{2}$	169.3	0.78	29.7
200	$\frac{1}{2}$	127.0	1.20	34.3
250	$\frac{1}{2}$	101.6	1.45	33.2
300	$\frac{1}{2}$	84.7	1.80	34.3
		Crystal II		
		$\Delta i/i_0=5.5\%$		
50	$\frac{1}{4}$	508.0	0.20	22.9
100	$\frac{1}{2}$	254.0	0.35	20.9
100	$\frac{1}{4}$	254.0	0.40	22.9
150	$\frac{1}{2}$	169.3	0.45	17.1
200	$\frac{1}{2}$	127.0	0.50	14.3
250	$\frac{1}{2}$	101.6	0.80	18.3
300	$\frac{1}{2}$	84.7	1.25	23.8

Eq. (7) with the assumed amounts of stray light. Table I summarizes the results.

An average of these data gives diffusion lengths of $L=30\ \mu$ and $L=20\ \mu$ for the two samples, respectively. With the experimental lifetimes, as determined under uniform illumination, a diffusion constant $D=2\times10^{-4}$ cm^2 sec^{-1} is obtained for both crystals.

Within the present assumptions and experimental errors, triplet diffusion is nearly isotropic in the *ab* plane of anthracene. It appears to be slightly lower along the *a* axis. An experiment with a screen with 160-μ holes showed differences in delayed fluorescence bigger than the ones observed with rulings of comparable opening dimensions, as would be expected form a two-dimensional diffusion effect. Experiments on triplet diffusion in the *ac* plane are planned as suitable samples become available.

CONCLUSIONS

In spite of the simplified model adopted for the spatial distribution of the exciting red light, agreement between experimental results and theoretical predictions of the diffusion equation has been obtained. The key result of this work is the demonstration of triplet-exciton diffusion by measurements, which to our knowledge, do not have an alternative interpretation. It appears that a diffusion equation correctly describes the triplet energy transfer in organic solids.

The mechanism for the motion of triplet excitons is still uncertain. The experimental value of $D=2\times10^{-4}$ cm^2 sec^{-1} reported here for the diffusion constant lies in between the theoretical values predictable from the hopping and band model calculations of Jortner *et al.*[7] Careful measurements of anisotropy and temperature dependence of the diffusion constant, as well as of effects of crystalline imperfections and surfaces on triplet migration, should lead to an understanding of the diffusion mechanism and allow a distinction between the hopping and band models.

ACKNOWLEDGMENTS

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