Exciton Diffusion in Naphthalene Crystals

A. A. Kazzaz* and A. B. Zahlan

Physics Department, American University of Beirut, Beirut, Lebanon

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Exciton capture by anthracene in naphthalene crystals is studied as a function of impurity concentration (4×10^{-8} to 4.8×10^{-3}), temperature, annealing, and wavelength of exciting radiation. It is shown that surface, incoherent, and possibly coherent free excitons participate in these excitonic processes. A method for annealing molecular crystals is described. Some observations on the temperature dependence of these processes are reported.

A NUMBER of papers[1-7] have appeared in the literature demonstrating the diffusional character of exciton motion in molecular crystals. McClure[8] and Ganguley and Chaudhury[9] have contributed review articles.

The status of the subject can be stated as follows: Simpson,[7] using microcrystalline films of anthracene and a tetracene "detector" film, found that the mean free path in such anthracene films (less than $1\,\mu$ thick) is $0.2\,\mu$. Borisov and Vishnevski[2] (some details of this paper are reproduced because it is not easily accessible) assumed that the exciton diffusion process is described by

$$D d^2 n/dx^2 + I_0 k e^{-kx} - n/\tau = 0, \qquad (1)$$

where $D =$ diffusion coefficient, $n(x)$ is the steady state exciton concentration at x, $k =$ extinction coefficient, $\tau =$ lifetime of the excitons, and I_0 is a constant proportional to light intensity per unit time. Applying the boundary conditions:

$$\begin{aligned} \text{at} \quad x=0, \quad & dn/dx = qn(0)/D = sn(0), \\ \text{at} \quad x=\infty, \quad & n = D\,dn/dx = 0, \end{aligned} \qquad (2)$$

they find the solution:

$$n(x) = [I_0 k/D(k^2-p^2)]\{[(s+k)/(s+p)]e^{-px} - e^{-kx}\}, \quad (3)$$

where $p = 1/l = (D\tau)^{\frac{1}{2}}$. Let

$$J = \beta \int_0^\infty n(x)dx = \beta I_0(k+p+s)/Dp(k+p)(p+s), \quad (4)$$

where J is the detection device current and β is a

* Present address: Physics Department, College of Science, University of Baghdad, Baghdad, Iraq.

[1] F. Lipsett and A. J. Dekker, Can. J. Phys. **30**, 165 (1952); Nature **173**, 736 (1954).

[2] M. D. Borisov and V. N. Vishnevski, Ukrain. Fiz. Zhur. **1**, 371 (1956) (translations of references 2, 3, and 5 are available from A. Zahlan).

[3] V. M. Agranovitch, I. Ya Kucherov, and A. N. Faidish, Ukrain. Fiz. Zhur. **2**, 61 (1957).

[4] J. B. Birks and G. T. Wright, Proc. Phys. Soc. (London) **B67**, 657 (1954).

[5] I. Ya Kucherov and A. N. Faidish, Dopovodi Akad. Nauk Ukr. RSR **1**, 57 (1956).

[6] H. C. Wolf, Z. Physik **145**, 116 (1956).

[7] O. Simpson, Proc. Roy. Soc. (London) **A238**, 402 (1956).

[8] D. McClure, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 9, p. 1.

[9] S. C. Ganguley and N. K. Chaudhury, Revs. Modern Phys. **31**, 990 (1959).

proportionality constant relating the total emission by the crystal to J. If the crystal is irradiated at λ_a, λ_b, λ_c, where the extinction coefficients are a, b, c, respectively, then, setting

$$(J_a/I_{0a})/(J_b/I_{0b}) = \alpha_{ab}, \quad (J_a/I_{0a})/(J_c/I_{0c}) = \alpha_{ac},$$

β and s can be eliminated from (4):

$$l = \frac{\begin{aligned}(1-\alpha_{ac})[c(1-\alpha_{ab})+b-a\alpha_{ab}] \\ -(1-\alpha_{ab})[b(1-\alpha_{ac})+c-a\alpha_{ac}]\end{aligned}}{b(1-\alpha_{ab})(c-a\alpha_{ac})-c(1-\alpha_{ac})(b-a\alpha_{ab})}. \quad (5)$$

Borisov and Vishnevski determined the absorption of 0.5-cm thick naphthalene and anthracene crystals in unpolarized light over the range 3000–3300 A and 3000–4000 A, respectively. J is also reported over the range 2500–3400 A for naphthalene and 2500–4000 A for anthracene—the (J,λ) curve for anthracene is corrected for reflected light. No correction for reabsorption was made. The authors do not report the method followed for the determination of the quantities I_{0b} and I_{0c}.

These workers reported a value of 0.2–0.3 μ for the exciton mean free path in naphthalene and 0.1–0.15 μ in anthracene. These results were obtained with thick crystals (0.5 cm). No information is given concerning purification and growth of the crystals used. These authors treated the surface [ultraviolet radiation in an acid or oxygen (?) atmosphere] to stop nonradiative surface processes. No information is available on such treatments.

We planned to use this method but found that the result hinges on the difference between two terms [see Eq. (5)] which differ by only a few percent; and, as will be discussed later, the thin crystals exhibited that much variation from crystal to crystal.

Agranovich and Faidish[10] solved the diffusion equation for the case of two excitons and a homogeneously distributed impurity. The solution is unwieldy and contains seven unknown parameters.

EXPERIMENTAL

Matheson, Coleman, and Bell naphthalene was refluxed with sodium and recrystallized five times from

[10] V. M. Agranovich and A. N. Faidish, Optika i Spektroskopiya **1**, 983 (1956). ACSIL Trans. No. 995.

alcohol distilled from zinc dust. The naphthalene was then sealed under vacuum in small tubes and zone-refined for 200 hr. The zone velocity was 0.25 cm/hr. Anthracene impurity concentrations of 10^{-7} up to 4.8×10^{-3} mole of anthracene per mole of naphthalene were prepared. C_p is defined as the anthracene concentration in mole per mole of naphthalene. Single crystals of naphthalene were grown from n-hexane (spectroscopic grade) on water in 6–15 hr.[11] Films were prepared by rapid sublimation on a cooled (about 120°K) quartz disk. The films were uniform, compact, transparent, and similar to those used by Simpson. All of the crystals and films were used immediately after preparation unless otherwise stated. The thickness of the sublimed film was determined by assuming it to be uniform and weighing the film. This work was limited to samples about 5 μ thick.

A Phillips (type 93110E) 100-w mercury lamp, a Carl Leiss double monochromator and an RCA photomultiplier type 6342 were used. The Hg lines at 3020, 2970, 2890, 2800, and 2650 A were used to excite the samples.

Only a small section (2-mm diameter) of the crystal was irradiated. Two readings were taken at every wavelength, one with and one without a Kodak No. 50 filter. The filter completely cut off the naphthalene fluorescence and transmitted only 1.60 to 1.77% of the anthracene fluorescence depending on C_p.

The photomultiplier currents were reduced to J_a and J_n, which are proportional to the number of quanta emitted by the anthracene and naphthalene, respectively.

The highest purity obtained is estimated, by extrapolating (see Fig. 1) the (J_a/J_n) vs C_p curve to zero concentration, as 4×10^{-8} mole of anthracene per mole of naphthalene. (All concentrations hereafter are given in such mole fractions.) We did not identify this impurity but assume from the narrow transmission region of the filter used (about 4500±300 A) that anthracene is the most likely one. The precise nature of this impurity is not essential to this study. [A. F. Prikhot'ko and M. P. Sphak, Optika i Spektroskopiya 6, 119 (1959), found that traces of methylnaphthalene in naphthalene lead to delayed emission at low temperature, the fluorescence beginning at 31 062 cm^{-1}; naphthalene fluorescence begins at 31 462 and 31 476 cm^{-1}. The naphthalene was purified by zone-refining. We did not look for this impurity because at the temperatures used in this study this impurity cannot be of any importance. H. Sponer, Y. Kanda, and L. A. Blackwell, J. Chem. Phys. 29, 721 (1958), found the delayed fluorescence lifetime to be greater than 1 msec at 4°K but the delayed fluorescence disappeared at 77°K.]
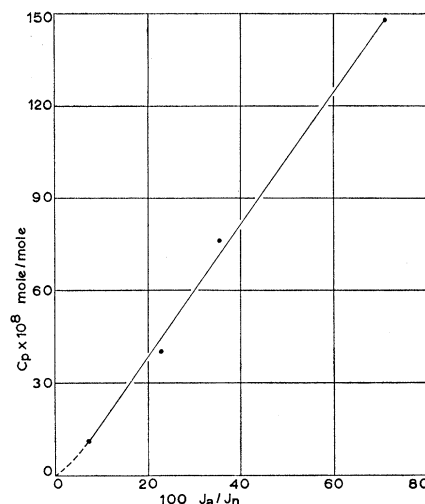

FIG. 1. The dependence of J_a/J_n on C_p, for grown crystals, at low concentrations of impurity.

RESULTS AND DISCUSSIONS

(1) Temperature Dependence and Annealing of Crystals

Agranovich and Korrobeev[12] studied theoretically the dependence of the mean free path on temperature. They find that $\langle l \rangle$ for free excitons should vary inversely with temperature. They report that $\langle l \rangle_{\text{free}} \simeq 20 \mu$ (a printing error gives the unlikely value of 20 A). This is roughly 100 times the published experimental values. These authors attribute this discrepancy either to the substantial role played by the localized excitons or to the presence of lattice defects. Scattering of free excitons by phonons leads to a $(D^{-1})_{\text{free}} \propto T^{\frac{1}{2}}$ dependence[12] while Triflaj[13] finds $D_{\text{loc}} \propto \exp(U_1/kT)$. Triflaj states that if the mean free path of the free exciton is determined by the presence of lattice defects, the diffusion coefficient must drop exponentially, as the temperature increases, in proportion to $\exp(U/kT)$, where U is the activation energy for the formation of defects.

There is no experimental information on the influence of bulk or surface crystalline defects on electronic processes in molecular crystals. High-purity (impurity concentration 4×10^{-8}) naphthalene crystals were annealed and the dependence of J_a, J_n on temperature, time, and wavelength was determined. If a crystal is cooled down to 170°K and then warmed up to about 250°K (in about 1 hr), (J_a/J_n) increases irreversibly. If this process is repeated several times, (J_a/J_n) increases in such a way as to approach some limit. Since this whole process was conducted with the crystal under vacuum, with or without continuous excitation, the only possible interpretation is that

[11] H. C. Wolf, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10, p. 1.

[12] V. M. Agranovich and Iu. V. Korrobeev, Optics and Spectroscopy 6, 155 (1959).
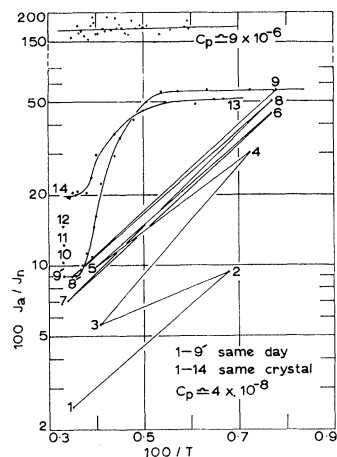[13] M. Triflaj, J. Czech. Phys. 6, No. 6 (1956); 8, 510 (1958).

FIG. 2. $\text{Log}(J_a/J_n)$ vs $100/T$ for 4×10^{-8} and 9×10^{-6} crystals. Point 1 is the starting point of the annealing cycles. $1 \to 14$ is for the same crystal. Points $1 \to 11$ follow in rapid succession; about 30 min elapses between successive points except for point 12 which is 96 hrs after point 1. Data at $\lambda = 2970$ A. The 9×10^{-6} curve is not typical in all details for high C_p. These curves are usually smoother, otherwise the same. Note that J_a/J_n at 9×10^{-6} is almost independent of T.

growth defects are annealed at least partially. The total fluorescence of the naphthalene also increases. Figure 2 shows the changes in $\log(J_a/J_n)$ at two temperatures with number of annealing steps and the dependence of (J_a/J_n) on T after the annealing treatments. Figure 3 shows the dependence of J_a, J_n, and J_a/J_n on T for a "fresh" (4×10^{-8}) crystal—no previous annealing. The same crystal exhibited different slopes depending on the number of annealing cycles it went through. Below 200°K the slope is almost independent of temperature and leads to an ϵ of the order of 50 cal/mole, where $\ln(J_a/J_n) = \epsilon/RT + \text{constant}$. The slope of the $\ln(J_a/J_n)$ vs $1/T$ curve above 200°K is very sensitive to the past treatment of the crystal (see Figs. 2 and 3). It is likely that the mean free path between 300° and 200°K, as suggested by Triflaj,[13] is limited by the equilibrium concentration of defects. The slope in the range 296°–200°K is 0.84 kcal/mole for a fresh crystal, Fig. 3, and increases to about 3 kcal/mole after 7 annealing cycles, Fig. 2. The dip at 250°K in Fig. 3 is observed in all the "fresh" (4×10^{-8}) crystals studied. This dip is annealed out easily, Fig. 2. The dip must be associated with capture processes since it appears only in the $\log(J_a/J_a^0)$ vs $1/T$ curve.

When impurities (concentration 10^{-5}, 10^{-4}) were introduced and the crystals annealed, no large changes were observed; see Fig. 2 (where only one case is shown). This result, in conjunction with the observations on crystals with impurity concentration 4×10^{-8}, indicates that the exciton mean free path is several times longer than indicated by the studies at high impurity concentration. The separation between two anthracene impurity molecules for the concentration 4×10^{-8} is roughly $0.4\,\mu$. The mean free path is then of the order of a few microns which is of the order of the dimensions of the crystal. This is why surface effects are very important at impurity concentration 4×10^{-8} (see Sec. 2 below). At impurity concentrations of 10^{-4} and 10^{-5}, surface effects and annealing are critical despite the fact that impurities limit the mean free path.

All of the work reported in the literature on naphthalene is for high impurity concentration, $C_p \geqslant 10^{-6}$.

(2) The Participation of Surface Excitons in Energy Migration and the Dependence on the Extinction Coefficient

The dependence of J_a/J_n on the extinction coefficient is the simplest deduction of the Agranovich-Faidish theory. In this model only (incoherent) free and localized excitons participate, the function of the surface is of a minor importance. Physically, the creation of excitons near the surface (high extinction coefficient) will lead to a low probability of capture by the impurity if it is assumed that the excitons, once they reach the surface, fluoresce or are quenched thermally. These assumptions are also supported by the studies of Faidish and Zima[14] on the variation of (J_a/J_n) as a function of thickness of the crystal. A reproducible dependence of J_a/J_n on the extinction coefficient is essential for the application of the Borisov-Vishnevski method.

To investigate the dependence of exciton trapping on surface processes, the ratio

$$A_\lambda = (J_a/J_n)_\lambda / (J_a/J_n)_{3020\,A} \qquad (6)$$

is defined. According to the two-bulk-exciton theory of Agranovitch and Faidish, A_λ is a function $(1/k)$ (k = extinction coefficient). This functional dependence of A_λ on k is already too complex in the simplified Agranovich-Faidish model. For naphthalene A_λ should be less than one at 2970, 2895, 2850, and 2650 A. A_λ could thus be considered as a rough measure of the role of the surface as a simple bulk exciton quencher or as participating in the energy transfer process through a surface exciton. Any participation by surface excitons will then tend to increase A_λ.
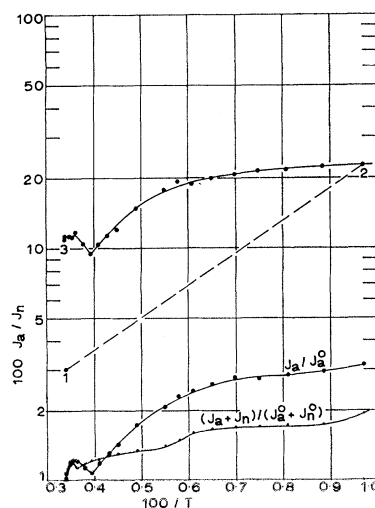

FIG. 3. $\text{Log}(J_a/J_n)$, J_a/J_a^0, $(J_a+J_n)/(J_a^0+J_n^0)$ all vs $100/T$ for a 4×10^{-8} fresh crystal. Point 1 represents the starting point. J_a^0, J_n^0 are the values of J_a, J_n at point 3.

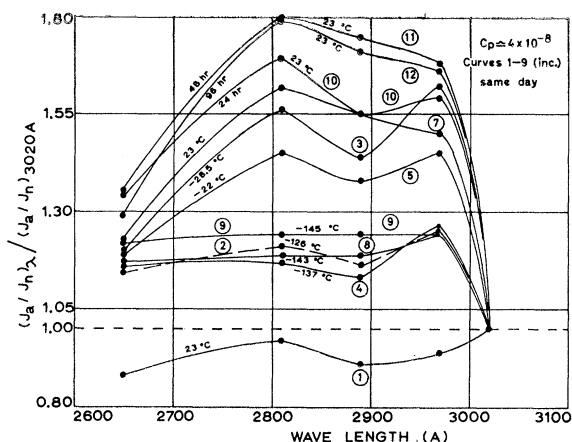[14] A. N. Faidish and V. L. Zima, Optics and Spectroscopy 6, 58 (1959).

FIG. 4. Plot of $(J_a/J_n)_\lambda/(J_a/J_n)_{3020\ A}$ vs λ. The numbers 1 to 12 on the curves refer to the points in Fig. 2. The curve for point 6 is similar to points 2, 4, 8 and has been left out. All data on the same crystal. The age of the crystal (curves 10, 11, 12) is with reference to curve 1.

The surface to volume ratio in the crystals used is too small to permit the direct observation of surface excitons in absorption. The extensive surface defects must, normally, limit the surface exciton mean free path. However, once the surface is annealed the mean free path increases and surface impurities begin to trap surface excitons. This immediately alters the boundary conditions as well as bulk-surface relationship.

The analysis of the data for the grown crystals shows that there is a considerable scatter in the value of A_λ from crystal to crystal; A_λ varies between 1.1 and 0.84. For sublimed films of impurity concentration 4×10^{-8}, A_λ is greater than one. This scatter in the value of A_λ must be due to variations in the surface of the crystals.

Curve 1 in Fig. 4 shows a plot of A_λ vs λ for a fresh-grown crystal of impurity concentration 4×10^{-8}. On subsequent annealing, as already explained, A_λ increases irreversibly and the remaining curves 2–12 give some detail on the "age" (that is annealing) and temperature dependence of A_λ. The total fluorescence of the crystal in Fig. 4 changes by 0 to 5% (for the 5 Hg lines) after 3 annealing cycles, while (J_a/J_n) increases by 360% and A_λ changes by some 60%.

Crystals containing impurity concentrations of the order of $10^{-5}-10^{-4}$ showed also irreversible changes but these changes are not as systematic as those exhibited in Fig. 4. In these cases $(J_a/J_n)_\lambda/(J_a/J_n)_{3020\ A}$ was less than one for most crystals and conditions. However there are exceptions. For example, a crystal with impurity concentration 2×10^{-4} exhibited a ratio ($\lambda=2970$ A) of 1.03 at 296°K, 0.98 at 129°K, and 0.84 when it was returned to 296°K; its total fluorescence increased by some 10% while the ratio (J_a/J_n) decreased, after this thermal treatment, by 18%.

The variations in the concentration and type of bulk and surface defects lead to the spread of experimental results (see Sec. 4) as measured by J_a/J_n and as

observed in fluorescence and phosphorescence studies of molecular crystals.[8]

These observations on the dependence of A_λ on the extinction coefficient as a function of annealing can be explained only through the introduction of surface excitons. Figure 4 shows that at room temperature in the annealed crystals (curves 10–12) the surface excitons contribute about half of the total impurity fluorescence. At about 130°K the role of the surface excitons decreases sharply and is of the order of 30%. At lower temperature (see Sec. 5) the participation of coherent free excitons becomes possible and these have a mean free path of the order of 20 μ. This increased range of bulk excitons diminishes the role of the surface.

If a crystal is placed in a tightly sealed quartz "box" an increase in naphthalene fluorescence and (J_a/J_n) at the rate of some 10% per day is observed over a period of 4 days and tending to a limit. This aging effect is due to the annealing of growth imperfections. Kucherov and Faidish[5] claim that there is a decrease in naphthalene fluorescence with age. The only time we noted such a decrease is when the crystal was allowed to evaporate. Thin microcrystalline films have a vapor pressure higher than that of the grown crystals and do evaporate very rapidly when they are less than 5 μ thick.

(3) Dependence of (J_a/J_n) on Impurity Concentration

Figure 5 shows the value of $J_a/(J_a+J_n)$ plotted against $\log C_p$ over the C_p range 10^{-7} to 4.8×10^{-3}. Kucherov and Faidish[5] report studies in the concentration range 10^{-6} to 10^{-3}. The 10^{-3} region is difficult as far as crystal growth is concerned. Most of the crystals obtained with concentration higher than 10^{-3} were poor and one has to prepare numerous samples to obtain one good crystal. At and above 10^{-3}, the anthracene concentration is high enough to require correction[6] for direct anthracene excitation. However J_a/J_n is so
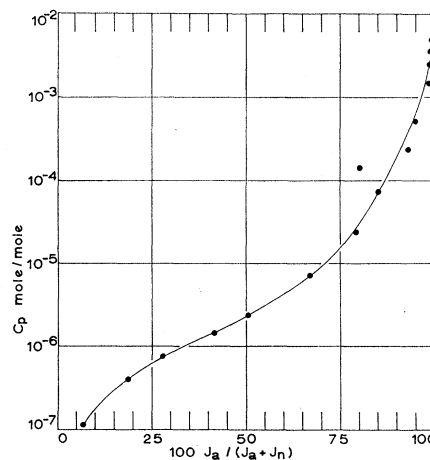

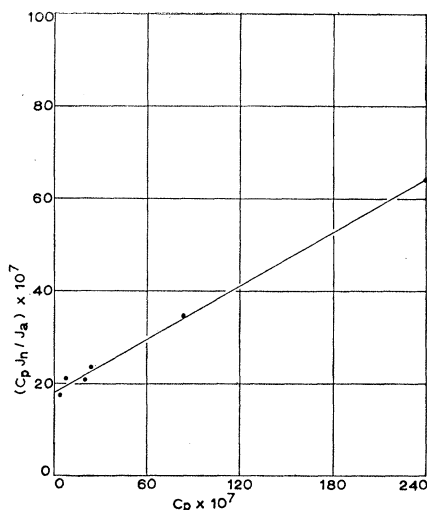FIG. 5. Plot of $J_a/(J_a+J_n)$ vs $\log C_p$ for grown crystals.

FIG. 6. Test of Eq. (7); see text.

large that corrections make little difference in Fig. 5. 100 J_a/J_n in grown crystals exceeds 100% for all $C_p \geqslant 2 \times 10^{-6}$. The results for grown crystals indicate a J_a/J_n, over the whole concentration range, higher than data reported until now. The results quoted in the literature are closer to the J_a/J_n ratios observed in micro-crystalline films, these are 2 to 3 times lower (see Sec. 4).

In view of the lack of adequate theoretical models, it is not possible to compute mean free paths from our data. In the impurity concentration range 10^{-7} to 4.8 $\times 10^{-3}$ with nonannealed crystals, energy transfer is due mainly to localized and incoherent free excitons.

The mean free path of the localized exciton is very short and it decays leading to fluorescence or thermal quenching unless the distance between two impurities is comparable to its mean free path. Experimental evidence is not clear on this point especially: that at the high impurity concentrations required to trap localized excitons the density and size of defects interfere strongly in these processes. Such defects must also influence the relative concentrations of free and localized excitons.

The J_a and J_n values are not corrected for reabsorption and quantum yields as is often done in the Russian literature.[5] These factors are so sensitive to the history of the crystal that we see no advantage in applying them at the moment. Thin crystals were used throughout to minimize the need for such corrections.

Experiments at low temperatures on crystals with impurity concentration 10^{-4} to 10^{-5} showed an increase in total fluorescence of some 40%. This increase is probably due to an increase in quantum yield and a decrease in reabsorption. Crystals with 10^{-7} impurity concentration exhibited a behavior totally different from the 4×10^{-8} impurity crystal: J_a/J_n increased only slightly at low temperature and there were no significant irreversible annealing effects on temperature cycling as those shown in Fig. 2. If we forget about the

annealing results on crystals of impurity concentration 4×10^{-8}, one can determine from Fig. 5 that at concentration 10^{-6} half,

$$J_a/(J_a+J_n) = 50\%,$$

of the free excitons are trapped. At this concentration the distance between impurities is roughly 750 A. The effects of annealing indicate either a much longer mean free path or the participation of coherent free excitons in the energy transfer processes (Sec. 5), or both.

In the limit $C_p \to 0$, $C_p > 0$ Eqs. (24) of Agranovich and Faidish[10] lead to

$$\lim_{C_p \to 0} (A_4 C_p J_n/J_a) = [(A_1+A_3)\mu_0^{\frac{1}{2}}+A_2+\mu_0 A_3]$$
$$+[\mu_1(A_1+A_2)\mu_0^{\frac{1}{2}}+A_3\mu_1]C_p. \quad (7)$$

Figure 6 shows a plot of $(C_p J_n/J_a)$ vs C_p. The linear relation is obeyed up to a concentration of 2.4×10^{-5}. In the limit $C_p \to 0$, $C_p \backsim 0$, (J_a/J_n) varies linearly with C_p. Figure 1 is such a plot. The relationship is not linear below 3×10^{-7}. The dashed line is extrapolated to $C_p=0$. It is this portion of the curve which was used to determine the initial purity of our material. The deviation of this plot from a straight line passing through the origin is most probably due to defects.

(4) Results Obtained using Microcrystalline Films

More than 40 microcrystalline films were studied. The general results are the same as for the grown crystals with the following exceptions (see also Sec. 2):

(a) The consistency among films and grown crystals prepared in identical manner is poor because of the variations in the relative importance of surface to bulk processes. At low impurity concentrations these variations are of the order of 10–20% but for crystals become large at $C_p \geqslant 10^{-5}$ when J_a/J_n varies between 6 and 3, depending on wavelength, while, for films, similar large variations begin at about $C_p \geqslant 10^{-4}$.

(b) Experiments designed to test the uniformity of the impurity distribution at high concentration, $C_p \geqslant 10^{-6}$, showed that the impurity is not homogeneously distributed.

(c) The values of (J_a/J_n) for the films are consistently smaller than those for crystals. At impurity concentration 7.2×10^{-7}, (J_a/J_n) for crystals is 35.5 ± 1.7 while for a film it is 7.9 ± 1.3. At 2.4×10^{-6}, these ratios are 103 ± 8 and 37 ± 6.7, respectively. This proves that the crystalline defect interrupt drastically the exciton mean free path.

(5) Coherence and Size of Excitons

Fox and Yatsiv[15] and Dexter[16] discussed coherence effects and problems related to the size of the exciton.

[15] D. Fox and S. Yatsiv, Phys. Rev. 108, 938 (1957).
[16] D. L. Dexter, Suppl. Nuovo cimento 7, 262 (1958).

There is thus the possibility for the existence of coherent free excitons and incoherent free excitons both in the sense of Dexter.[16] This distinction has not been made by experimentalists because all observations have been performed on the incoherent free excitons only. Fox and Yatsiv estimated that in anthracene a coherent free exciton would be shared by some 10^5 molecules. Dexter[16] estimates that the thermal velocity of the coherent exciton is 10^7 cm/sec. The lifetime of naphthalene fluorescence[17] is about 10^{-9} sec. The mean free path of a coherent exciton is then about 100μ.

The importance of the surface relative to the bulk decreases sharply at about $250° \pm 25°K$ (Sec. 2). It is difficult to see why the mean free path of incoherent bulk excitons should be more sensitive to temperature than the mean free path of surface excitons. It is for this reason that coherent excitons are believed to participate in these processes, thus increasing J_a/J_n due to their longer mean free path. The "size" of the impurity as extended by the defect surrounding it must be important in the trapping of the diffuse coherent excitons since on further annealing J_a/J_n curve $13 \rightarrow 14$ increases above $250°K$ but decreases below $225°K$ as compared to $10 \rightarrow 11$, Fig. 2. This "size" effect is

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[17] A. Schmillen, Z. Naturforsch. **8**, 213 (1953), reports the mean life of crystalline anthracene fluorescence to be about 10^{-9} sec. Napthalene will probably have a similar lifetime. The problem of lifetimes is apparently in a confused state. M. Kasha and R. V. Nauman, J. Chem. Phys. **17**, 516 (1949), report for naphthalene in EPA at $77°K$ a value of 3.3×10^{-5} sec.

probably also important in the trapping of the other excitons.

As indicated in Sec. 3 on increasing the impurity concentration from 4×10^{-8} to 10^{-7} the increase in crystalline defects was sufficient to prevent the appearance of coherent excitons and to reverse the importance of surface to bulk processes. Apparently this is the critical impurity concentration region for the observation of crystalline excitations that involve a large number of molecules.

(6) Dependence on Film Thickness

Faidish and Zima[16] report that at an impurity concentration (tetracene/anthracene) of 10^{-6} the anthracene fluorescence is almost independent of the crystal thickness between 0.2 and 40μ, but that at higher impurity levels, the fluorescence of anthracene decreases with increasing thickness. We found that for 4×10^{-8} films the value of J_a/J_n was almost independent of thickness for films below 10μ. However, at 10μ and above, J_a/J_n increases very rapidly with thickness due to reabsorption of naphthalene fluorescence. We subscribe to the explanation put forth by Faidish and Zima. This is the reason why we limited our studies to crystals about 5μ thick.