

## Exciton Diffusion in Naphthalene Crystals

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Exciton capture by anthracene in naphthalene crystals is studied as a function of impurity concentration ( $4 \times 10^{-8}$  to  $4.8 \times 10^{-9}$ ), 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<sup>1-7</sup> have appeared in the literature demonstrating the diffusional character of exciton motion in molecular crystals. McClure<sup>8</sup> and Ganguley and Chaudhury<sup>9</sup> have contributed review articles.

The status of the subject can be stated as follows: Simpson,<sup>7</sup> 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<sup>2</sup> (some details of this paper are reproduced because it is not easily accessible) assumed that the exciton diffusion process is described by

$$Dd^2n/dx^2 + I_0ke^{-kx} - n/\tau = 0, \quad (1)$$

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:

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

they find the solution:

$$n(x) = [I_0k/D(k^2 - p^2)] \{ [(s+k)/(s+p)]e^{-px} - e^{-kx} \}, \quad (3)$$

where  $p = 1/l = (D\tau)^{-1/2}$ . 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  $\beta$  is a

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<sup>1</sup> F. Lipsett and A. J. Dekker, Can. J. Phys. **30**, 165 (1952); Nature **173**, 736 (1954).

<sup>2</sup> 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).

<sup>3</sup> V. M. Agranovich, I. Ya Kucherov, and A. N. Faishish, Ukrain. Fiz. Zhur. **2**, 61 (1957).

<sup>4</sup> J. B. Birks and G. T. Wright, Proc. Phys. Soc. (London) **B67**, 657 (1954).

<sup>5</sup> I. Ya Kucherov and A. N. Faishish, Dopovodi Akad. Nauk Ukr. RSR **1**, 57 (1956).

<sup>6</sup> H. C. Wolf, Z. Physik **145**, 116 (1956).

<sup>7</sup> O. Simpson, Proc. Roy. Soc. (London) **A238**, 402 (1956).

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

<sup>9</sup> 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  $\lambda_a, \lambda_b, \lambda_c$ , where the extinction coefficients are  $a, b, c$ , respectively, then, setting

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

$\beta$  and  $s$  can be eliminated from (4):

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

Borisov and Vishnevski determined the absorption of 0.5-cm thick naphthalene and anthracene crystals in unpolarized light over the range 3000–3300 Å and 3000–4000 Å, respectively.  $J$  is also reported over the range 2500–3400 Å for naphthalene and 2500–4000 Å for anthracene—the  $(J, \lambda)$  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  $0.2$ – $0.3 \mu$  for the exciton mean free path in naphthalene and  $0.1$ – $0.15 \mu$  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 Faishish<sup>10</sup> 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 re-fluxed with sodium and recrystallized five times from

<sup>10</sup> V. M. Agranovich and A. N. Faishish, 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  $4.8 \times 10^{-8}$  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.<sup>11</sup> 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  $\mu$  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 Å 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  $4 \times 10^{-8}$  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  $4500 \pm 300$  Å) 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  $31\,062\text{ cm}^{-1}$ ; naphthalene fluorescence begins at  $31\,462$  and  $31\,476\text{ cm}^{-1}$ . 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.]

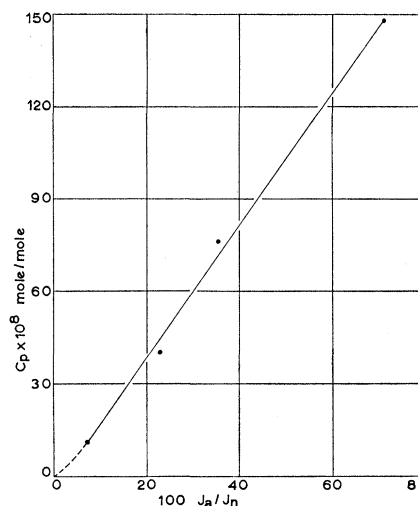


FIG. 1. The dependence of  $J_a/J_n$  on  $C_p$  for grown crystals, at low concentrations of impurity.

## RESULTS AND DISCUSSIONS

### (1) Temperature Dependence and Annealing of Crystals

Agranovich and Korrobeevev<sup>12</sup> 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  $\langle l \rangle_{\text{free}} \approx 20\text{ Å}$  (a printing error gives the unlikely value of 20 Å). 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  $(D^{-1})_{\text{free}} \propto T^{1/2}$  dependence<sup>12</sup> while Trifla<sup>13</sup> finds  $D_{\text{loc}} \propto \exp(U_1/kT)$ . Trifla<sup>13</sup> 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  $4 \times 10^{-8}$ ) 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

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

<sup>12</sup> V. M. Agranovich and Iu. V. Korrobeevev, *Optics and Spectroscopy* **6**, 155 (1959).

<sup>13</sup> M. Trifla, *J. Czech. Phys.* **6**, No. 6 (1956); **8**, 510 (1958).

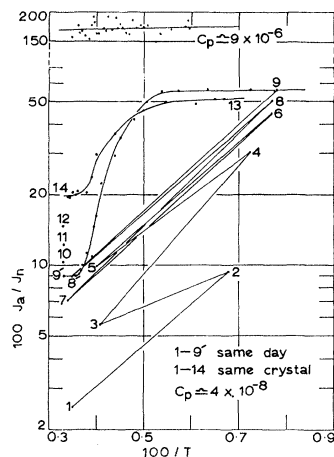


FIG. 2.  $\log(J_a/J_n)$  vs  $100/T$  for  $4 \times 10^{-8}$  and  $9 \times 10^{-6}$  crystals. Point 1 is the starting point of the annealing cycles. 1  $\rightarrow$  14 is for the same crystal. Points 1  $\rightarrow$  11 follow in rapid succession; about 30 min elapses between successive points except for point 12 which is 96 hrs after point 1. Data at  $\lambda = 2970$  Å. The  $9 \times 10^{-6}$  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  $9 \times 10^{-6}$  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" ( $4 \times 10^{-8}$ ) crystal—no previous annealing. The same crystal exhibited different slopes depending on the number of annealing cycles it went through. Below  $200^\circ\text{K}$  the slope is almost independent of temperature and leads to an  $\epsilon$  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  $200^\circ\text{K}$  is very sensitive to the past treatment of the crystal (see Figs. 2 and 3). It is likely that the mean free path between  $300^\circ$  and  $200^\circ\text{K}$ , as suggested by Trifaj,<sup>13</sup> is limited by the equilibrium concentration of defects. The slope in the range  $296^\circ$ – $200^\circ\text{K}$  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  $250^\circ\text{K}$  in Fig. 3 is observed in all the "fresh" ( $4 \times 10^{-8}$ ) crystals studied. This dip is annealed out easily, Fig. 2. The dip must be associated with capture processes since it appears only in the  $\log(J_a/J_n)$  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  $4 \times 10^{-8}$ , 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  $4 \times 10^{-8}$  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  $4 \times 10^{-8}$  (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,  $C_p \geq 10^{-6}$ .

## (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<sup>14</sup> 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

$$A_\lambda = (J_a/J_n)_\lambda / (J_a/J_n)_{3020 \text{ Å}} \quad (6)$$

is defined. According to the two-bulk-exciton theory of Agranovitch and Faidish,  $A_\lambda$  is a function  $(1/k)$  ( $k$ =extinction coefficient). This functional dependence of  $A_\lambda$  on  $k$  is already too complex in the simplified Agranovich-Faidish model. For naphthalene  $A_\lambda$  should be less than one at 2970, 2895, 2850, and 2650 Å.  $A_\lambda$  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  $A_\lambda$ .

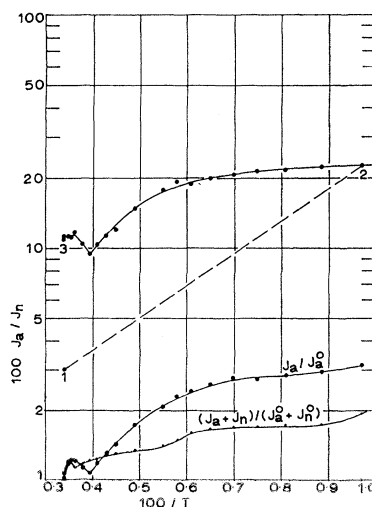


FIG. 3.  $\log(J_a/J_n)$ ,  $J_a/J_n^0$ ,  $(J_a+J_n)/(J_a^0+J_n^0)$  all vs  $100/T$  for a  $4 \times 10^{-8}$  fresh crystal. Point 1 represents the starting point.  $J_a^0$ ,  $J_n^0$  are the values of  $J_a$ ,  $J_n$  at point 3.

<sup>14</sup> A. N. Faidish and V. L. Zima, Optics and Spectroscopy 6, 58 (1959).

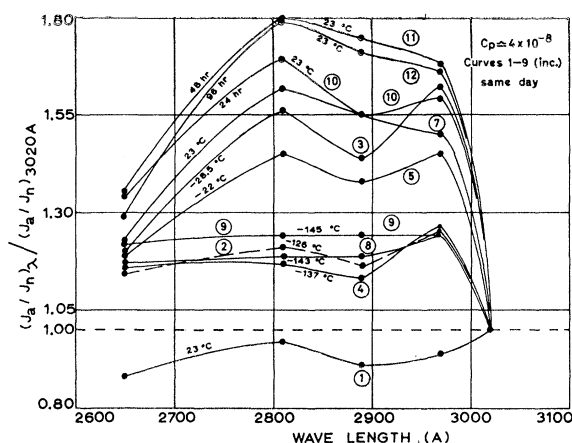


FIG. 4. Plot of  $(J_a/J_n)_\lambda / (J_a/J_n)_{3020 \text{ Å}}$  vs  $\lambda$ . The numbers 1 to 12 on the curves refer to the points in Fig. 2. The curve for point 6 is similar to points 2, 4, 8 and has been left out. All data on the same crystal. The age of the crystal (curves 10, 11, 12) is with 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  $A_\lambda$  from crystal to crystal;  $A_\lambda$  varies between 1.1 and 0.84. For sublimed films of impurity concentration  $4 \times 10^{-8}$ ,  $A_\lambda$  is greater than one. This scatter in the value of  $A_\lambda$  must be due to variations in the surface of the crystals.

Curve 1 in Fig. 4 shows a plot of  $A_\lambda$  vs  $\lambda$  for a fresh-grown crystal of impurity concentration  $4 \times 10^{-8}$ . On subsequent annealing, as already explained,  $A_\lambda$  increases irreversibly and the remaining curves 2–12 give some detail on the "age" (that is annealing) and temperature dependence of  $A_\lambda$ . 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  $A_\lambda$  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  $(J_a/J_n)_\lambda / (J_a/J_n)_{3020 \text{ Å}}$  was less than one for most crystals and conditions. However there are exceptions. For example, a crystal with impurity concentration  $2 \times 10^{-4}$  exhibited a ratio ( $\lambda = 2970 \text{ Å}$ ) 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.<sup>8</sup>

These observations on the dependence of  $A_\lambda$  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  $20 \mu$ . 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. Kuchero and Faishish<sup>5</sup> 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  $5 \mu$  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  $4.8 \times 10^{-3}$ . Kuchero and Faishish<sup>5</sup> 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<sup>6</sup> for direct anthracene excitation. However  $J_a/J_n$  is so

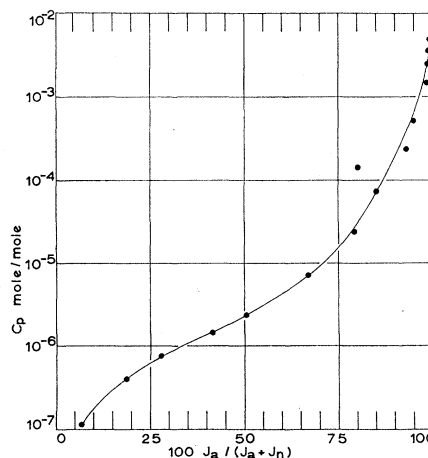


FIG. 5. Plot of  $J_a/(J_a + J_n)$  vs  $\log C_p$  for grown crystals.

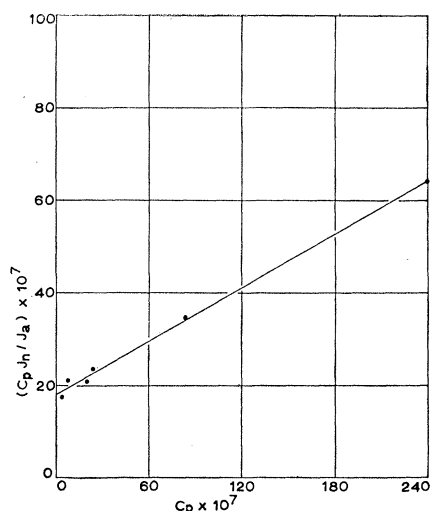


FIG. 6. Test of Eq. (7); see text.

large that corrections make little difference in Fig. 5. 100  $J_a/J_n$  in grown crystals exceeds 100% for all  $C_p \geq 2 \times 10^{-6}$ . 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 microcrystalline 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.<sup>5</sup> 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  $4 \times 10^{-8}$  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  $4 \times 10^{-8}$ , 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 Å. 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  $C_p \rightarrow 0$ ,  $C_p > 0$  Eqs. (24) of Agranovich and Faïdich<sup>10</sup> lead to

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

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  $2.4 \times 10^{-5}$ . In the limit  $C_p \rightarrow 0$ ,  $C_p \simeq 0$ ,  $(J_a/J_n)$  varies linearly with  $C_p$ . Figure 1 is such a plot. The relationship is not linear below  $3 \times 10^{-7}$ . 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  $C_p \geq 10^{-5}$  when  $J_a/J_n$  varies between 6 and 3, depending on wavelength, while, for films, similar large variations begin at about  $C_p \geq 10^{-4}$ .

(b) Experiments designed to test the uniformity of the impurity distribution at high concentration,  $C_p \geq 10^{-6}$ , 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  $7.2 \times 10^{-7}$ ,  $(J_a/J_n)$  for crystals is  $35.5 \pm 1.7$  while for a film it is  $7.9 \pm 1.3$ . At  $2.4 \times 10^{-6}$ , these ratios are  $103 \pm 8$  and  $37 \pm 6.7$ , respectively. This proves that the crystalline defect interrupt drastically the exciton mean free path.

#### (5) Coherence and Size of Excitons

Fox and Yatsiv<sup>15</sup> and Dexter<sup>16</sup> discussed coherence effects and problems related to the size of the exciton.

<sup>15</sup> D. Fox and S. Yatsiv, Phys. Rev. **108**, 938 (1957).

<sup>16</sup> 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.<sup>16</sup> 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<sup>16</sup> estimates that the thermal velocity of the coherent exciton is  $10^7$  cm/sec. The lifetime of naphthalene fluorescence<sup>17</sup> is about  $10^{-9}$  sec. The mean free path of a coherent exciton is then about  $100 \mu$ .

The importance of the surface relative to the bulk decreases sharply at about  $250^\circ \pm 25^\circ \text{K}$  (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  $250^\circ \text{K}$  but decreases below  $225^\circ \text{K}$  as compared to 10  $\rightarrow$  11, Fig. 2. This "size" effect is

probably also important in the trapping of the other excitons.

As indicated in Sec. 3 on increasing the impurity concentration from  $4 \times 10^{-8}$  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<sup>16</sup> 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  $40 \mu$ , but that at higher impurity levels, the fluorescence of anthracene decreases with increasing thickness. We found that for  $4 \times 10^{-8}$  films the value of  $J_a/J_n$  was almost independent of thickness for films below  $10 \mu$ . However, at  $10 \mu$  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  $5 \mu$  thick.

<sup>17</sup> A. Schmillen, Z. Naturforsch. **8**, 213 (1953), reports the mean life of crystalline anthracene fluorescence to be about  $10^{-9}$  sec. Naphthalene 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  $77^\circ \text{K}$  a value of  $3.3 \times 10^{-6}$  sec.

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