proposed by Kondo[9] and by Hamilton and Jensen[10] for La leads to superconductivity. The sharp rise of T_c with pressure found in La[11] as well as in Ba points towards the same origin of superconductivity.

(2) If the proximity of an f band is irrelevant to the superconductivity of barium, it may be a consequence of the development of d character in the electron wave functions as suggested by the work of Vasvari, Animalu, and Heine[12] on the band structure of alkaline-earth metals or in analogy to Sternheimer's $6s \rightarrow 5d$ electron transfer in cesium.[13] In this case, we would expect cesium also to become superconducting under pressure. Similar arguments should hold for strontium and rubidium. On the other hand, all these three elements also have $4f$ spectroscopic energy levels of similar energy as Ba.[14] An extended investigation for superconductivity under pressure of alkali metals and alkaline earths will be necessary to decide this question.

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EVIDENCE FOR LONG-RANGE EXCITON-IMPURITY INTERACTION IN TETRACENE-DOPED ANTHRACENE CRYSTALS*

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It is shown that diffusion of singlet excitons cannot explain the time dependence of the fluorescence intensity in tetracene-doped anthracene crystals; however, the predictions of a long-range energy-transfer mechanism can be made to agree with experimental results.

The mechanism of energy transfer in organic crystals has been the subject of extensive investigations and in the most recent work on tetracene-doped anthracene crystals and similar systems, energy transfer is attributed to diffusion of singlet excitons.[1] It has generally been concluded that the exciton-impurity interaction is a short-range interaction, and the exciton diffusion coefficient D is on the order of 10^{-3} cm^2 sec^{-1}. In this paper we present experimental data on the time dependence of energy transfer from an anthracene host lattice to tetracene-impurity molecules which cannot be satisfactorily explained by this simple exciton-diffusion theory. The results can be explained by a long-range exciton-impurity interaction, and if the excitons move, the results place an upper limit on the order of 5×10^{-5} cm^2 sec^{-1} on their diffusion coefficient.

Vapor-grown crystals of anthracene doped with 1 and 83 ppm tetracene were investigated.[2] The tetracene concentration was determined from the fluorescence spectra by the method of Kreps, Druin, and Czorny.[3] The samples were excited by a 600-keV x-ray source having a total pulse duration of about 6 nsec and a pulse width at half-maximum of about 2 nsec. The fluorescence emission from the samples was detected by an ITT F4030 (S11) photomultiplier tube and displayed and photographed on a Tektronix Model No. 519 oscilloscope. The anthracene and tetracene fluorescence were separately isolated by appropriate filters.

The results of these measurements are shown in Figs. 1 and 2. The experimental points which are shown are the average obtained from three decay pictures. The spread in the data for the three pictures was ±0.03 or less.

If energy transfer is attributed to the diffusion of singlet excitons as is done in recent papers on tetracene-doped anthracene,[4-6] the equations describing the time rate of change of anthracene exciton concentration n_A and the concentration of excited tetracene molecules n_T are

$$\dot{n}_A(t) = G(t) - \beta_A n_A(t) - k n_A(t), \tag{1}$$

$$\dot{n}_T(t) = k n_A(t) - \beta_T n_T(t). \tag{2}$$

Here $G(t)$ is the rate of generation of anthracene singlet excitons, assumed to be proportional to the instantaneous intensity of the excitation pulse, β_A and β_T are the reciprocal lifetimes of the anthracene excitons τ_A and the excited impurity tetracene molecules τ_T, respectively, including both radiative and nonradiative processes but in the absence of energy transfer, and k is the probability that a tetracene molecule will trap an exciton times the concentration of tetracene-impurity molecules. Direct excitation of the tetracene molecules has been neglected since over the concentration range studied this will be negligible compared with excitation by energy transfer as evidenced by the fact that in a crystal containing 1 part in 10^5 tetracene molecules on the order of half the fluorescent light comes from tetracene and the quantum efficiency of anthracene fluorescence is about 1. The expression generally used for k is $k = 4\pi D R N_T$, where R is the interaction distance and N_T is the concentration of tetracene-impurity molecules. If k is independent of time, the solution to Eqs. (1) and (2) can be written as

$$n_A(t) = \exp[-(\beta_A + k)t] \times \int_0^t G(\xi)\exp[(\beta_A + k)\xi]d\xi, \tag{3}$$

$$n_T(t) = k\exp[-\beta_T t]\int_0^t \exp(\xi\beta_T) n_A(\xi)d\xi. \tag{4}$$

The anthracene and tetracene fluorescence intensitites are proportional to the anthracene ex-

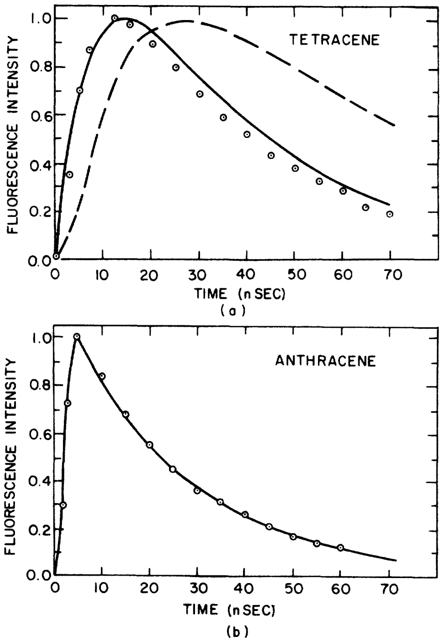

FIG. 1. Time dependence of the fluorescence intensity in anthracene doped with 1 ppm tetracene. See text for explanation of theoretical lines.

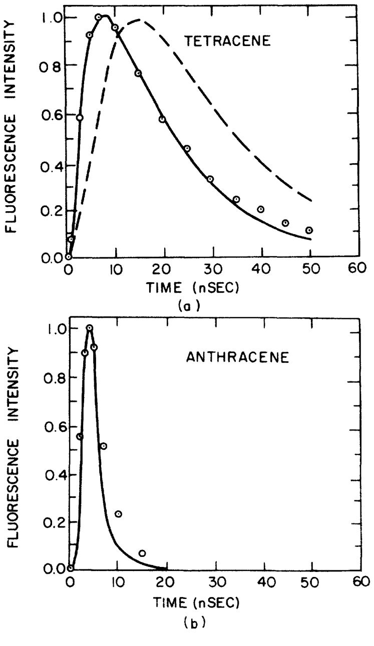

FIG. 2. Time dependence of the fluorescence intensity in anthracene doped with 83 ppm tetracene. See text for explanation of theoretical lines.

citon concentration and to the concentration of excited tetracene molecules, respectively. These equations were numerically integrated using the experimentally determined shape of $G(\xi)$ and assuming $\tau_A = 27$ nsec and $\tau_T = 13$ nsec. The predictions of Eqs. (3) and (4) are shown as solid lines in Figs. 1(b) and 2(b) and as dashed lines in Figs. 1(a) and 2(a). Within the accuracy of the experimental data, this model can be made to agree with the anthracene fluorescence time dependence but not with that of the tetracene. The apparent discrepancy in Fig. 2(b) is attributed to the inability of the measuring circuit to follow the extremely fast decay. The choice of τ_T and τ_A will be discussed in more detail later, but it should be emphasized that simply shortening the tetracene lifetime will not provide agreement between theory and experiment.

Long-range resonant dipole-dipole interaction is another mechanism which has been proposed to explain the energy transfer in crystals.[7,8] In this model an excited anthracene molecule can transfer its excitation energy directly to an unexcited tetracene molecule and diffusion of excitons is not involved. The energy-transfer probability for this type of interaction is inversely proportional to the sixth power of the distance over which the energy is transferred. Thus, the excited anthracene molecules located close to a tetracene molecule transfer their energy more rapidly than those that are far from tetracene impurities.

If we consider very short-pulse excitation, Eqs. (1) and (2) can still be used to describe the kinetics of the fluorescence intensity for this model. However, for the process now under consideration k is a function of time. The time dependence of the anthracene excited-state concentration becomes[7,9]

$$n_A(t) = n_A(0)\exp[-\beta_A t - \gamma(\pi\beta_A t)^{1/2}], \tag{5}$$

and that of the tetracene excited molecules is

$$n_T(t) = \gamma\beta_A^{1/2}\exp(-\beta_T t) \times \int_0^t \exp(\xi\beta_T) n_A(\xi)\xi^{-1/2}d\xi, \tag{6}$$

where $\gamma = N_T/C_0$. The "critical concentration" is defined by $C_0 = (\frac{4}{3}\pi R_0^3)^{-1}$, where R_0 is the distance between the anthracene exciton and tetracene impurity at which the energy-transfer probability is equal to the probability for de-excitation in the absence of energy transfer.

For comparison with experimental results the finite width of the exciting pulse must be taken into account. This was accomplished by treating the real pulse as a series of equally spaced delta functions whose magnitudes are proportional to the height of the pulse at the time of the function. Each delta function will produce curves with the shape of Eq. (5) with a different $n_A(0)$. The sum of these curves can then be compared with the experimental results. The time dependence of the anthracene fluorescence intensity determined using this model can be made to agree with the experimental data and gives the same solid lines shown in Figs. 1(b) and 2(b) as did the exciton model. However, unlike the exciton model, the long-range interaction model can also be made to agree with the observed time dependence of the tetracene fluorescence intensity as illustrated by the solid lines in Figs. 1(a) and 2(a).

In obtaining the theoretical predictions, it was assumed that $\tau_A = 27$ nsec, the experimentally observed value, and the values of τ_T and γ were adjusted to obtain a good fit with the observed anthracene and tetracene fluorescence from both samples simultaneously. The value used for τ_T was 13 nsec, consistent with that obtained by Galanin and Chizhikova[10] for the decay of the fluorescence of tetracene in anthracene when only the tetracene molecules were excited. A major problem encountered in the interpretation of these data by long-range interaction is that the value of γ needed to obtain a good fit for both samples yields a critical energy-transfer distance of ~130 Å. This is much greater than the value of ~30 Å predicted theoretically from consideration of the overlap of the anthracene-emission and tetracene-absorption spectra.[10,11]

Because of this discrepancy in R_0 attempts have been made to fit the data by other models. For example, the commonly used expression for k in the exciton-diffusion model is not complete. There is a second term which is important at short times. The complete expression for k is given by[12] $k = 4\pi DRN_T[1 + R(\pi Dt)^{-1/2}]$. Even if this expression for k is used and those excitons created within a distance R of a tetracene molecule are taken into account in solving Eqs. (1) and (2), no agreement can be obtained between the theoretical predictions and the observed time evolution of the tetracene emission.

Yokota and Tanimoto[13] have developed expressions for energy transfer in which both long-range dipole-dipole interaction and exciton diffusion are taken into account. For $D = 0$ the expressions they obtain reduce to those in Eqs. (5) and (6). For values of $R_0 \approx 130$ Å and $0 \leq D \leq 3 \times 10^{-6}$ cm^2 sec^{-1} the theoretical predictions of this theory do not deviate from the solid curves in Figs. 1(a) and 2(a). For values of $D \geq 5 \times 10^{-5}$ cm^2 sec^{-1} no agreement between theory and experiment can be obtained.

To summarize, the theoretical explanation of the time evolution of the anthracene and tetracene fluorescence intensity requires a model based on long-range exciton-impurity interaction. An upper limit on the order of 5×10^{-5} cm^2 sec^{-1} is placed on the exciton-diffusion coefficient. This value is much less than 10^{-3} cm^2 sec^{-1}, the approximate value reported by a number of laboratories using different experimental techniques.[5,14,15] The experiment most often cited as evidence of exciton motion is that reported by Simpson.[14] However, we find that it is possible also to fit Simpson's data using long-range dipole-dipole interaction with $R_0 \sim 130$ Å. The results reported here indicate that the model discussed by several authors[1,14] of an exciton hopping randomly from one anthracene molecule to the neighboring one until it happens to hop onto a tetracene impurity molecule is incorrect. So far we are unable to account for the discrepancy between the value of R_0 predicted theoretically from spectral overlap considerations and that obtained as a phenomenological parameter in the treatment of our fluorescence decay data.

We mention in conclusion that the anomalously fast rise of the tetracene fluorescence intensity has been observed with uv excitation as well as with x-ray excitation. This observation eliminates the possibility that the anomalous behavior was associated with the mode of excitation. The x-ray experiment was more definitive than the uv experiment, however, because the excitation pulse width was smaller and the x rays provided bulk excitation rather than surface excitation. It should also be pointed out that the long-range interaction observed here may be important in exciton-exciton annihilation studies where it has been assumed that interaction takes place only between excitons on neighboring molecules.[16]

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