ter would become less restrictive. It is interesting to note that Enz (Ref. 9) obtained v'_{II} by considering high frequencies.

[32]To verify this, carry out the eigenvector expansion, substitute in the explicit expression for the eigenvectors given by Eqs. (4.13) and (4.26), let $\omega_{\vec{k}s} = v_s |\vec{k}|$ and $\vec{v}_{ks} = v_s \hat{k}$ (where the v_s are the first-sound velocities), and rearrange terms.

[33]Note that when anisotropy is allowed for, one can have $v_{II} = v'_{II}$ without all of the first-sound velocities being the same. If $v_{II} = v'_{II}$ and if normal processes dominate, the conditions for driftless and for drifting second sound will both be satisfied. Obviously, the essential condition for drifting second sound will be satisfied. That the conditions for driftless second sound will also be satisfied follows from Eq. (6.4) and $\bar{v}_{II} = v_{II} = v'_{II}$. Also, note that when the propagation velocities are equal, the different types of second sound are experimentally indistinguishable.

[34]Morse and Feshbach (Ref. 2) use a first-sound velocity c in forming their correction to the diffusion equation, as they are primarily interested in investigating how an upper bound on the propagation velocity affects diffusion. The present discussion shows that under certain conditions a better value for their c would be the velocity of second sound v_{ss}.

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[36]R. J. von Gutfeld and A. H. Nethercot, Jr., Phys. Rev. Letters 17, 868 (1966). In their Table II, von Gutfeld and Nethercot give a mean free path of 2.4×10^{-2} cm at 37 °K for their sample. Their heat pulse generator and their detector appear to have been separated by at least 5×10^{-1} cm, which is approximately 20 mean free paths.

[37]See Ref. 16, pp. 1752–1753.

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COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in The Physical Review or Physical Review Letters; (2) addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.

Comments on Random Walk and Diffusion as Models for Exciton Migration*

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It has been shown that exciton diffusion cannot explain the time dependence of host-sensitized energy transfer in doped organic crystals. It is claimed in a recent publication that formulating exciton migration as a random-walk problem eliminates any discrepancies in the observed and predicted time dependences of the energy transfer. In this paper we show that the two models for exciton migration give exactly the same theoretical predictions, and the anomalous time dependence remains unexplained.

This note is a comment on a recent paper by Rosenstock[1] in which it is claimed that random-walk and diffusion models for energy migration give different theoretical predictions for the time dependence of fluorescence intensities.

We recently demonstrated that studying the complete time evolution of the fluorescence intensities of sensitizers and activators is an important tech-

nique for investigating energy transfer in solids.[2-4] This elucidates the time dependence of the processess involved and can thus easily distinguish between exciton diffusion and long-range resonant interaction. Previous investigations of energy transfer were made by measuring relative fluorescence intensities or decay times.

When this technique was applied to the system of tetracene-doped anthracene, it was found that the usual mathematical formulation of singlet exciton diffusion theory cannot explain the observed time dependences of the luminescence intensities. The results indicate that energy transfer is more efficient at short times than at long times which is characteristic of long-range resonant interaction. It was found that the best fit to the data is obtained using a combined theory of diffusion plus long-range interaction. However, in order to obtain this fit it was necessary to use a value for the phenomenological critical energy transfer distance parameter R_0 which is much greater than that estimated from spectral considerations, and a value for the diffusion coefficient D which is much less than that determined by other measurements. These anomalies remain unexplained. The results are quite surprising since it is generally thought that host-sensitized energy transfer in this and similar crystal systems takes place by exciton diffusion

In the paper by Rosenstock[1] it is claimed that our data can be satisfactorily explained by expressing the exciton migration in a random-walk formulation. In the present paper we show that this in not true. The random-walk model for exciton migration predicts the same time dependence for the luminescence intensities as does the diffusion model which we used previously. Thus, if both the rise and decay of the fluorescence intensities are considered the anomalies observed in the time dependence of the energy transfer cannot be explained.

As Rosenstock states, the diffusion model may be considered an approximation to the random-walk model. However, this is a valid approximation for a large number of particles and a large number of steps n in the walk.[5] These criteria are fulfilled for the case of interest here, and Rosenstock employs limits for large n in his random-walk formulation. (See, for example, footnote 7 of Ref. 1.) Thus, we would expect the random-walk model and diffusion model to give exactly the same theoretical predictions for the time dependence of the luminescence intensities.

The apparent discrepancy between our fit to the data with the diffusion model and Rosenstock's fit using the random-walk model arises from the fact that we fit the total time evolution of the fluorescent intensities, rise and decay, whereas Rosenstock fits only the decay portion of the curve. As pointed out in Ref. 2, it is the anomalously fast rise of the tetracene fluorescence in the lightly doped sample which must be explained. The decay portion of the curves is consistent with intensity measurements made previously[6,7] and can be fit with exciton diffusion theory using $D = 5\times10^{-4}$ cm^2 sec^{-1} and an interaction distance of 10 Å. This value of the diffusion coefficient is consistent with values measured by other techniques.[7,8]

Thus, the important criteria in fitting our data is the theoretical prediction of the rise time of the activator fluorescence intensity. This can be found from Eq. (7) of Ref. 1,

$$I^T(t) = b/\{1+[(a-b)/(1-F)C]\}^{-1} \times (e^{-bt/\tau} - e^{-[a+(1-F)C]t/\tau}) \quad , \tag{1}$$

where the meanings of the various symbols are defined in Ref. 1. The time at which the activator fluorescence intensity reaches it maximum value t_{max} can be found by setting the first time derivative of $I^T(t)$ equal to zero. This gives

$$t_{max} = [(b-a)/\tau - (1-F)C/\tau]^{-1} \ln[b/(a+(1-F)C)] \, . \tag{2}$$

Using the values for the decay times given in Ref. 2 and $F = 0.3$ from Ref. 1, we find that for the sample with 1-ppm tetracene, $t_{max} = 18$ nsec. (Note that for the slightly larger decay-time values used in Ref. 1, $t_{max} = 21$ nsec.) The data shown in Ref. 2 and used in Ref. 1 exhibit a 12-nsec rise time for the activator fluorescence of this sample. The theoretical predictions of diffusion theory give a t_{max} for this sample of 20 nsec. Thus, the rise time prediction of the random-walk model is consistent with that of the diffusion model and is not consistent with experimental observations.

The equations above apply directly to an exciting pulse which is infinitely sharp but do not account for the finite width of the exciting pulse used to obtain the experimental data of Ref. 2. Data obtained from δ-function excitation are shown in Refs. 3 and 4, and the observed t_{max} is approximately 10 nsec. The prediction of diffusion theory in this case is 18 nsec. Therefore, the concluding remarks of the preceding paragraph remain the same for δ-function excitation.

The connection between Eqs. (3) and (4) of Ref. 2 and Eqs. (6) and (7) of Ref. 1 can be easily shown. We start from the former set of equations[2]:

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

$$n_T(t) = k e^{-\beta_T t} \int_0^t e^{\xi\beta_T} n_A(\xi) \, d\xi \quad , \tag{4}$$

where the various symbols are defined in Ref. 2. If the exciting pulse shape $G(\xi)$ is assumed to be a δ function, Eq. (3) immediately gives

$$n_A(t) = n_A(0) e^{-(\beta_A+k)t} \quad . \tag{5}$$

Substituting this into Eq. (4) and integrating gives

$$n_T(t) = [kn_A(0)/(\beta_A + k - \beta_T)](e^{-\beta_T t} - e^{-(\beta_A + k)t}) \quad . \qquad (6)$$

Note that in both Refs. 1 and 2 direct activator excitation is considered negligible as has been assumed in deriving Eq. (6). Neglecting the coefficients of the exponential factors which are lost in normalizing the expressions, Eqs. (6) and (7) of Ref. 1 are exactly the same as Eqs. (5) and (6). The notation is simply changed as follows: $\beta_A \to a/\tau$, $\beta_T \to b/\tau$, $k \to (1-F)C/\tau$.

In summary, we feel that the random-walk calculations of Rosenstock are mathematically interesting, but they do not resolve the anomalies observed in the time evolution of the fluorescence intensities in tetracene-doped anthracene. Instead they give the same predictions as exciton diffusion theory, as should be expected. We conclude by emphasizing that due to the anomalous R_0 we do not feel that the results of Ref. 2 represent proof of the existence of long-range energy transfer in this system. They simply show that the current theories of energy transfer are not adequate for explaining phenomena occurring in short times and indicate the necessity for a time dependence similar to that of the long-range-interaction mechanism.

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uv Resonant Raman Scattering in ZnO

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Multiphonon scattering has been observed in ZnO by means of uv laser Raman studies. Phonon-scattering shifts greater than 4000 cm^{-1} are observed. Comparisons are made with other resonant Raman scattering studies, which now include the related series ZnTe, ZnSe, ZnO, and ZnS. A discussion of multiphonon linewidths is given.

Recently, resonant Raman scattering studies have been performed on a wide class of semiconductors, including CdS,[1] ZnSe,[2] InAs,[3] InSb,[4] ZnTe,[5] GaP,[6] and ZnS.[7] In the most recent paper,[7] it was observed that the number of multiphonon lines observed in III–V's and II–VI's at resonance varied monotonically with the polaron coupling coefficients in the materials examined. Since ZnO is known to have a large polaron coupling coefficient,[8] we have examined it in the present experiment as a comparison with earlier studies. The band gap in ZnO is at about 3400 Å, and so a uv laser is required as the excitation source for resonant scattering. We have employed a 1-m helium-cadmium laser of 4-mm bore and 3-Torr helium pressure, operating with 1 g of Cd isotope 114 in a sidearm at ~280 °C. The source emits 6 mW of cw power at the 3250-Å Cd II transition wavelength.

The spectrum obtained at ambient temperatures is shown in Fig. 1. Note the presence of emission lines from Cd I and II and from He I. Detection was by means of a Spex 1400 double monochromator, an EMI 6256 phototube with quartz window and collection optics, and a Keithley 610B electrometer.

The spectrum as shown consists of a broad luminescence envelope peaking at about 3750 Å, with relatively sharp lines superimposed upon it. These sharp lines are at frequency shifts which are multiples of the 1-LO zone-center frequency of 585 cm^{-1} and have been discussed in some detail for