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Temperature Dependence of Sensitized Fluorescence in Naphthalene Crystals

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Introduction

The mechanism of energy transport in organic molecular crystals can be studied by sensitized fluorescence. One can analyze nearly all of the experimental results on sensitized fluorescence so far reported by a hopping model.[1] In this model, energy is hopping from molecule to molecule with a characteristic time of about 10^{-13} sec (incoherent exciton). Since one does not observe an activation energy for energy migration in pure organic crystals, there is no firm theoretical foundation for the hopping model, and it seems more satisfactory to explain energy transfer by a free exciton (coherent exciton) mechanism.

In the hopping model only the nearest neighbours of an excited molecule are important for an energy transport. In the band model, larger regions of the crystal cooperate and crystal properties like phonons determine the exciton diffusion and the efficiency of energy transport. Now the question arises: Is there any crucial experiment which allows a decision for or against the hopping model or the band model of energy migration in crystals like naphthalene?

Such a crucial experiment is the measurement of the temperature dependence of energy transfer. If coherent excitons which make something like diffusion are responsible for energy migration, and if scattering by phonons is the most important exciton scattering mechanism, then one expects an increase of the diffusion length and the efficiency of energy transfer with decreasing temperature. Agranovich and Konobeev[2] have shown, that in this case the diffusion coefficient D is proportional to $1/\sqrt{T}$ in the temperature region above a Debye temperature.

Experiment

Figure 1 shows the ratio of guest to host fluorescence as a function of temperature in an extremely pure naphthalene crystal containing 5×10^{-5} parts of anthracene as guest. The ratio I_A/I_N increases with decreasing temperature between 100 and 6°K. A proportionality to $1/\sqrt{T}$ is a good first approximation. The decrease below 6°K is not yet understood and will not be discussed in the following. The same temperature dependence is observed for crystals with lower anthracene concentrations.

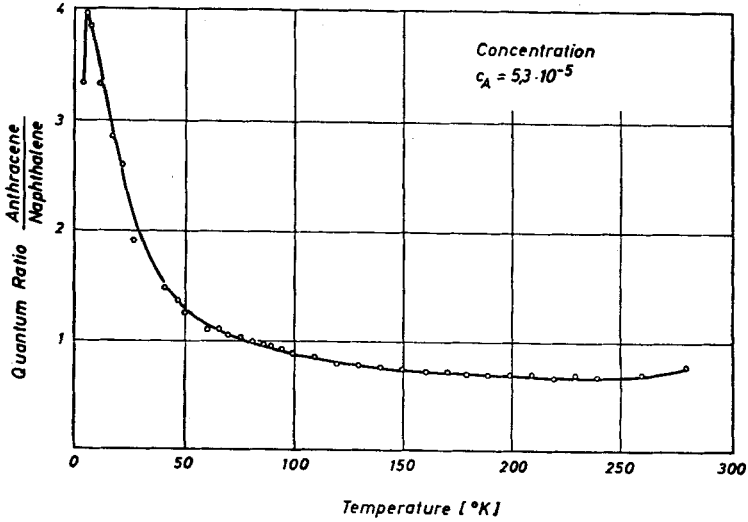

Figure 1. Ratio of anthracene to naphthalene quanta in the fluorescence of a naphthalene crystal containing $5 \cdot 10^{-5}$ parts of anthracene.

Discussion

Assuming exciton diffusion, and assuming that capture of the exciton by a guest molecule occurs only at a distance smaller than or equal to R (radiationless decay of excitons is neglected), the intensity ratio $I_{\text{Guest}}/I_{\text{Host}}$ at low guest concentration is given by the following equation:

$$I_G/I_H = 4\pi DRN_G\tau_H$$

(D = exciton diffusion coefficient
N_G = number of guest molecules per cm^3
τ_H = decay time of host exciton fluorescence).

Taking the values from Fig. 1 (concentration 5×10^{-5}, $I_G/I_H = 4$ at low temperature, 0.7 at high temperature, $\tau_H = 10^{-7}$ sec) we find $DR \simeq 10^{-11}$ cm^3 sec^{-1} at low temperature and $DR = 2 \times 10^{-12}$ cm^3 sec^{-1} at high temperature. The exciton capture radius R is unknown. If we assume that $R = 10^{-7}$ cm and independent of temperature we find $D \simeq 10^{-4}$ cm^2 sec^{-1} at low temperature and $D \simeq 2 \times 10^{-5}$ cm^2 sec^{-1} at high temperature.

The exciton diffusion length calculated from $L = \sqrt{D\tau}$ is $L \simeq 300$ Å at low temperature, $L \simeq 140$ Å at high temperature. Whereas the absolute values of D and L are uncertain mainly because we do not know R, the temperature dependence of energy transfer as measured in Fig. 1 seems to indicate that phonon scattering is the most important exciton scattering mechanism in the temperature region studied. This temperature dependence cannot be explained by a simple hopping model for exciton migration.

REFERENCES

1. Wolf, H. C., Festkörperprobleme Band 4, S. 57 (1965) Verlag Vieweg, Braunschweig.
2. Agranovich, V. M. and Konobeev, Yu. V., Soviet Physics Solid State **5**, 999 (1963).