Table I. Coefficients a and b of Eq. (1) for Ar, O_2, He^4, and He^3.

Element	a	b $(T<T_c)$
Ar	1.8	8
O_2	2.4	10
He^4	0.62	2.0
He^3	0.37	1.7

ment with the conjecture of Yang and Yang.[4] We note that the coefficient 0.62 for He^4 is very close to that observed by Buckingham and Fairbank[5] for the specific heat along the saturated vapor curve at the λ point of He^4 (0.64) and may have particular significance in explaining the quantum transition.

Preliminary measurements of C_v for He^4 at densities not as close to ρ_c as the measurements presented above indicate that in the two-phase region $d^2\mu/dT^2$, where μ is the chemical potential, does not approach zero as T approaches T_c. This differs from the result of the two-dimensional lattice gas and supports the prediction of Yang and Yang.[4] The behavior of C_v in the one-phase region is a sensitive and complicated function of density. It will be discussed elsewhere.

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DIFFUSION OF TRIPLET EXCITONS IN ANTHRACENE*

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We have performed two types of experiments which indicate that the diffusion coefficient for triplet excitons in anthracene crystals is on the order of 0.4×10^{-2} to 2×10^{-2} cm^2 sec^{-1}. The results are particularly significant since they are compatible with coherent motion of triplet excitons (mean-free path greater than the lattice spacing) and give inconsistent results for the hopping or incoherent model of energy transfer unless present estimates of the hopping rate are grossly in error.

In a recent review article on excitons, Knox[1] pointed out that exciton diffusion by coherent motion has not been adequately demonstrated. Experimental observations on triplet excitons in anthracene[2,3] have shown that there was a very good possibility that diffusion effects could be observed in this system, and Avakian and Merrifield[4] have recently published results demonstrating this effect. Their results, however, appeared to be consistent with the hopping model.

Our first experiment consisted of studying the effect of crystal thickness on the time dependence of the fluorescent light intensity emitted by a crystal of anthracene after excitation by a Q-spoiled ruby laser. Crystals were mounted on a microscope slide with a polished surface in contact with the glass. The ruby-laser light was incident on the crystal through the glass, and the crystal thickness was varied by shaving off the back surface with a microtome.

It has been well established[2,3] that the concentration, n, of triplet excitons in a thick anthracene crystal can be described by the equation

$$dn/dt = -\beta n - \gamma n^2, \tag{1}$$

where β is the reciprocal of the exciton lifetime and γ is the exciton-exciton annihilation rate constant. The exciton-exciton annihilation process produces fluorescence, and by studying the time dependence of the light emitted by a crystal the time dependence of the exciton concentration can be inferred. The number of fluorescent quanta emitted per unit volume is equal to $\frac{1}{2}\gamma n^2$, where $\gamma \cong 2.5 \times 10^{-11}$ cm^3 sec^{-1}.

In this experiment a marked decrease of the apparent lifetime of the triplet excitons with decreasing crystal thickness was observed. Since the initial fluorescence flux per unit volume did not vary significantly with crystal thickness, it was concluded that γ was constant. If one wishes to attribute the decrease of the apparent lifetime to diffusion with surface quenching, Eq. (1) must be generalized to

$$\frac{\partial n}{\partial t} = -\beta n - \gamma n^2 + D\frac{\partial^2 n}{\partial x^2}, \tag{2}$$

where D is the diffusion coefficient for the triplet excitons. Under the conditions $\gamma n^2 \ll \beta n$ (weak illumination), uniform initial density, and surface quenching, the solution of this equation becomes

$$n(x,t) = \frac{4}{\pi} n_0 \sum_{k=0}^{\infty} \frac{1}{2k+1} \exp\left\{-\left[\beta + \frac{(2k+1)^2\pi^2 D}{L^2}\right]t\right\} \times \sin\left(\frac{2k+1}{L}\pi x\right).$$

For $t > 5\times10^{-2} \times L^2/D$, Eq. (2) approaches $dn/dt = -\beta' n$, with $n = (4/\pi)n_0 e^{-\beta' t}\sin(\pi x/L)$, where

$$\beta' = \beta + \pi^2 D/L^2, \tag{3}$$

and L is the crystal thickness. Experimental results for β' derived under the conditions described above are shown in Fig. 1. The magnitude of the effect is demonstrated by the fact that the thinnest crystal used in Fig. 1 is 0.1 mm. Similar results were obtained on thin crystals grown by sublimation, and therefore the results cannot be explained in terms of defects being introduced by the microtome. From plots such as Fig. 1 diffusion coefficients were found to vary from around 0.4×10^{-2} cm^2/sec for several samples cleaved from large Harshaw crystals, through 0.7×10^{-2} cm^2/sec for two samples cleaved from a home-grown crystal, up to 2×10^{-2} cm^2/sec for one Harshaw sample.

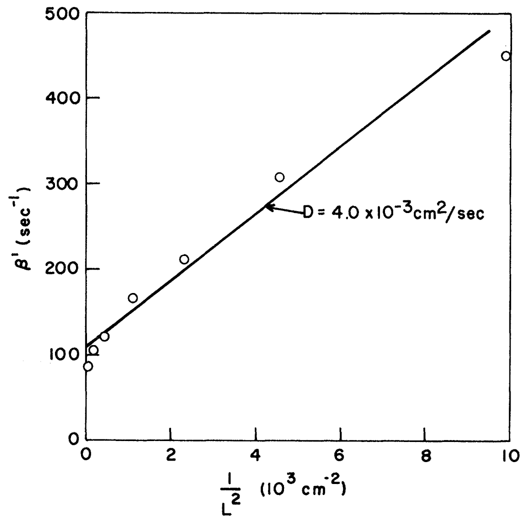

FIG. 1. Reciprocal of the lifetime of triplet excitons as a function of (crystal thickness)$^{-2}$ for a Harshaw crystal.

One cannot explain the results of this experiment solely by using in Eq. (1) a thickness-dependent β which is equal to β'. Assuming the applicability of Eq. (1), it is possible to obtain β from the experimental data for short times.[3] For the 0.1-mm crystal the short time β was three times larger than β'. A numerical solution of Eq. (2), assuming a uniform initial concentration and surface quenching, predicts a larger apparent short-time β, in agreement with the experimental observations.

Our second experiment consisted of measuring the intensity of the delayed fluorescence as a function of the penetration depth of the exciting light in a thick crystal. It has been shown that triplet excitons and thus delayed fluorescence can be produced by light which initially produces singlet excitons.[5] Our second experiment utilized this mechanism to produce triplet excitons at varying depths in the crystal. The experiment was carried out under essentially steady-state conditions and at low light intensity so that γn^2 could be neglected compared to βn. The equation which governs the triplet exciton concentration under these conditions is

$$\frac{dn}{dt}=0=cI_0e^{-\alpha x}-\beta n+D\frac{\partial^2 n}{\partial x^2}, \qquad (4)$$

where c is a proportionality constant and α is the absorption coefficient of the incident light. This equation plus the assumption that $n=0$ at the crystal surface predicts that the intensity of the delayed fluorescent light should go through a maximum as the wavelength is varied.

The experimental results obtained for one crystal are shown in Fig. 2. Solution of Eq. (4) with $D=10^{-2}$ cm^2 sec^{-1} (a value consistent with our first experiment) and $\beta=100$ predicts that the maximum would occur at $\alpha\sim 70$ cm^{-1}, in good agreement with the experimental observations. If D were assumed to be 10^{-4} cm^2 sec^{-1} (more consistent with previous estimates[4,6]), the maximum should have occurred at $\alpha\sim 500$ cm^{-1}.

The magnitude of the diffusion coefficient determined from these experiments makes it possible to distinguish between the two different mechanisms that have been used to discuss the diffusion of triplet excitons in anthracene crystals, the hopping model and the band model.[6]

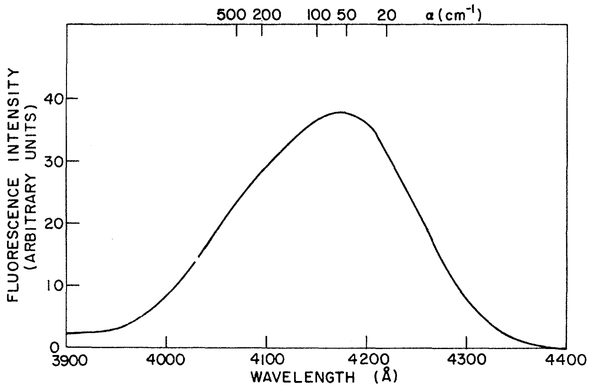

FIG. 2. Variation of the intensity of delayed fluorescence with wavelength of the exciting light. The wavelength range of the exciting light was 25 Å wide at the half-intensity points. Absorption-coefficient data were obtained from I. Nakada, J. Phys. Soc. Japan 20, 346 (1965).

The hopping model predicts $D=a^2/2\tau$, where a is the hopping distance and τ is the time per hop. Theoretical estimates[6] of $1/\tau$ range from 6×10^9 to 3×10^{10} sec^{-1}, and a is approximately 6×10^{-8} cm. These results predict that D would be between 1.1×10^{-5} and 5.4×10^{-5} cm^2 sec^{-1}, two orders of magnitude smaller than the experimentally observed values.

The band model predicts

$$D=\tfrac{1}{2}v\lambda,$$

where v is the instantaneous velocity of the exciton and λ is its mean-free path. Theoretical estimates of v vary between 10^4 and 10^5 cm/sec, and with the values of D observed experimentally, λ is predicted to lie between 6 and 400 Å, a range which is quite consistent with the model.

We believe that the expressions used in recent papers which relate the diffusion coefficient to the rate of collision of excitons with excitons[6] or impurities[7] in the coherent transfer model are incorrect. Kinetic theory of gases gives the collision-rate constant as σv where σ is the collision cross section and v is the instantaneous velocity. This rate constant was given by Jortner et al.[6] as $8\pi D\langle R\rangle$ where $\langle R\rangle$ is the collision distance. The fundamental difference between these two expressions is that the kinetic-theory result does not depend on the exciton mean-free path, whereas the relation containing the diffusion coefficient does, since $D=\frac{1}{2}\lambda v$.

Jortner et al. obtained the expression $8\pi D\langle R\rangle$ from the first term of a formula given by Chandrasekhar[8] for the rate of coagulation in a solution,

$$8\pi D\langle R\rangle\left[1+\frac{\langle R\rangle}{(2\pi Dt)^{1/2}}\right].$$

The first term is not applicable to the exciton collision problem since it represents the steady-state flow set up by the alteration of the distribution by the continued presence of a particle sink. The rate of interest for the present problem should be given by the limit of the second term as $t\to 0$ which is $8\pi^{1/2}D\langle R\rangle^2/\lambda$, since this represents the collision rate in an unaltered distribution. Using the relation $D=\frac{1}{2}\lambda v$, the true rate becomes $4\pi^{1/2}\langle R\rangle^2 v$, which is similar to the kinetic-theory result σv, since $\sigma=\pi\langle R\rangle^2$.

Similarly, Agranovich and Konobeev,[7] by an "elementary calculation," arrive at $4\pi D\langle R\rangle$ as the rate constant for exciton capture by an impurity. In view of the above discussion we believe that their interpretation that previous experimental results demonstrate coherent motion for singlet excitons in naphthalene is incorrect.

Most determinations of the diffusion coefficient reported in this paper were made for diffusion perpendicular to the *ab* plane. For diffusion in the *ab* plane we found a value of D within the range cited in the first paragraph. Theoretical predictions[6] indicate a large anisotropy, $D_{\perp ab}/D_{\parallel ab} \sim 10^{-3}$, which was not observed.

The results reported here are consistent with those reported by Avakian and Merrifield[4] of a diffusion distance of $7\,\mu$ in a $20\,\mu$-thick crystal. Our results predict a $9\,\mu$ diffusion distance from the relation $l=(2D\tau)^{1/2}$, assuming $D=4\times10^{-3}$ cm^2/sec and the effective $\beta=(\tau)^{-1}=\pi^2D/L^2$, where $L=20\,\mu$. Our results are inconsistent with theirs for the thicker crystals.

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ANOMALOUS ENERGY LOSSES OF PROTONS CHANNELED IN SINGLE-CRYSTAL GERMANIUM*

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The process of "channeling," i.e., the crystallographic orientation dependence of the energy loss of particles which are incident on a crystalline solid,[1-3] has been invoked to explain anomalously small energy losses of charged particles incident along crystallographic orientations having "channels" of low electronic density.[4-6] Recently, channeling was used to account for the crystallographic orientation dependence of charged-particle reactions[7,8] and x-ray production.[9] The orientation dependence of the transmission of charged particles has also been observed photographically,[10,11] demonstrating the phenomena of interplaner channeling.

In previous investigations[4,6] when protons were incident on silicon crystals along crystallographic channeling directions, the energy spectrum of the emergent protons showed a high-energy tail indicative of a continuum of lower than normal energy losses in the crystals. The most marked results in silicon were reported to occur when the beam was incident along the $\langle 110\rangle$ direction, which is the most open direction in a diamond-type lattice.

In the present investigation the energy and angular dependence of protons channeled in germanium have been studied, with high angular resolution.[12-14] The results show that under certain conditions a clearly resolved peak is observed at energies well above the normal energy-loss peak, indicating the existence of a channeling process having a specific energy loss. Furthermore, the energy loss of this peak is a function of crystallographic orientation.

The description of the scattering chamber has been given elsewhere.[5] The beam of protons emergent from the crystal was finely col-