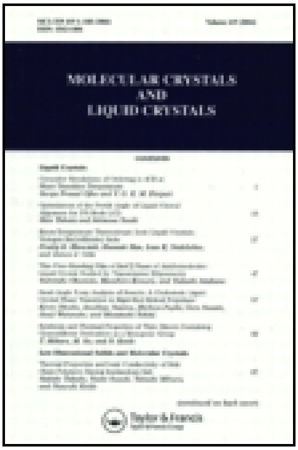

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: T. B. El Kareh & H. C. Wolf (1968): The fluorescence decay times of the two Davydov-components in naphthalene crystals, Molecular Crystals, 4:1-4, 195-200

To link to this article: http://dx.doi.org/10.1080/15421406808082912

Molecular Crystals, 1968. Vol. 4, pp. 195–200

Printed in Germany

The fluorescence decay times of the two Davydov-components in naphthalene crystals

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Abstract—The fluorescence decay time of purest naphthalene crystals has been measured as a function of temperature (300°K–4°K) and thickness. The radiative lifetimes of the two Davydov-components are measured as $\tau_a = 115 \pm 5$ nsec and $\tau_b = 33 \pm 5$ nsec.

1. Introduction

The lowest electronic singulet states of organic molecules are split into exciton bands in the crystalline state. If there are two molecules in the unit cell, two exciton bands are formed. Both are origins for the fluorescence of the crystal. The energetic distance between them is determined by the well known Davydov-splitting. Normally, the oscillator strength of the different Davydov components of one electronic transition are different. Therefore one expects two different decay times for the exciton luminescence in crystals with two molecules per unit cell.

We tried to measure these two decay times τ_a and τ_b for naphthalene crystals. In naphthalene, the origins for exciton luminescence are situated at 31475 (a-component) and 31625 cm^{-1} (b-component) above the ground state. The Davydov-splitting is 150 cm^{-1}. The oscillator strength for the higher Davydov-component is approximately 4 times greater than that of the lower component.[1]

2. Experimental

We measured the fluorescence decay of naphthalene crystals as a function of temperature between 300°K and 4°K, and of thickness between 1 μ and 3 mm. The crystals were excited by light pulses of short duration ($T_{1/2} = 9$ nsec) emitted by a sparkgap in air. We selected the wavelength region between 3400 Å and 2900 Å for excitation using a filter combination whose transmission maximum lied at 3130 Å. As detectors we used a Philips 56 AVP photomultiplier and a Tektronix 585A oszilloscope. The detector risetime was 4 nsec. The sensitivity of the whole setup was high enough to photograph single fluorescence decay curves on the oszilloscope screen and to follow the decay over a region of $1^{1}/_{2}$ intensity decades.

A typical curve is shown in Fig. 1. In the time interval between 50 nsec and 350 nsec after fluorescence has reached its maximum the decay was always exponential. We used this time interval to determine the decay time τ. When no scattered exciting light reached the photomultiplier the decay during the first 50 nsec was somewhat slower than the measured τ (Fig. 1). This initial part of the decay curve is at least partially explained by the fact that the duration of the exciting light pulse is not infinitesimally short compared to the fluorescence decay time.

Especially at low temperature correction must be applied for scattered exciting light which often cannot be completely eliminated by the filters and geometrical arrangement. In that case the decay curve has a short component at its beginning. The intensity of scattered exciting light in naphthalene crystals increases at low temperature.

We measured the average values of τ for many crystals. The accuracy of the measured values is estimated to be ±5 nsec.

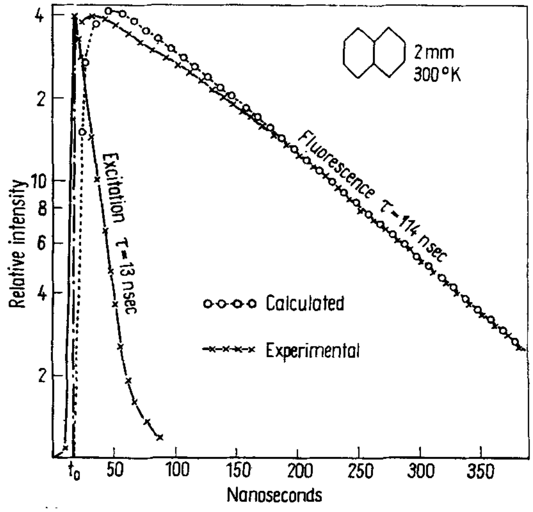

Figure 1. A typical fluorescence decay curve. The experimental curve is compared with a calculated curve which takes into account the final length of the exciting light pulse.

Thick crystals were grown from melt. Thin crystals were produced from solution on water surface or by sublimation. Thick crystals had a higher quality as to perfectness and purity.

3. Results and discussion

The measured values for τ are presented in Table 1. At 4°K the total fluorescence intensity originates at the lower Davydov-component. Therefore we conclude that

$$\tau_a = 115 \text{ nsec} \pm 5 \text{ nsec}.$$

At room temperature reabsorption is very strong. By plotting the τ values as a function of thickness d at room temperature (Fig. 2) and extrapolating to $d = 0$ we get $\tau \cong 40$ nsec. This resulting decay time can be considered as composed of two components τ_a and τ_b with vanishing reabsorption. τ_b can be calculated from the relation

$$\frac{1}{\tau} = (1 - A)\left(\frac{1}{\tau_b} e^{-\Delta E/kT} + \frac{1}{\tau_a}\right),$$

where τ is the measured decay time, τ_a and τ_b the decay times for emission from the Davydov-levels *a* and *b*, ΔE the Davydov-splitting (150 cm^{-1}) and A the reabsorbed fraction of primary fluorescence. (Fig. 3).

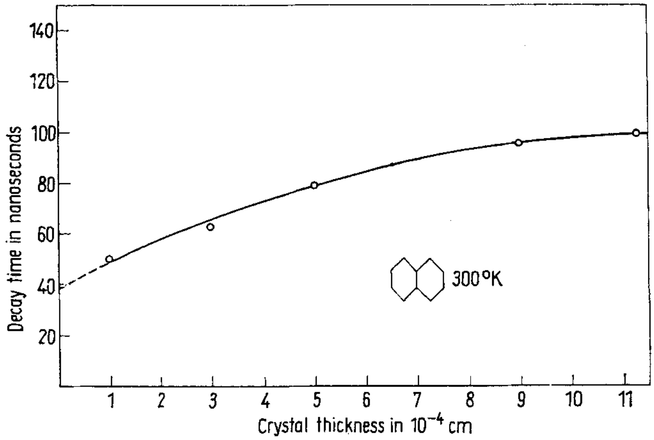

Figure 2. Fluorescence decay time of naphthalene at room temperature as a function of crystal thickness.

TABLE 1 Fluorescence decay time of naphthalene crystals as a function of temperature (°K) and thickness (d). (Times in nanoseconds)

°K / d	300	260	240	220	180	160	140	120	100	80	60	40	20	4,2	Production of crystal
1–3 mm	116	106	103	97	105	110	111	113	125	126	121	117	115	115	From zone melting Tube
100 μm	101	85	90	98	100	103	100	1102	104	104	100	96	98	98	By sublimation
8–10 μm	96	94	80	82	78	80	76	78	76	81	78	80	78	78	From solution on water
4–6 μm	79	71	69	72	68	60	59	56	59	60	58	57	56	56	from Solution on water
1–3 μm	62	60	58	57	60	54	54	56	54	55	53	53	54	53	from Solution on water
<1 μm	46														from Solution on water
10 μm	64			78	78	79	78	80	83	85	95	96	95	95	Evaporated layer

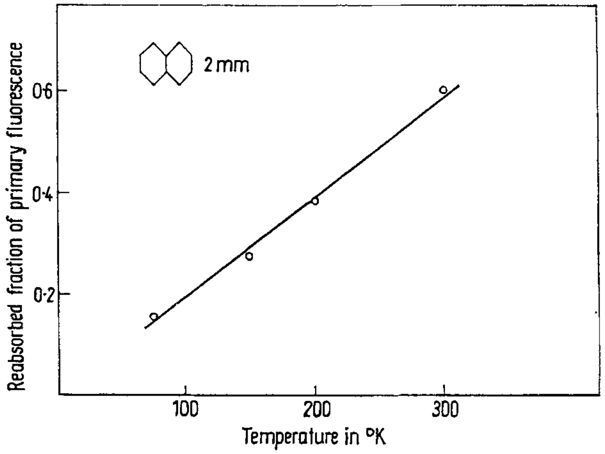

Figure 3. Reabsorbed fraction of primary fluorescence of naphthalene crystals (thickness 2 mm) as a function of temperature. This curve was measured by integrating fluorescence spectra.

Setting the measured τ-values for thick crystals (Table 1) the related values of A (Fig. 3) and $\tau_a = 115$ nsec in the above relation one finds

$$\tau_b = 33 \text{ nsec} \pm 5 \text{ nsec}.$$

The temperature dependence of the measured values of τ is explained as follows: Reabsorption decreases with decreasing temperature which tends to make τ shorter. At the same time the fraction of emission from the a-level increases with decreasing temperature which tends to make τ longer. As a result of these two effects which influence τ in opposite directions one gets a minimum for τ at about 202°K and a maximum at about 80°K for thick crystals.

The temperature dependence of the measured τ values of microcrystals (thickness below 20 μ) is inconsistent with the above model. Fluorescence spectra show that crystals grown from solution on a water surface contain impurities which act as traps. In fact we could show that while the effect of these traps on τ is negligible at room temperature they decrease markedly the values of τ at low temperatures. We conclude that the low temperature values of thin crystals (on water) do not belong to the intrinsic fluorescence of naphthalene.

Although the decay time of evaporated microcrystals decreases with increasing temperature (Table 1) as expected for microcrystals, they cannot be attributed to pure naphthalene because the spectra show the occurance of naphthalene dimers.

Our result for thick crystals at room temperature is in good agreement with the value given by Singh and Bradley.[2] We cannot explain the difference between this value and the result of Birks, King and Munro.[3] We are not aware of other low temperature decay times or τ values for the two Davydov-components.

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