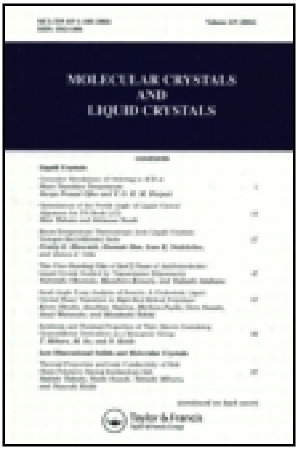

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The Temperature Dependence of the Energy Transfer in Anthracene Doped Single Crystals of Phenanthrene

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The Temperature Dependence of the Energy Transfer in Anthracene Doped Single Crystals of Phenanthrene

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The fluorescence spectra and the fluorescence decay time of of emission bands excited by short light pulses of pure and anthracene doped phenanthrene single crystals were examined for temperatures of 4 to 300 K.

For low temperatures the spectra include an emission from X-traps shifted to smaller wavenumbers by 317 cm^{-1} in addition to the excititon emission (and the anthracene emission for doped crystals). The relative large lifetime of the excition states (τ=45 - 60 ns) determines the decay time of both the exciton emission and the sensibilized X-traps and anthracene emission for all temperatures. The dependance on the temperature unambiguously shows that the excition energy transfer to the anthracene is missing below 50 K.

This is explained by the hypothesis that the anthracene molecules interact only with the highest level of the exciton band. Furthermore, it is to be claimed that the decay time of the directly excited X-traps should be relatively small.

INTRODUCTION

The fluorescence behaviour of single crystals of carefully purified phenanthrene and phenanthrene doped with anthracene was analysed to get further informations about the energy transfer processes.

By his examinations of the phenanthracene – anthracene mixed crystals Belitz[1] was able to demonstrate definitely the energy transfer by excitons. He found a value of 56000 for the energy transfer constant in accordance with the intensity measurements of Benz and Wolf[2] for the same system.

Besides the exciton emission (0–0 transition at 28590 cm^{-1} Benz and Wolf found an emission shifted to the red and caused by the so called X-traps. At low temperatures these X-traps, competing with the anthracene impurity, capture the excitions.

The high sensibility of the single photon counting method used in the following investigations made it possible to measure the fluorescence decay of small bands ($\sim$ 200 cm^{-1}) after spectral separation. Thus, the decay behaviour of the phenanthrene excitons, of the X-traps and of the anthracene emission could be measured farely separated in the range from 4 – 300 K.

The experimental method, the derived results and the applicable conclusions are described in the following.

THE CRYSTALS

The pure and doped phenanthrene crystals under investigation had been grown by F. Belitz[1] using the method of Bridgman and Stockbarger. The substances were purified (described in detail in reference[1]) chromatographically and by zone-melting. The pure phenanthrene crystals had negligible concentrations of anthracene as can be seen in figure 4.

EXPERIMENTAL ARRANGEMENT

The He-cryostat

Using a He-evaporater-cryostat the crystals could be cooled down to 4,2 K. The crystals were excited and the fluorescence was observed from the same side through two quartz windows 90° apart. To avoid mechanical strains the crystals were loosely held at the sampleholder by papermasks. Immediatly after the cleavage the crystals were brought into the He-athmosphere to avoid damaging by air.

The lifetime measurements

The lifetimes were measured by the single photon counting method[3]. The crystals were excited periodically (3 kHz) by light pulses of short duration (2,5 ns FWHM) emitted by a hydrogen-sparkgap working at a pressure of 10 to 15 athmospheres. The trailing edge of the excitation pulse existed of a superposition of two exponential components with time constants of 2,4 and 4,5 nsec respectively (Figure 1).

On account of the decay time being very short compared to the fluorescence decay of the measured crystals, the decay curves were analysed neglecting the finite decay of the light pulse.

For excitation of fluorescence a spectral range about 400 Å at 3130 Å was isolated from the total emission of the lamp using an interference-reflexions-

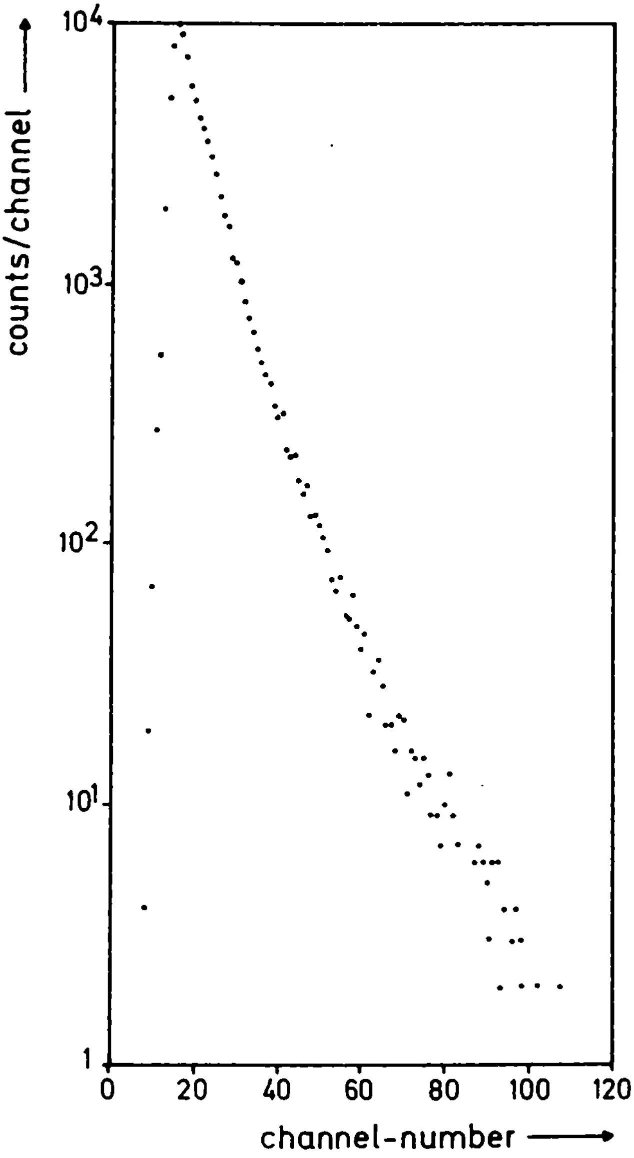

FIGURE 1 Light pulse – measured at 3130 Å by the single photon counting apparatures Time scale – 0,38 nsec per channel.

filter (Schott and Gen, Mainz). The fluorescence was analysed by a 0,75 m Czerny-Turner-Spectrometer having behind the exit-slit an RCA 8850 multiplier for photon counting. Figure 2 shows the experimental arrangement. A critical review of the principles of the applied method is given by Binkert et al.[4]

The decay times were extracted from the data by plotting the intensity logarithmically over a linear time scale. The statistical error at the end of the third decade should be as low as 30%. Therefore we needed measuring times of 2 to 30 minutes depending on the intensity. To gauge the instrument we used cables with well known delay. The reproducibility of our results is within 2%.

The scanning of spectra

The spectral intensity of the fluorescence (exciting wavelength = 3130 Å) was measured by a 0,75 m Czerny-Turner-Spectrometer and a photon counting equipment. The multiplier pulses were given into a multi-channel analyser whose channel numbers were coupled to the wavelength scale of the spectro-

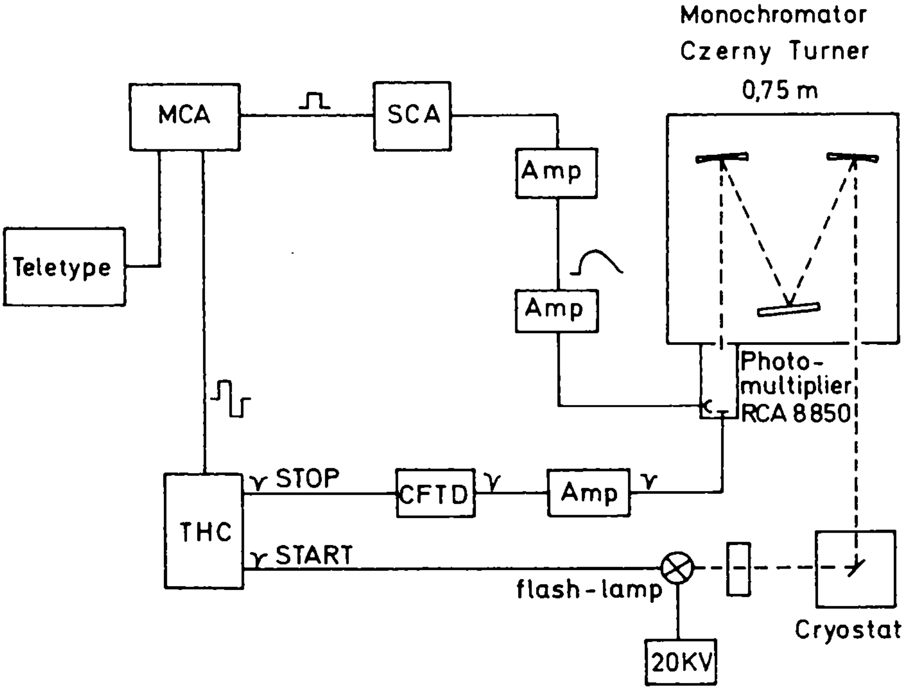

FIGURE 2 Block diagramm of the single photon lifetime instrument, MCA – Northern NS 633, 256 – channel analyzer, SCA – Ortec 406 A single channel analyzer CFTD – Ortec 435 constant fraction timing discriminator, THC – Ortec 347 A time to pulse height converter.

meter. The total resolution given by the number of channels per wavelength unit was about 0,5 Å. No corrections were made concerning the wavelength-dependent sensitivity of the monochromator-multiplier arrangement.

RESULTS

The fluorescence spectra

Figure 3 shows the fluorescence spectrum of a pure phenanthrene single crystal at 4,2 K. The spectrum is analysed in Table 1. Recent data were used concerning IR and Raman spectra given by Witt und Mecke[5]. Our values agree satisfactory with those published by Benz and Wolf[2].

We assumed the 0–0 transition to be at 28597 cm^{-1} as was shown by Craig and Gordon[6]. The band near 28280 cm^{-1} (in Figure 3 only a shoulder can be seen) can be identified to be the 0-0 transition of a X-series. The differences of wavenumbers correspond to the ground state vibration energy of phenanthrene (tab. 1). Craig and Gordon found the same band at 28280 cm^{-1} within the absorption spectrum of a sample of synthetized phenanthrene. Therefore we suppose that the X-series is a phenanthrene transition perturbed by lattice defects.

Table 2 gives a survey of further bands observable as well in the absorption as in the emission spectrum. The bands near 28523 cm^{-1}, 28401 cm^{-1} and 28387 cm^{-1} could be interpreted, as we assume, as 0–0 transitions of further X-centres; but we could not observe vibration bands belonging to these transitions. Also we found no vibration bands belonging to the band at 28253 cm^{-1}. This band vanishes at 100 K which implies the band to be a X-emission. This band is superposed by another one belonging to the ground state vibration of phenanthrene at 406 cm^{-1}. At low temperatures the total spectrum can accordingly be divided at least into two parts: The phenanthrene emission (P-bands) and the X-emission. After Benz and Wolf[2] the emission of the P-bands relative to the X-bands is intensified by increasing temperature.

As can be seen from table 1 some of the measured bands can be definitely assigned to one of these two components. This is important in respect to the lifetime measurement of individual fluorescence bands.

Figure 4 shows the fluorescence spectrum of a doped phenenthrene crystal at 15 K recorded by F. Bayer in our institute. The anthracene concentration was 10^{-4} mol/mol.

TABLE 1

Analysis of the fluorescence spectrum of a phenanthrene crystal at 4,2 K

Nr.	wavenumber (cm^{-1})	distance from $0-0_P$ (28597 cm^{-1})	distance from $0-0_{IV}$ (cm^{-1})	Analysis[a)]	Analysis after Benz and Wolf[2]			
					wavenumber	distance $0-0_P$	relation	
							identified	possible
1	28597			$0-0_P$	28590		$0-0_P$	
2	28513	84		$0-0_I$	28520			$0-0_I$
3	28401	196		$0-0_{II}$	–			
4	28387	210		$0-0_{III}$	28385			$0-0_{II}$
5	28353	244		244 (245)	28350	250		P
6	28280	317	0–0 einer X-Serie	$0-0_{IV}$	28275			$0-0_{III}$
7	28253	344		X	28240		X	
8	28162	435		435 (428)	28160	430		P
9	28038	559	242 (245)?	559 (547)?	28040	550		P
	–	–			27985	605		P
	–	–			27940			
10	27880	717		717 (714)	27880	710	P	
11	27856	741		741 (735)	27850	740	P	
12	27736	861		861 (865)	27745	845		P
	–	–			27645	945		P
13	27574	1023	708 (717)	X	27570			X
14	27540	1057	740 (735)	X	27530			X
15	27453	1134	817 (819)?	1140 (1144)?	27450	1140	P	
16	27425	1172	865 (865)	X	27410	1180	P	

17	27252	1345		1345 (1350)	27245	1345		P
18	27205	1392			27215			P
19	27080	1517		1517 (1522)	27105	1490		P
20	27037	1560	1243 (1245)	X	27030	1560	P	
21	26934	1663	1346 (1350)	X	26910		X	
22	26844	1753	1438 (1441)	X	26833		X	
23	26816	1781		430+1350	26800	1790	P	
24	26686	1911			26670			
25	26635	1962			–			
	–	–			26552			
26	26526	2071		713+1350	26515			
	–	–			26483			
27	26439	2158			26423			
28	26400	2197		865+1350	26370			
	–	–			26305	2285	P	
	–	–			26270	2320	P	
29	26108	2389			26075			
	–	–			25985			
	–	–			25890	2700		P
30	25584	3015			25565			
31	25496	3101			25475		X	
	–	–			25395			
32	25338	3259			25310			
33	25250	3347			25285			
34	25085	3512			25070			
	–	–			24898			
	–	–			24808			

a) wavenumbers in brackets give the results obtained by K. Witt and R. Mecke[5]

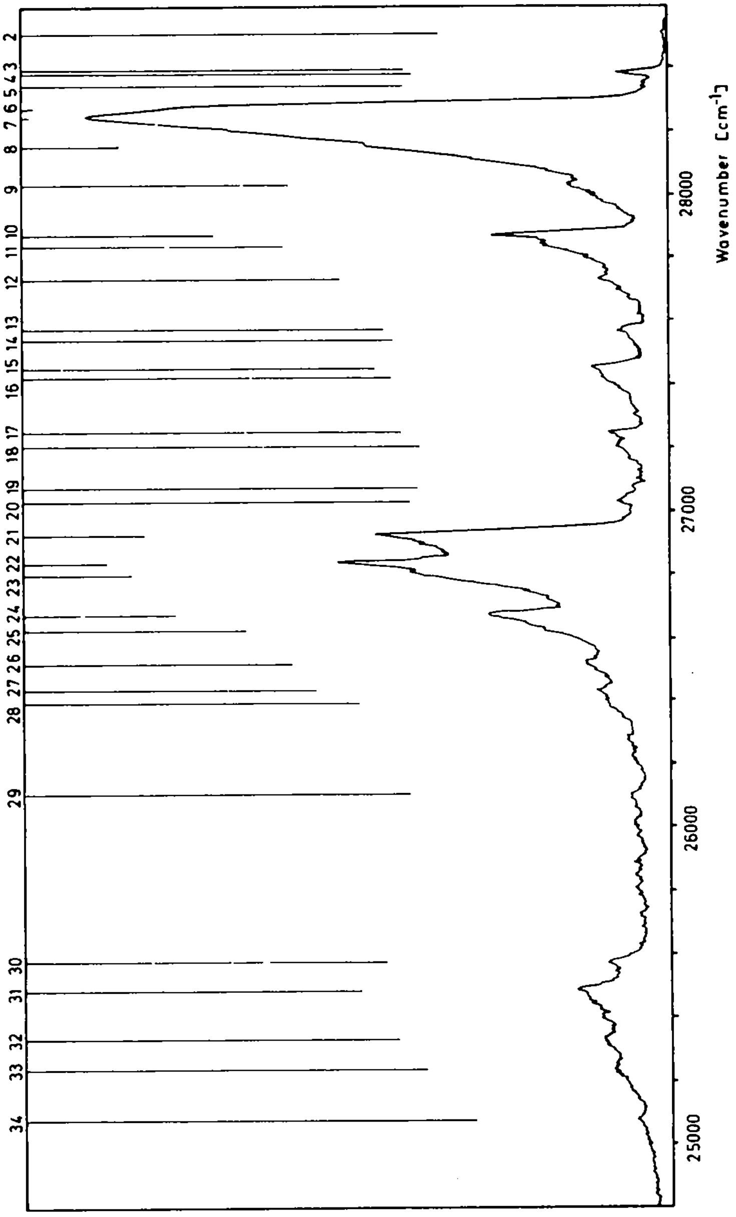

FIGURE 3 Fluorescence spectrum of phenanthrene single crystal excited by 3130 Å – radiation at 4,2 K.

TABLE 2

fluorescence		absorption[a)]	
wavenumber (cm^{-1})	$\Delta\tilde{\nu}$ from $0-0_P$	wavenumber (cm^{-1})	$\Delta\tilde{\nu}$ from $0-0_P$
.....	..	28533	44
28513	84	28513	84
28401	196	28406	191
28387	210	28380	217
28280	317	28285	312

a) given by Craig and Gordon[6]

The temperature dependence of lifetimes in pure and doped phenanthrene crystals

a The selection of bands for the lifetime measurements Because it is possible to distinguish between P- and X-bands in the fluorescence spectrum the temperature dependency of the fluorescence decay time of these bands were measured separately. For this purpose we selected the following bands: 1. 28345 cm^{-1}, 2. 27880 cm^{-1}, 3. 26881 cm^{-1}, 4. 26518 cm^{-1} and in addition the anthracene band at 24679 cm^{-1} for mixed crystals. The spectral band width for the lifetime measurements was about 200 cm^{-1}. The selection of the bands was governed by the following aspects:

a) the intensity
b) the identification as P- or X-bands
c) the possibility of separation from neighbouring (possibly unknown) bands.

The band at 27880 cm^{-1} is due to a P-emission. The center of a X-emission, intensive at low temperatures, lies in the spectral range about 26881 cm^{-1}. The P-band at 26518 cm^{-1} is weak for low temperatures and the separation from neighbouring (unknown) bands is worse. The situation near 28345 cm^{-1} is less obvious. Probably we have here a superposition of one P- and several X-bands. The very intensive X-band at 28553 cm^{-1} presumably dominates at low temperatures whereas for high temperatures the phenanthrene emission prevails.

The anthracene band in doped crystals is the most intensive one and the phenanthrene bands superposed are negligible.

We intended to show up differences in the behaviour of the decay times especially at low temperatures.

b The fluorescence decay times The lifetimes of the bands mentioned above were measured on pure and doped phenanthrene crystals (10^{-5} and 10^{-4} M/M A) as function of the temperature. Figures 5, 6 and 7 show examples of decay

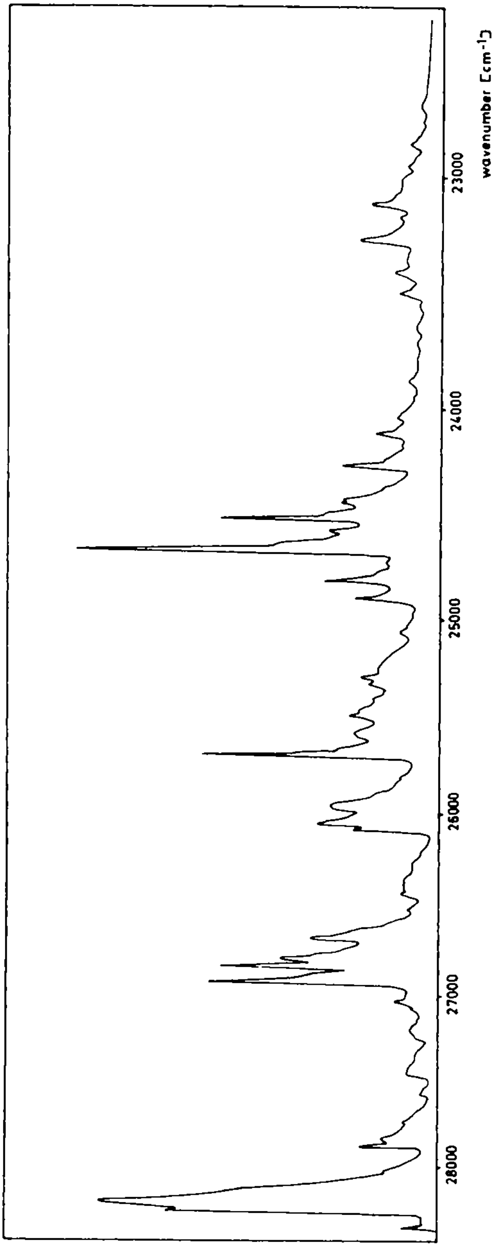

FIGURE 4 Fluorescence spectrum of the system phenanthrene – anthracene (10^{-4} mol/mol) excited by 3130 Å – radiation at 15 K.

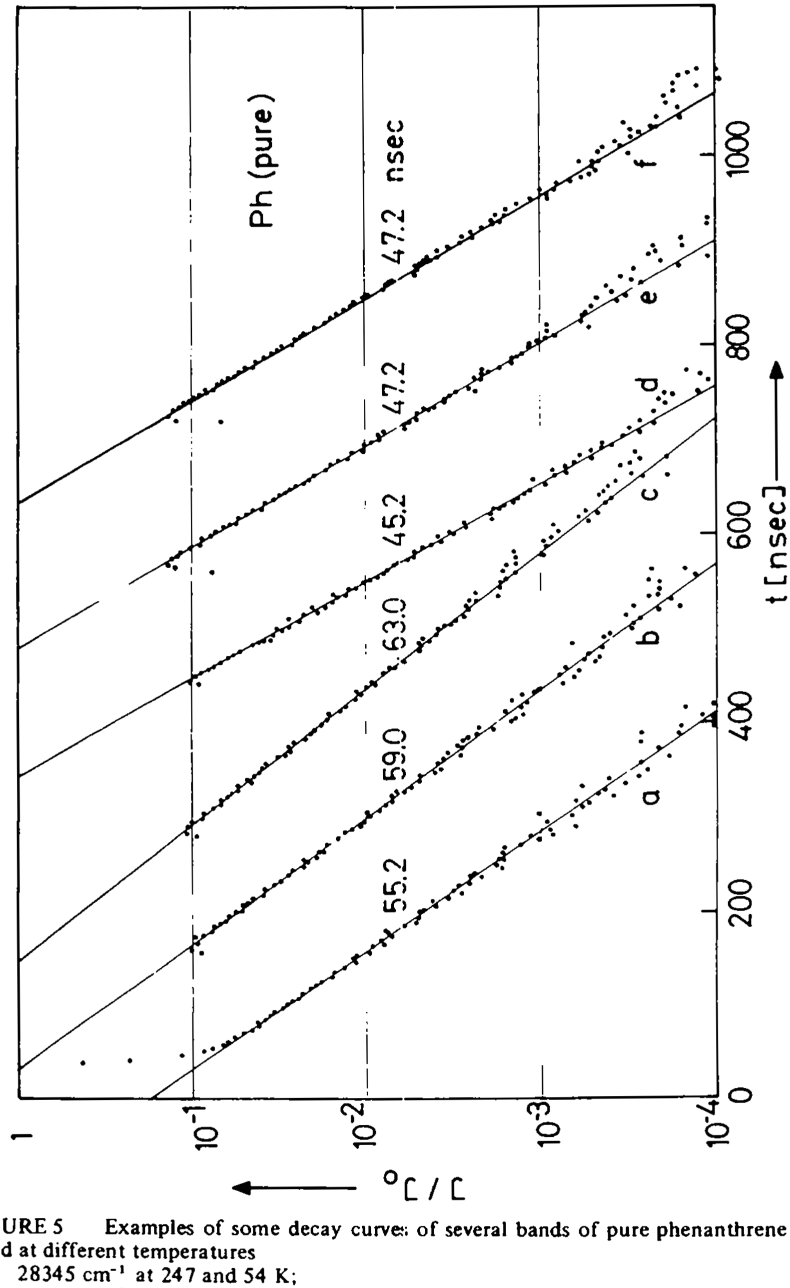

FIGURE 5 Examples of some decay curves of several bands of pure phenanthrene measured at different temperatures

a,d) 28345 cm^{-1} at 247 and 54 K;
b,e) 27880 cm^{-1} at 246 and 22 K;
c,f) 26881 cm^{-1} at 245 and 24 K.

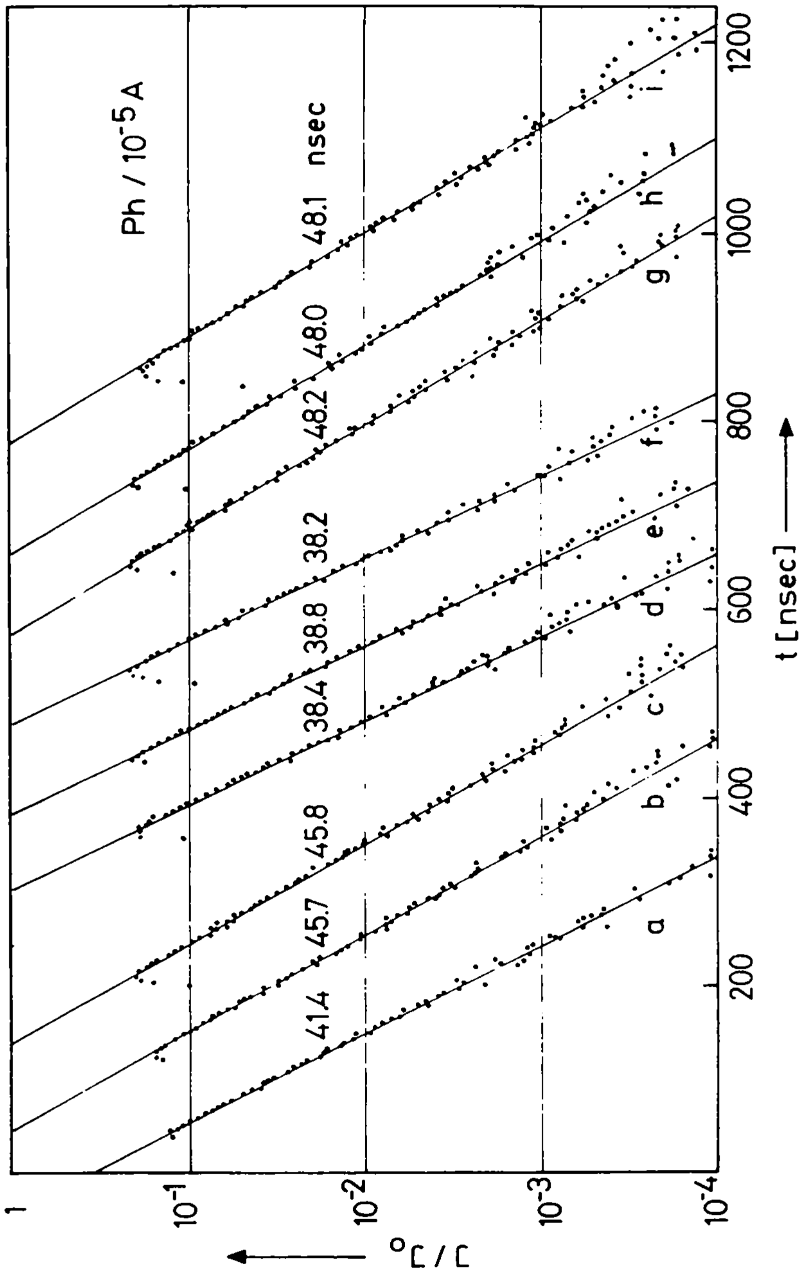

FIGURE 6 Examples of some decay curves of several band of phenanthrene – anthracene measured at different temperatures. $C_A = 10^{-5}$ mol/mol.
a,d,g,) 27880 cm^{-1} at 292, 149 and 36 K;
b,e,h,) 26881 cm^{-1} at 291, 147 and 31 K;
c,f,i,) 24679 cm^{-1} at 188, 142 and 28 K.

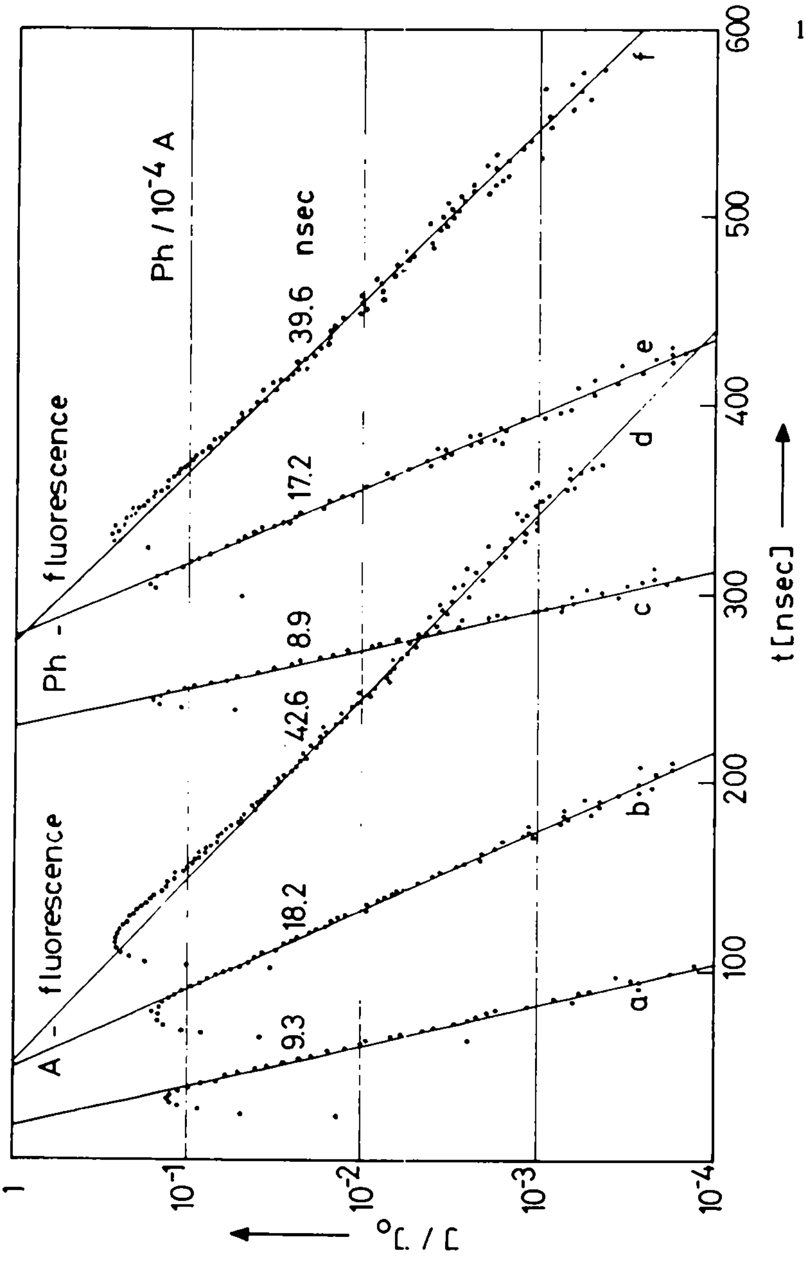

FIGURE 7 Examples of some decay curves of phenanthrene – anthracene measured at the 24679 cm^{-1} band and the 26881 cm^{-1} band at different temperatures. $C_A = 10^{-4}$ mol/mol

a,b,c) 24679 cm^{-1} at 273, 71 and 46 K;

d,e,f) 26881 cm^{-1} at 260, 72 and 51 K.

curves measured for various temperatures. The drop of the fluorescence intensity with time was observed through three decades.

The curves in Figures 5 and 6 show an exact exponential decay of the fluorescence whereas the decay curves of Figure 7, measured at low temperatures, have an additional short but weak decay component which probably is due to surface effects[1,7]. This component was not observed in the case of well cleveaged surfaces. The fluorescence measured at the anthracene band near 24679 cm^{-1} show a rise–adventised by the small curvature at the maximum – depending on the molecular lifetime of anthracene. It changes from 6 ns to 11 ns at room temperature and lower temperatures than 150 K respectively.[8]

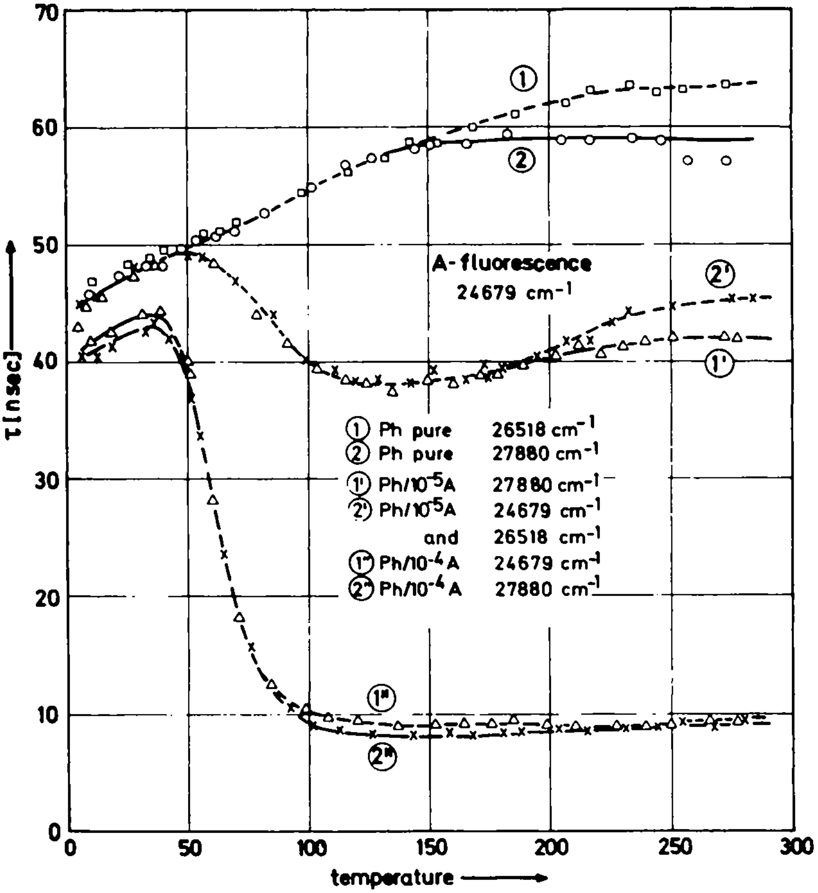

FIGURE 8 Temperature dependence of the decay times of several bands of the pure and anthracene doped phenanthrene crystals.

In contrast to this the fluorescence decay of the phenanthrene and X-bands have a rise time comparable to the decay time of the exciting light pulse.

Figures 8 and 9 show the temperature dependent lifetime of all the bands of pure and doped crystals under investigation. The curves number 1 and 2 of Figures 8 and 9 present the values of the pure crystals. An identical behaviour of fluorescence decay is found for the P-bands at 27880 cm^{-1} and 26881 cm^{-1} and the X-band at 26518 cm^{-1}. This is true especially for temperatures below 150 K. The lifetimes of the bands mentioned above decrease almost linearly with decreasing temperature.

A deviation from this behaviour is observed only for the short wave band near 28345 cm^{-1} (Figure 9, curve 2), whose values of $\tau(T)$ change in a different

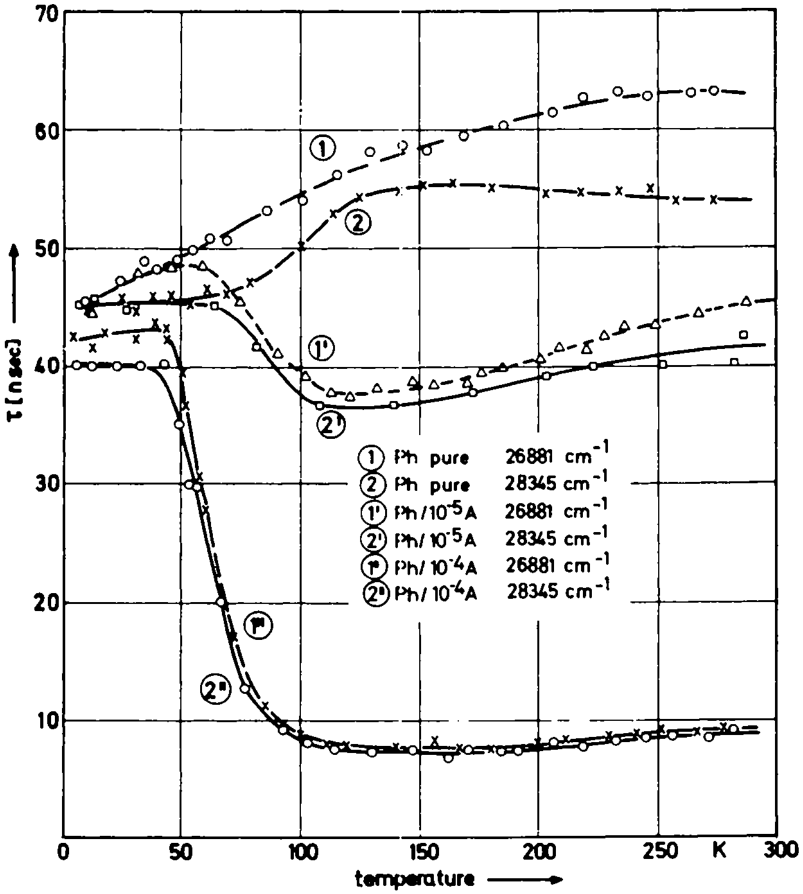

FIGURE 9 Temperature dependence of the decay times of several bands of the pure and anthracene doped phenanthrene crystals.

manner at temperatures below 130 K. No explanation could be found till now. The same phenomenon was observed on anthracene doped phenanthrene crystals.

Excepting the 28345 cm^{-1} band, identical lifetimes were measured for the P- and X-bands as well as for the A-bands within the whole temperature range (Figures 8 and 9, curves 1', 2' and 1", 2").

At high temperatures the incorporation of anthracene diminishes the lifetimes of the excitons. In doped crystals these change very much in the temperature range from 50 to 120 K and below 50 K coincide with those of the pure phenanthrene crystal (see Figures 6 and 7).

Decay times of the A-band measured on phenanthrene crystals doped with 10^{-4} mol/mol anthracene are well above the lifetimes of the phenanthrene fluorescence between 100 and 200 K. This is due to the higher value of the molecular lifetime of anthracene compared with the lifetime of the quenched phenanthrene fluorescence. Therefore the former determines the decay constant.

THE ENERGY TRANSFER

The results quoted above should be explained by the well known concept of the energy transfer by excitons. An unambiguous evidence for the exciton capture is the decrease of the exciton lifetime with increasing concentration of the guestmolecules[1,9,10,11] – anthracene in our case. At low temperatures the decrease of energy transfer often is caused by shallow traps due to (unknown) impurities or disturbed exciton states (X-traps). A high temperature the shallow traps are emptied by the thermal energy. A comprehensive article on the subject of energy transfer in organic molecular crystals is given by H. C. Wolf[12] where further references can be found.

The pure phenanthrene crystal

For pure crystals with X-traps this concept leads at low temperatures to the transition scheme shown in Figure 10. This yields $\tau = (\alpha+\beta)^{-1}$ for the lifetime of the exciton fluorescence, where the energy transfer probability β depends on the X-trap concentration. The X-trap fluorescence should have two components of decay, $(\alpha+\beta)^{-1}$ and δ^{-1}. The larger of the two determines the decay, the lower the rise of the fluorescence.

If there are present several X-traps of different trap depth and concentration, β should be replaced by $\sum_i \beta_i (c_i)$.

Especially pure phenanthrene crystals show identical decay times for P-(exciton) bands and X-bands within the whole temperature range. The X-emission has no significant rise time (Except the excitation-flash). Direct excitation of the X-traps is negligible considering their low concentration. Taking into account that the measured decay times of P- and X-emission are identical we are led to the conclusion that the lifetime of X-traps can not be essentially larger than the duration of the exciting light pulse. That is to say the exciton band is the longliving reservoir determining the decay times of all emissions (for excitons, X-traps and anthracene).

Direct experimental proof for the existence of this very short molecular lifetime of the X-traps of phenanthrene has not been given until now. But our measurements on phenanthrene doped 2,3 dimethylnaphthalene crystals yielded a molecuar phenanthrene decay time of 12 nsec, much shorter than the phenanthrene crystal lifetime.

One expects a temperature dependence of the lifetime of the exciton band because of the thermally stimulated radiationless transition combined with decreasing quantum yield and because of the thermal depopulation of the X-traps and the temperature dependence of energy transfer. The splitting of the exciton band (Davydov-splitting) lets the lifetimes depend on the relative population density in the case of different oscillator strength of the two components.

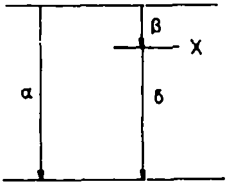

FIGURE 10 Transition scheme at 4,2 K.
α,δ – radiative transition probabilities;
β – energy transfer probability, dependent on the X-trap concentration.

Benz and Wolf[2] report a quantum yield of 0,6 at 4,2 K and 0,3 at 100 K for phenanthrene (50 X zone refined). As Craig and Gordon reported[6] the value of the Davydov-spliting is 60–70 cm^{-1} and the oscillator strength of the higher component is greater than that of the lower by a factor of two. Both facts would lower the exciton lifetime of the pure crystal with increasing temperature. In contradiction to this we observed lifetimes decreasing with decreasing temperature, which is explained by exciton capture into the X-traps.

The almost linear decrease of τ below 150 K is eventually caused by the participation of some types of X-centres with different trap depth or by a temperature dependent probability for the energy transfer into the X-traps. This could be in accordance with the conception of Agranovich and Konobeev[13] predicting an increase of the exciton diffusion constant D with decreasing temperatures.

The anthracene doped crystals

We summarize the most important facts:

1) The decay time of the anthracene fluorescence is identical with that of the P- and X-bands. This is exactly true at $T < 200$ K.

2) At temperatures $T>50$ K the energy transfer is due to the excitions. The excition lifetime decreases with increasing anthracene concentration. The Stern-Volmer relation τ (O)/τ (C) = 1 + k c gives a transfer constant of k = $5X10^4$ for $T > 80$ K in accordance with Belitz[1] and Benz and Wolf[2].

3) No shortening of the excition lifetime can be seen on anthracene doped crystals at $T < 50$ K even not at higher anthracene concentrations (10^{-4} mol/mol).

4) Nevertheless, for $T < 50$ K, we have a surprisingly high intensity of anthracene emission in the fluorescence spectrum amounting to 60–70% of the total intensity at 10^{-4} mol/mol (see Figure 4).

It should be clear from 1. that the anthracene emission is fed directly or indirectly from the exciton band at all temperatures. For $T > 50$ K we have the direct process of a capture from the exciton band (see 2.), which in turn is missing below 50 K as stated in 3. We must conclude that the energy transfer by excitons to the anthracene is thermally stimulated.

On the other hand, the observation of the intensive sensitized fluorescence of X-traps at lower temperatures shows without any doubt that a migration and therefore an energy transfer by excitons to the X-traps is possible without thermal excitation.

The activation energy needed for the energy transfer process to the anthracene molecules is ascribed to the transition cf the excitons from the lower to the higher Davydov level. The exciton transition from the two Davydov bands are polarized perpendicular to each other. We suppose the lowest electron transition (S_1) of the anthracene molecules, having definite orientation with respect to the lattice, to be mainly (or only) coupled to the higher Davydov level. Hence, there

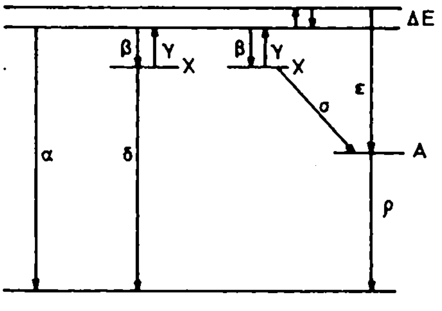

FIGURE 11 Transition scheme
α,δ,ρ – radiative transition probabilities,
β,ϵ – energy transfer probabilities, dependent on the concentration of the anthracene and X-traps respectively,
σ – energy transfer probability $X \rightarrow A$,
γ – detrapping probality (a function of temperature),
ΔE – Davydov-splitting, the thermally actived processes are missing at low temperatures.

is no direct energy transfer by excitons to anthracene below 50 K. However, the anthracene fluorescence is not essentially reduced (in agreement with the observation of Benz and Wolf). For these temperatures the anthracene fluorescence is sensitized either by absorption of the P- and X-emission or by radiationless energy transfer from the X-traps. In their work Benz and Wolf assume a radiationless energy transfer based on the observation that the anthracene fluorescence is intensified by higher X-trap concentration. The relatively high anthracene intensity is not well explained by the process of radiation absorption. Therefore we suggest the transition scheme of Figure 11 for the fluorescence processes in anthracene doped phenanthrene crystals.

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