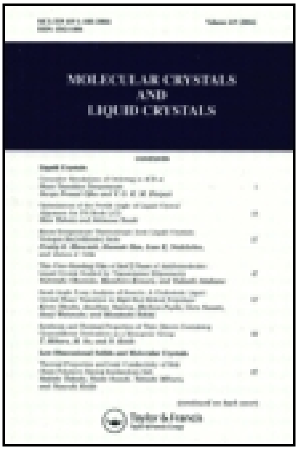

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Emissive States of Chrysene Crystal

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Emissive States of Chrysene Crystal

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Absorption spectra and fluorescence spectra of extremely purified chrysene crystal are observed at the temperature range from 3 K to 300 K. At 3 K absorption spectrum is resolved to be four series and these series are inferred to due to the crystal field splitting. The largest splitting is 330 cm^{-1}. On the other hand fluorescence spectra are resolved to be two series and intensity ratio of the two series depends upon the crystal temperature. The emissive states are considered to be the highest and the lowest states of the four split states of the lowest excited singlet state.

Chrysene crystal is known to emit both prompt and delayed fluorescences. Only broad fluorescences at temperatures above 77 K have been reported,[1-4] and vibrational analysis of these spectra has never been tried. Wegner *et al.* detected the splitting of broad bands of the fluorescence at room temperature and explained it by the Davydov splitting.[2] However, in the other three reports the splitting of broad bands was not observed.

In this report, it is confirmed that there are two series in the fluorescence of chrysene crystal at room temperature. Absorption spectra of the crystal are also observed and is compared with the fluorescence spectra.

EXPERIMENTAL

Purification of chrysene: Chrysene (Rutgerswerke) was refined with a recrystallization method and with a zone melting method. *N,N*-dimethylformamide and ethanol were used as recrystallizing solvents and a zone-melting apparatus with a heater-temperature-controlling mechanism[5] was used for extensive zone refining. No impurity was detected in refined crystals with a high-speed-liquid chromatography.[6] The refined crystal of which the triplet exciton lifetime was above 48 ms[7] was used for the measurements. Lamella single crystals were prepared by sublimation.

Spectrometry: An Aminco–Bowman spectrophotofluorometer model SPF-500 was used for the measurements of prompt and delayed fluorescence spectra. With this apparatus prompt and delayed fluorescence were observed at the perpendicular direction to the excitation light axis. The excitation source was a 250 W Xenon short arc lamp with an integral parabolic reflector. A 320 nm line was used as an exciting light for the measurements of both spectra. The spectral response of the photomultiplier tube (R 928) and the spectral transmittance of the monochromator have not been taken into account. For the delayed fluorescence a rotating drum phosphoroscope (5000 r.p.m.) was used to separate delayed emission from prompt emission. UV absorption spectra of the chrysene crystal were measured with a Cary spectrophotometer (model 17 DX). In these measurements the crystal temperature was varied with a cryostat (Oxford Electronic Instruments, model CF-204). A Raman spectrum of the chrysene powder was observed at room temperature at the spectral range from 10 cm^{-1} to 2000 cm^{-1}, a 515 nm line of Ar ion laser being used as an incident light.

RESULTS AND DISCUSSION

Absorption spectra

Absorption spectra were observed with lamella single crystals. The thickness of these lamella was determined to be about 4 μm by the observation of interference fringe of visible light. The plane of these lamellas was assigned to be the (001) plane of monoclinic crystal by the X-ray reflection spectrum.

The absorption spectrum of the ^1L_b ($B_u \leftarrow A_g$) band of chrysene crystal is shown in Figure 1. At room temperature peaks are at 366, 358, and 348 nm. The vibrational structure is similar to that observed in solution except shoulders at 370 and 362 nm. Energy difference (1400 cm^{-1}) between the two peaks at 366 and 348 nm corresponds to the ring stretching vibration (1387 cm^{-1}) observed in Raman spectrum.

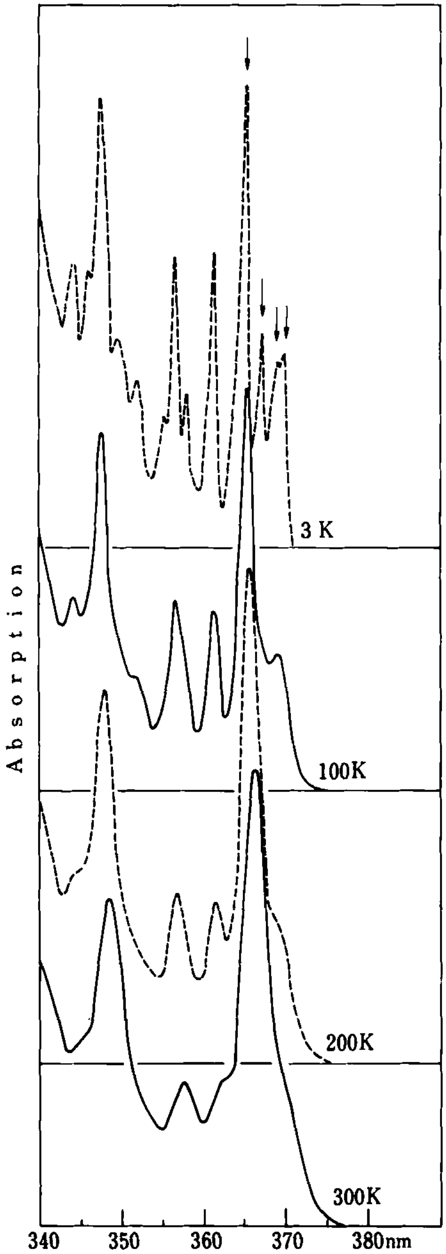

FIGURE 1 Absorption spectra of chrysene lamella. Arrows show the peaks at 369.7, 368.9, 367.1, and 365.3 nm.

As the temperature decreases, peaks appear instead of shoulders. At 3 K three sharp peaks are observed at 369.7, 368.9, and 367.1 nm instead of a shoulder observed at room temperature. Absorption spectrum at 3 K is consistently resolved to be four series. The intense peak at 365.3 nm and the above three peaks are assigned as the absorption lines from ground state to pure electronic S_1 level (Table I). Vibrational energies are somewhat different in the four series. Since these absorption spectra are observed with the extremely purified crystals, four absorption series are thought not to be caused by impurities in the crystal. The facts that the plane of the lamella is assigned by the X-ray reflection spectrum and that the peak intensities at 369.7, 368.9, and 367.1 nm are comparable to that of 365.3 nm suggest that these four series of absorption are not the set of absorptions of crystal defects and intrinsic absorption of chrysene. Consequently these four series of absorption are inferred to be the transitions to the splitted states in the crystal field.

Chrysene crystal is known to be monoclinic with the space group $I_{2/c}$, where four molecules are contained in unit cell.[8] In chrysene B_u state of a molecule splits into four states in crystal, two A_u and two B_u states. According to group theory, all the transitions from the ground state to the splitted states are optically allowed. Since ^1L_b band corresponds to the transition from A_g to B_u,[9] the appearance of four series of absorptions does not contradict the above symmetry consideration. In the case of chrysene crystal Davydov splittings have been calculated to be negligibly small with the first approximation where only the dipole-dipole interactions are considered for the crystal-field-splitting, resulting from small oscillator strength of the ^1L_b band.[10] However, in the case of the ^1L_b bands of naphthalene and phenanthrene, in spite of negligibly small splittings expected with the first approximation,[11] observed splittings are 150 cm^{-1} and about 50 cm^{-1}, respectively.[12–14] The observed largest splitting in the chrysene crystal is 330 cm^{-1} and is relatively large compared with the ones in the ^1L_b bands of naphthalene and phenanthrene crystals.

Thus, four series (A, B, C and D in Table I) are observed in the absorption spectra with the chrysene single crystal. The A, B, C and D series are in order of decreasing excitation energies. Only relatively intense A series are observed as clear peaks at 300 K. As the temperature decreases blue shift of A series are observed. The magnitude of the blue shift at 100 K is about 1 nm, which is comparable to that of observed in the ^1L_b band of a phenanthrene single crystal.[14] On the other hand, B, C and D series appear as peaks at the temperatures lower than 200 K.

TABLE I

Vibrational analysis of the absorption spectra.

Solution in DMF at r.t.		Lamella at 3 K				
Peak (nm)	Difference from 361.5 nm band (cm^{-1})	Peak (nm)	A Difference from 365.3 nm band (cm^{-1})	B Difference from 367.1 nm band (cm^{-1})	C Difference from 368.9 nm band (cm^{-1})	D Difference from 369.7 nm band (cm^{-1})
		369.7				0
		368.9			0	
		367.1		0		
		365.3	0			
361.5	0	361.4				621
		360.2			654	
		357.9		700		
		356.6	668			
354.0	666	355.3				
		353.0				
		352.0				1360
		350.2			1447	
		349.3		1388		
		347.7	1385			
345.0	1381	345.7				
		344.2				2004
		341.2		2067		
		339.7	2062			

0–0 band of D series appears as shoulder at 300 K and other peaks belonging to B and C series appear at the temperatures lower than 100 K. 0–0 band of D series shows no red shift in the temperature range from 300 K to 3 K.

In the case of the ^1L_a band of the anthracene, *b* component shifts to red and a component does not shift when the crystal temperature decreases.[15] Red shifts of ^1L_a bands have been reported with anthracene,[16] tetracene,[17] and pentacene[18] single crystals when the high pressure is supplied. In general, as the temperature decreases, and as the high pressure is supplied, it is expected that the distances between molecules in the crystal are shortened, and that the intermolecular interactions become stronger. In that case, it is expected that the energy of the $^1\pi\pi^*$ absorption bands become lower and that the Davydov splittings increase. Therefore, as the temperature decreases the D series of chrysene crystal are expected to show a red shift. But such a red shift cannot be observed. From this result, it may be concluded that the energy of the ^1L_b band does not decrease with decreases in temperature. As the cause of the blue shift of A series, increases of the energy of the ^1L_b band and of the Davydov splitting with decreases in temperature may be mentioned. However, a clear conclusion about this point cannot be obtained at this stage.

Prompt fluorescence spectra

The fluorescence spectrum of the chrysene lamella at 4.2 K is shown in Figure 2. Main peaks are observed at 371.5, 391.7, 414.2, and 438.9 nm. The energy intervals of these peaks are about 1380 cm^{-1} and correspond to totally symmetrical ring stretching vibration as also observed in the absorption spectra. Weak peaks are also observed at 375.9, 396.0 and 418.5 nm and their energy differences from the corresponding main peaks are about 290 cm^{-1}. In the Raman spectrum of chrysene crystal a relatively strong peak is observed at 295 cm^{-1}, corresponding to the A_g skeletal out-of-plane vibration. The distinct progression observed in the fluorescence spectrum at 4.2 K consists of these two vibrations and is denoted D′ series fluorescence.

In the temperature range from 4.2 K to 70 K, the observed prompt fluorescences does not change except that the peak intensity at 371.5 nm reduces by the reabsorption of the fluorescence. Figure 3 shows that at 100 K new bands are observed at 366.5, 385.7, 407.6 and 432.3 nm. These new bands are denoted as A′ series. The peak intensity in A′ series increases with the rise of the temperature, while the intensity of the peaks in D′ series reduces. The energy intervals of the A′ series

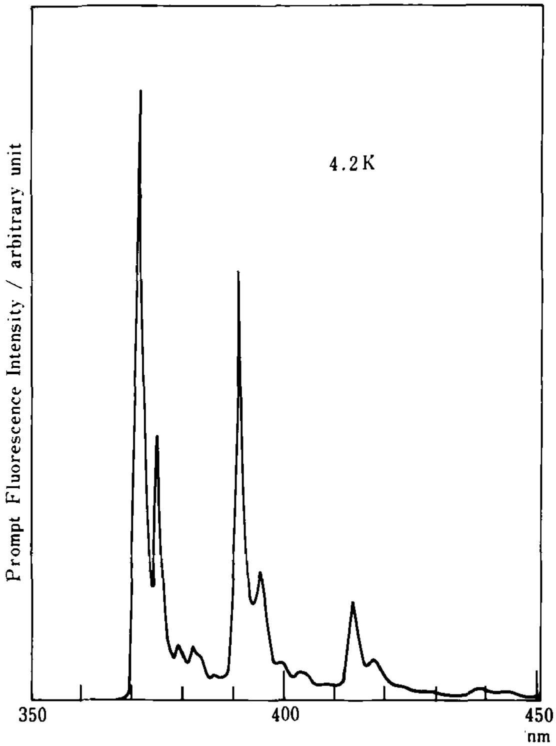

FIGURE 2 Prompt fluorescence spectra of chrysene lamella at 4.2 K. Spectral band width was 0.5 nm.

bands are also consistently assigned as the ring stretching vibration (Table II). The energy difference of A′ and D′ series is 370 cm^{-1}. At 220 K the fluorescence spectrum consists of A′ series as major and D′ series as minor and is quenched at 366.5 and 371.5 nm because of the reabsorption of fluorescence. As the reabsorption by a hot band causes the reduction of the peak intensity at 385.7 nm it seems as if the peak at 385.7 nm shifted to red slightly and reduced at 270 K. Figure 4 shows the fluorescence observed with another lamella at 295 K. Since in this lamella the effect of the reabsorption is relatively small, the strong intensity at 371.5 nm is observed. At this temperature, two series are both observed, the intensity of both A′ and D′ series reduces as a whole. The facts that both A′ and D′ series have the same vibrational structure and that main progression have the ring stretching vibration observed in Raman spectrum show that both A′ and D′ series are the emissions from chrysene molecules. Both emissive states are inferred to be prepared by some physically different circumstances.

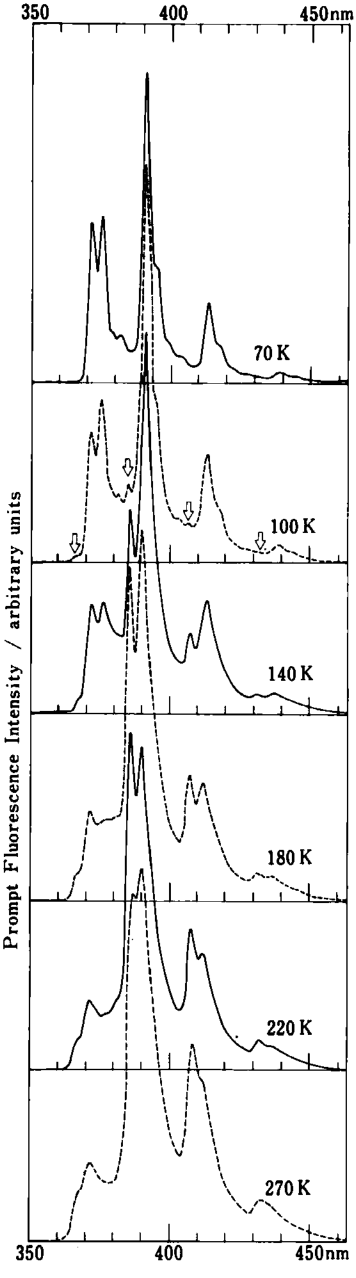

FIGURE 3 Prompt fluorescence spectra of chrysene lamella. Spectral band width was 1 nm. Arrows show the A′ series emission.

TABLE II

Vibrational analysis of prompt fluorescence

4 K (D′ series)			140 K		
Emission (nm)	Difference from 371.5 nm band (cm^{-1})	Assignment	Emission (nm)	A′ series Difference from 366.5 nm band (cm^{-1})	D′ series Difference from 371.5 nm band (cm^{-1})
			366.5	0	
371.5	0		371.5		0
375.9	302	295(R)			
			385.7	1357	
391.7	1384	1387(R)	391.7		1384
396.0	1662	1387 + 295			
			407.6	2750	
414.2	2771	1387 × 2	414.2		2771
418.5	3019	1387 × 2 + 295			
			432.3	4152	
438.9	4129	1387 × 3	438.9		4129

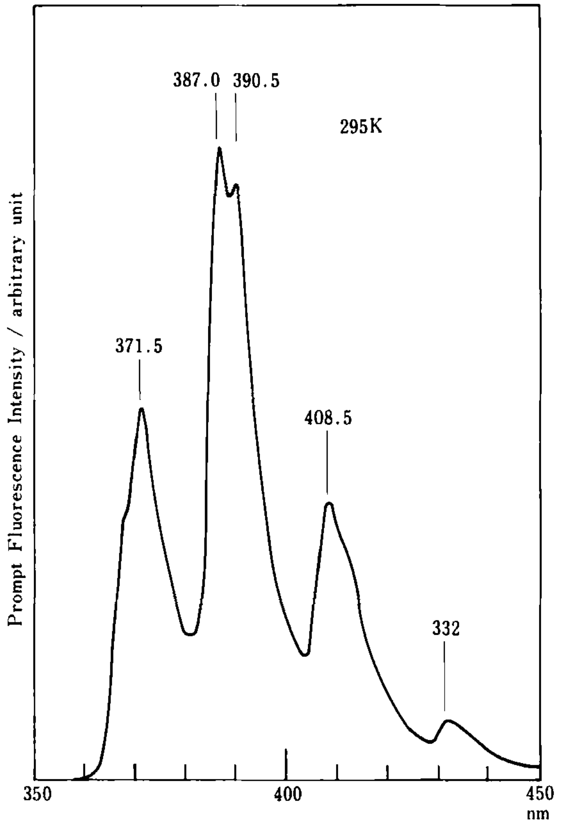

FIGURE 4 Prompt fluorescence spectra of chrysene lamella at 295 K. Spectral band width was 0.5 nm.

A similar temperature change in the prompt fluorescence is observed with polycrystalline chrysene prepared by various kinds of crystallizations, recrystallization from solvents, rapid and slow solidifications from melt.This fact suggests that two series of fluorescences are intrinsic for the chrysene crystal and are not due to defects in the crystal. The activation energy to increase the intensity of A′ series is estimated to be about 100 cm^{-1} from Arrhenius plot in both cases of lamella and polycrystal. It is considerably small compared with the energy difference of A′ and D′ series. In our measurements where a 320 nm line was used as an excitation light, the chrysene molecules could be excited to the S_2 state (^1L_a). In this case, it is thought that the $S_2 \rightarrow S_1$ internal conversion controls the population of the S_1 splitting levels in which the Boltzmann distribution does not come about.

Origin states of two fluorescence series

Thus two intrinsic fluorescence spectra are observed as is reported by Wegner *et al.*[2] On the other hand, A′ fluorescence series starts at the same wavelength as the A series absorption while D′ fluorescence series starts at almost the same wavelength as the D series absorption. These facts support that two series of fluorescences are due to the transitions from the state split in the crystal field. The highest and the lowest states of the four split states are the emissive states. The emissions from the middle two states are thought not to be detected clearly because of their weakness.

Delayed fluorescence spectra

Figure 5 shows the delayed fluorescence of polycrystalline chrysene. In the delayed fluorescence only D′ series is observed in the temperature

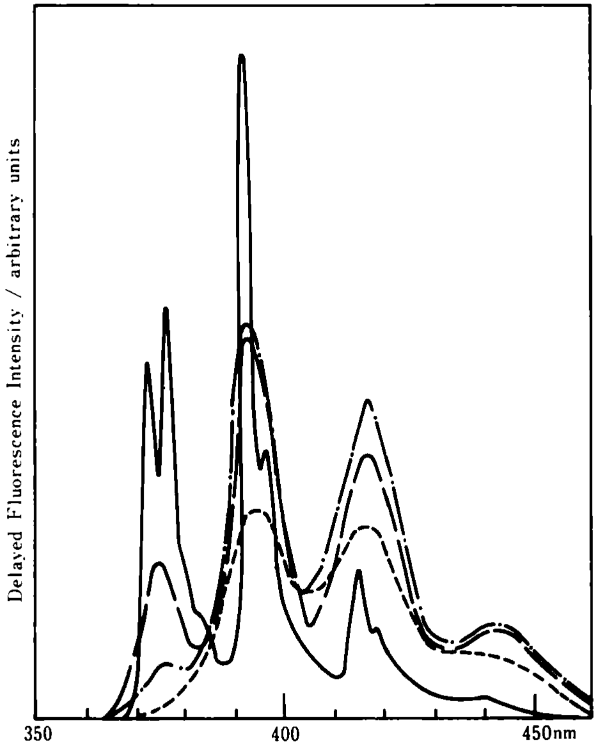

FIGURE 5 Delayed fluorescence of polycrystalline chrysene at 4.2 K (solid line), 70 K (broken line), 110 K (dotted broken line), and 295 K (dotted line); spectral band width were 1,4,4, and 5 nm, respectively.

range from 4.2 K to 295 K. *T–T* annihilation is deduced to pump only the lowest split state in the chrysene crystal.

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