1003. *Luminescence from Anthracene Crystals and its Temperature-dependence.*

By L. E. Lyons and J. W. White.

The variation of the luminescence from crystals of anthracene is reported over the temperature range 4—300° K. Changes occur most markedly over certain ranges, some bands increasing, others decreasing, in intensity. Factors causing the variation include (i) the increasing importance at higher temperatures of origins of relatively high energy; (ii) a Franck–Condon type of intensity distribution; (iii) reabsorption; (iv) thermal degradation (which is especially important above 130° K). The " edge " bands are considered in terms of the interaction of phonons and excitons, free or trapped. Oxygen has small but definite effects on the variation in luminescence.

THE luminescence from anthracene crystals is not yet understood although the electronic spectrum of anthracene crystals has been investigated by a number of workers recently.[1-3] The " edge-bands " which appear often in both absorption and fluorescence have been studied particularly by some authors,[1,2] and various theories have been advanced to account for them. The present work studied the temperature dependence of these bands and of the other regions of luminescence.

EXPERIMENTAL

The luminescence was excited by a mercury " black " lamp applied continuously, and was detected with a 1P28 photomultiplier attached to a " Uvispek " monochromator, the wavelength drum being driven by a synchronous motor. The 100 c./sec. signal was fed to a phase detector, an amplifier which had a maximum gain of 10^7, and a pen recorder of which the full-scale deflection was produced by 5 mv. The sensitivity of the apparatus was limited by the noise of the photomultiplier so that only those light levels above 10^5 quanta/sec. on the photomultiplier could be observed. In earlier experiments a constant-deviation spectrometer was converted into an automatic instrument by moving the prism mount periodically with the aid of a synchronous motor. This apparatus was capable of recording photographically the whole spectrum shown instantaneously on the screen of a cathode-ray tube. The rapidity of recording was obtained in order to follow rapid changes in the spectrum arising from a fast warm-up of the sample. The changes in the spectrum were in fact so slow that rapid registration was unnecessary and the luminometer first described was therefore most used. The temperature of the sample was varied by first cooling it to 4° K in a liquid-helium cell and then allowing the helium to evaporate and the sample to warm-up at a natural rate. The temperature was measured with three devices. A standard platinum-resistance thermometer was used to calibrate a manganin resistance thermometer which was the main measuring device. Two copper–constantan thermocouples were calibrated against the platinum thermometer and were able to be coupled to a pen-recorder to obtain a permanent record of warming curves. One thermocouple measured the temperature of the face of the sample, the other that of the radiation shield.

The anthracene had been purified by distillation with ethylene glycol, sublimation, and chromatography.

RESULTS

The variation of the luminescence spectrum with temperature is shown in Fig. 1 for a polycrystalline sample. The spectrum varied in details from sample to sample but for

[1] Pesteil and Barbaron, *J. Phys. Radium*, 1954, **15**, 92; Sidman, *Physical Rev.*, 1956, **102**, 96; Ferguson and Schneider, *Canad. J. Chem.*, 1958, **36**, 1070; *J. Chem. Phys.*, 1958, **28**, 761; Fugol and Shulga, *Optika i Spektroskopiya*, 1958, **5**, 34.

[2] Craig and Hobbins, *J.*, 1955, 539, 2309; Kallmann, Kramer, and Sucov, *J. Chem. Phys.*, 1955, **23**, 1043; Bree and Lyons, *J.*, 1956, 2662; Lyons and Morris, *J.*, 1959, 1551; Wolf, *Z. Naturforsch.*, 1958, **13a**, 414.

[3] Prikhotjko and Fugol, *Optika i Spektroskopiya*, 1958, **4**, 335.

both polycrystalline samples and single crystals there was a general result in nearly all cases, *viz.*, that as the temperature rose the intensity in each of the three main regions of luminescence shifted to higher energies. Superposed on this result was the increasing reabsorption of the luminescence in the region 24,000—25,000 cm.$^{-1}$, producing a gradual partial disappearance of the peak which had a maximum at about 24,700 cm.$^{-1}$ at 4° K. Despite the effect of reabsorption, it can be seen in Fig. 1 that there is a steady increase in the luminescence occurring above 25,000 cm.$^{-1}$ as the temperature is raised.

The variation in intensity of some individual bands with temperature is shown in Fig. 2. All bands do not behave similarly. The following types of behaviour were observed together with intermediate cases.

(i) The band shows a marked decrease in intensity as the temperature rises from 4° to 100° K, thereafter remaining weak. Examples are those at 24,900, 24,870, 24,815, 24,660, 24,600, 24,485, 23,515, 23,350, and 23,150 cm.$^{-1}$.
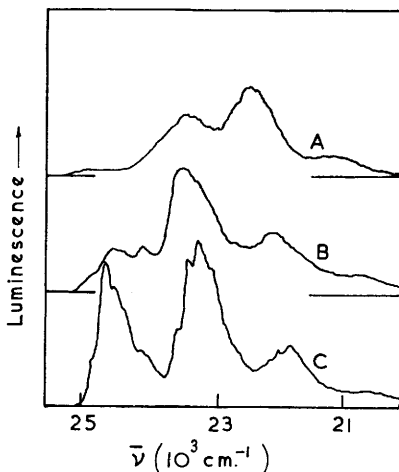

Fig. 1. *The luminescence spectrum of an anthracene crystal 5 μ thick at various temperatures.*

A, 300° K. *B*, 78° K. *C*, 4° K.

(ii) The band shows a marked increase in intensity between 0° and 100° K. Above 100° K the intensity remains constant over a range of temperature and then decreases, as does the band at 23,610 cm.$^{-1}$, or else remains approximately constant, as does that at 25,050 cm.$^{-1}$. Luminescence increases with temperature, *e.g.*, for bands at 25,310, 25,275, 25,170, 25,120, 25,070, 24,980, 23,915, 23,795, 23,660, 22,940, 22,690, 22,435, and 22,215 cm.$^{-1}$.

(ii) The band may not change greatly in intensity with temperature, *e.g.*, those at 24,050 and 22,065 cm.$^{-1}$.

Regions in which the intensity increases as the temperature was raised to 100° K were found to alternate with those in which the intensity decreased. Increases occurred generally in the regions 25,500—24,950, 24,000—23,600, and 22,800—22,200; decreases in the regions 24,900—24,400, 23,450—23,000, and 22,100—21,500. In certain cases slight variations were observed from one experiment to another. The limits of the regions of increase and decrease are therefore approximate.

Oxygen had small but definite effects on the temperature-dependence curves. The introduction of 0·1 mm. of oxygen on to an outgassed sample caused an immediate increase in the temperature (about 70° K) at which a marked change in luminescence occurred [see Fig. 2(*c*)]. Oxygen (0·1 mm.) made the high-energy tail on the luminescence spectrum more intense but was not essential for its appearance. The 24,960 cm.$^{-1}$ band was doubled in intensity by oxygen. The 23,610 cm.$^{-1}$ band varied in intensity between 4° and 50° K only in the absence of oxygen [Fig. 2(*c*)].

The gross features of the spectrum at 4° K are the three main groups of peaks and a fourth of lower intensity. These groups are separated by approximately 1400 cm.$^{-1}$, an

Fig. 2(*a*). *Variation of the intensity of luminescence of particular bands with temperature between 30° and 300° K.*
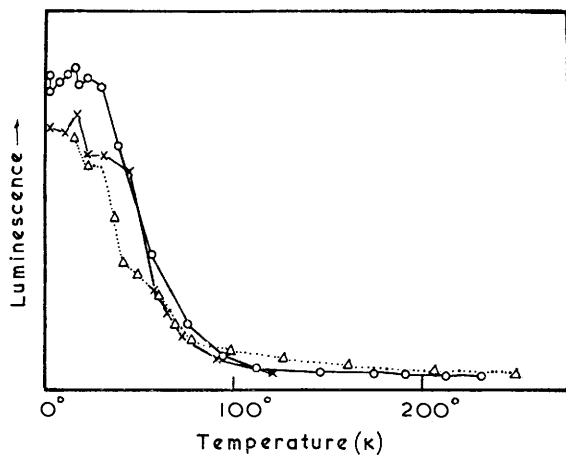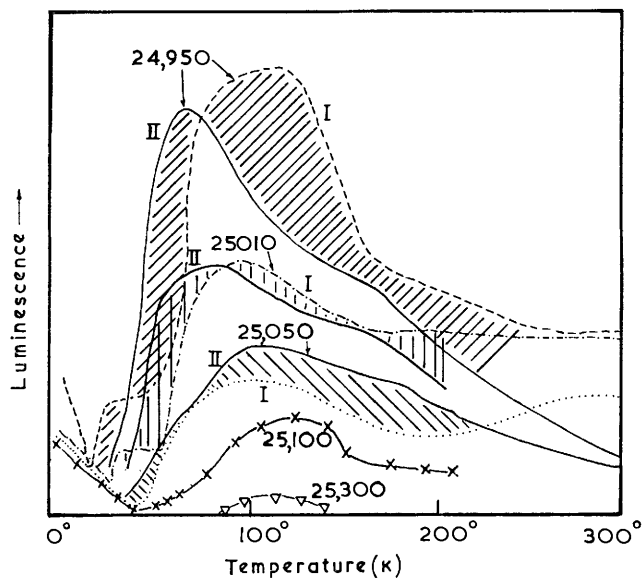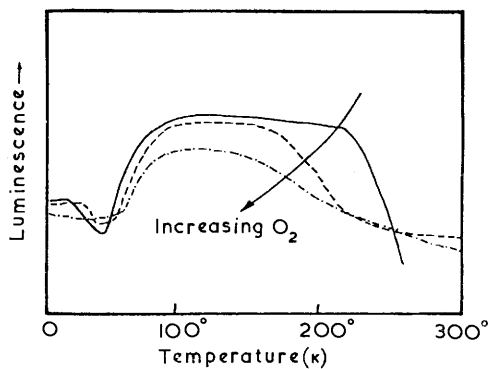
I, *Polycrystal.*   II, *Single crystal.*

Fig. 2(*b*). *Examples of luminescence at 24,680 cm.$^{-1}$ which decreases with increase of temperature.*

Three separate experiments are shown.

Fig. 2(*c*). *Effect of oxygen on the temperature dependence of the luminescence at 23,610 cm.$^{-1}$.*

interval which is close to a well-known frequency of a totally symmetrical vibration in molecular anthracene. At higher temperatures the separation of approximately 1400 cm.$^{-1}$ is still discernible although the reabsorption makes it less obvious in some cases. Thus, although at higher temperatures the main groups of peaks are different in energy from those which occur at 4° K, yet the intervals between the main groups are more nearly constant with temperature. These considerations suggest the important conclusion that at different temperatures the luminescence spectrum is built upon different origins. This change of origin is the basis for understanding the variation of the spectrum with temperature. The problem is then to explain why the origins shift with temperature.

The existence in crystals of anthracene and of other similar substances of various edge bands which have been observed in both absorption and fluorescence is now well established. The existence of a considerable number of electronic origins in the crystal is therefore an accepted fact. The nature of these origins has not yet been explained. Adding the results of the present work to that already reported by others, we now think that edge

FIG. 3. *Comparison of the observed luminescence at* 24,985, 25,030, 25,070, 25,110 *cm.*$^{-1}$ *with the calculated occupancy of those levels relative to* 24,930 *cm.*$^{-1}$ *as the base level.*
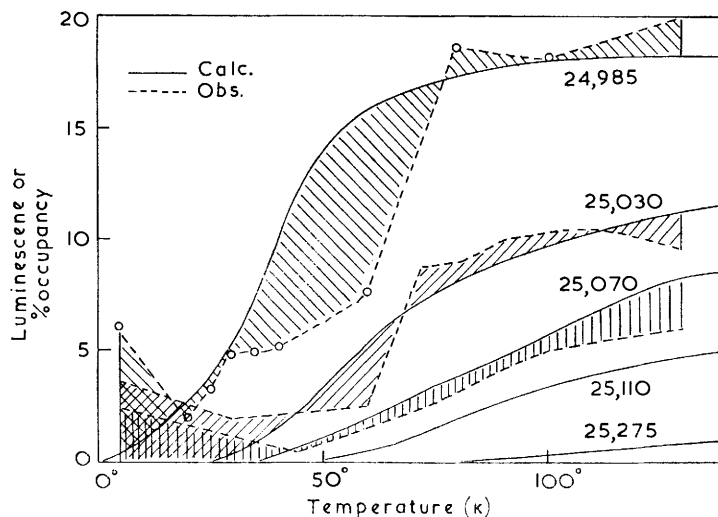
bands include bands at 25,370, 25,310, 25,275, 25,170, 25,110, 25,070, 25,030, 24,985, 24,930, 24,870, 24,815, 24,770, 24,715, and 24,670 cm.$^{-1}$. The error is probably 5—10 cm.$^{-1}$ in many cases. Of these, those which already have been found both in absorption and fluorescence are at 25,110, 24,985, 24,930, 24,870, 24,815, 24,770, and 24,670 cm.$^{-1}$. A large number of other bands were found in the present work at an intensity too weak for certain recording. Those reported in the above list are those of whose existence there is little doubt.

The question now arises whether or not there is any thermal equilibrium amongst the various luminescing levels. The assumption of thermal equilibrium, governed by Boltz-mann statistics, gives at least a partial explanation of the variation in intensity of various bands with temperature, at least up to 100° K. As the temperature is raised the occupancy of the base level decreases, that of any other level increases, at least at first. The broad similarity of curves, calculated on Boltzmann statistics, to the results in Fig. 2(*a*) suggests that this type of explanation of the luminescence might be useful. Fig. 3 shows calculated occupancies and observed luminescence for a series of levels spaced at 40—50 cm.$^{-1}$ as shown. The ordinate for the 24,985 cm.$^{-1}$ curve only has been chosen to give agreement at 120° K. The level near 24,950 cm.$^{-1}$ on this view is therefore nearer to the base level

than the 25,010 cm.$^{-1}$ level.   The base level is therefore tentatively placed at 24,900 cm.$^{-1}$. The behaviour of the luminescence near 24,900 cm.$^{-1}$ is as follows.   Between 4° and 30° K the intensity drops rapidly, then increases until 90° K is reached, above which temperature the intensity again falls.   The occupancy of the base level on the statistical assumptions continuously decreases and the simple statistical picture might explain the initial drop in intensity at 24,900 cm.$^{-1}$, but cannot explain the subsequent rise.   The rate of the initial decrease in the base level is greater than a 40 cm.$^{-1}$ interval would predict.   A level about 10 cm.$^{-1}$ above the base gives a better quantitative result.   A further difficulty for the simple explanation is that luminescence from levels above the base level is not predicted at very low temperatures.   For 24,950 cm.$^{-1}$ there is a decrease as the temperature rises to about 20° K; for 25,050 cm.$^{-1}$ a decrease to about 45° K.   Only above these temperatures does the luminescence increase.   The decreases are not predicted on the simple assumption

FIG. 4.   *A luminescence curve observed at 6° K and curves calculated from it for 100° K and 214° K: thermal distribution over origins equally spaced at 40 cm.$^{-1}$ is assumed, and a similar shape of the luminescence curve associated with each origin.*
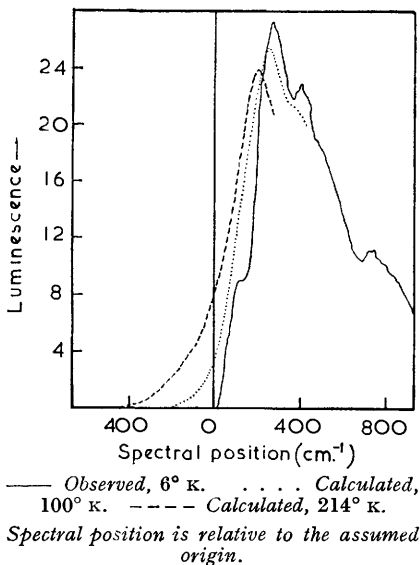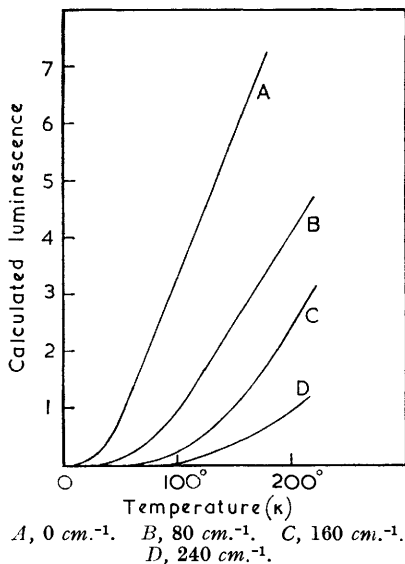
FIG. 5.   *Intensities of luminescence at 40, 80, 160, and 240 cm.$^{-1}$ from the origin of lowest energy, upon similar assumptions to those used for Fig. 4.*

——— *Observed, 6° K.*   . . . . *Calculated, 100° K.*   – – – – *Calculated, 214° K.*

Spectral position is relative to the assumed origin.

A, 0 cm.$^{-1}$.   B, 80 cm.$^{-1}$.   C, 160 cm.$^{-1}$. D, 240 cm.$^{-1}$.

used if the base level is near to 24,900 cm.$^{-1}$.   If the base level is at a higher energy, then a problem remains, but it is to explain the increase in luminescence following a decrease.

In general, luminescence at a position in the spectrum can be associated either with an origin at that position, in which case the occupancy of the originating level is the determining factor, or else with an origin or origins at higher energies, in which case the occupancy of the higher levels is important together with the distribution of intensity throughout the luminescent spectrum based on the relevant origins.   In anthracene crystals both in absorption and luminescence there appears to be a strong Franck–Condon effect.   This effect causes the maximum of luminescence to occur at about 300 cm.$^{-1}$ below the origin.   The equilibrium positions of the molecules in the excited crystal are therefore different from those in the ground state.   If we assume, and this is an approximation, that the distribution of intensity is independent of the origin with which it is associated then the curves of Figs. 4 and 5 are calculated.

Fig. 4 shows the curve observed at 6° K and others calculated from it for 100° K and 214° K.   The growth of the high-energy tail and the shift of the maximum are indicated.

Fig. 5 shows the luminescence as a function of temperature for various spectral positions. The scale is such that the luminescence is 27 units at the peak of the spectrum. Fig. 5 includes the changes brought about by introducing Franck–Condon assumptions. There is no decrease with a temperature rise. Any observed decrease must therefore be attributed to a thermal degradation which converts energy of the excited state into heat. Such a degradation takes place generally, and is observed here as a general decrease in luminescence above about 140° K.

Yet another process which must be considered is the effect of reabsorption and its consequence of a greater luminescence at lower energies and less at higher energies. The overall result is shown clearly in Fig. 1. It is noteworthy that the high-energy tail on the luminescence spectrum appears at higher temperatures in a region where the overall luminescence decreases markedly. Reabsorption effects are greater the greater the energy in the spectrum and the greater the temperature. The extinction coefficient will be given, a near continuum of vibrational levels of suitable symmetry being assumed, by $\varepsilon(\nu) = \varepsilon_0 \exp [h(\nu - \nu_0)/kT]$ where ε_0 is the value of ε at ν_0, the origin of the absorption. For more than one origin the single exponential term is replaced by a sum. Such a relation can explain the overall decrease of luminescence at the higher energies as the temperature is raised to 300° K. Reabsorption must therefore play a part in the final full theory of the variation of the luminescence spectrum with temperature. Its effects may be neglected (i) at sufficiently low temperatures, (ii) when the temperature is changed over a sufficiently small range, (iii) when $(\nu - \nu_0)$ is sufficiently large, and (iv) when ε is sufficiently small.

The main conclusions of the foregoing discussion are not likely to be altered by considerations of reabsorption, *i.e.*, that a Boltzmann distribution over the existing origins and a Franck–Condon effect are both important in these spectra.

The nature of the various origins has not so far been considered. Sidman [1] suggested that trapped exciton levels existed at energies lower than the free exciton levels. The interaction of trapped excitons with phonons and their consequent detrapping is a process which does not seem to have been considered previously. The effect of temperature on luminescence arising from trapped excitons must inevitably require a discussion of such an interaction. It seems likely that excitons in hollow traps will leave the traps at sufficiently high temperatures and become mobile. This type of explanation fits very nicely with the effect of temperature on the luminescence from anthracene crystals containing naphthacene.[4]

In addition, those transitions should be observable in both absorption and luminescence which involve absorption or an emission of a phonon simultaneously with the change in electronic energy.[5] The exciton wave-vector is approximately equal to $\pm p$, where p is the wave-vector of the phonon. It has been shown [6] that such transitions might explain both the energy and the polarisation of the edge bands [3] of luminescence of anthracene at low temperatures. Therefore there is no need at present to postulate impurities as necessary for the explanation of the luminescence. However, it is not yet possible to exclude completely such an explanation, especially in view of the demonstrated influence of oxygen. The final explanation must take account of the interaction of phonons with both free and trapped excitons and the observed results on both pure and mixed crystals, after the effects of oxygen have been excluded.

THE UNIVERSITY OF SYDNEY, SYDNEY, N.S.W., AUSTRALIA.

[4] Lyons and White, *J. Chem. Phys.*, 1958, **29**, 447; White, M.Sc. Thesis, Sydney, 1959.
[5] Davydov, *Izvest. Akad. Nauk*, S.S.S.R., *Ser. Fiz.*, 1951, **15**, 606.
[6] Lyons, Proc. Conference on Electronic Conduction of Organic Solids, held at Duke University, 1960 (to be published).