

LETTERS TO THE EDITOR

CATHODOLUMINESCENCE OF Eu^{3+} IN LaCl_3

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CRYSTAL phosphors activated by trivalent europium possess intense luminescence under photo- and cathode-ray excitations¹⁻⁵. The purpose of the present work is to study the differences in spectral characteristics of Eu^{3+} activated lanthanum chloride phosphor on excitation by cathode rays and ultraviolet radiation.

Europium chloride was prepared by dissolving europium oxide (99.9% purity, Koch-Light Laboratory, England) in concentrated hydrochloric acid (G.R. Grade). The solution is then evaporated and desiccated. The phosphor sample was prepared by fusing a mass of LaCl_3 (99.9% pure) mixed with desired quantity of europium chloride in a furnace at about 800°C in chlorine atmosphere.

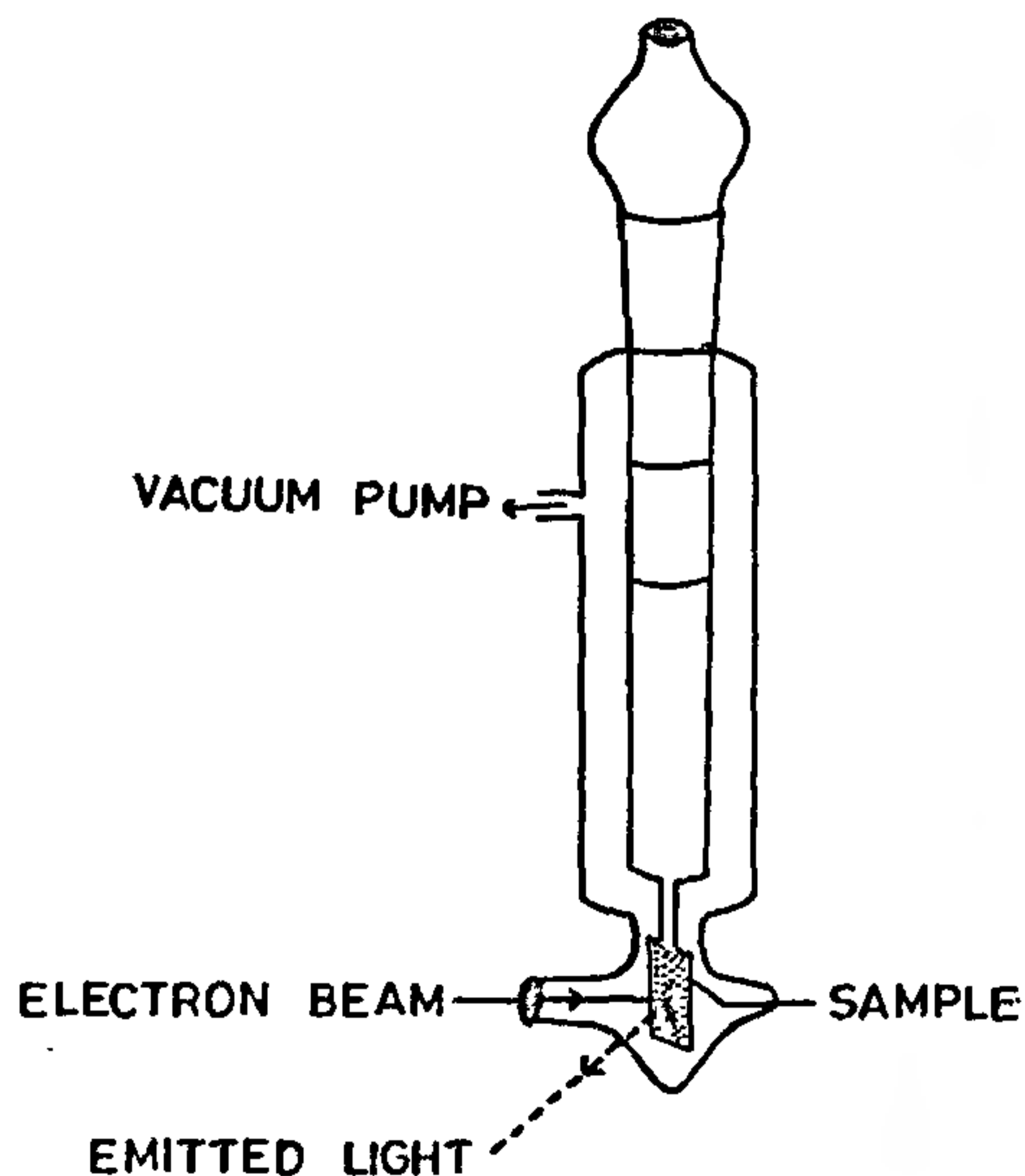


Figure 1. Block diagram of cathodoluminescence apparatus.

† However, a broad band at 507 nm and an intense sharp peak at 500 nm is observed in CRE only, the nature of which is uncertain.

Cathodoluminescence apparatus (shown in figure 1) was fabricated for the study of the emission by cathode-ray excitation. The electron beam was obtained from an electron gun having an anode, cathode, grid and oxide coated filament. The anode voltage was supplied with a voltage doubler (6000 volts) and the electron beam thus produced was magnetically focussed on the phosphor plaque. The phosphor plaque was prepared by settling the phosphor onto a 1.5×2.5 cm copper plate. The phosphor plaque was kept in a glass cylinder which was connected with the electron gun by a quick fit joint and the emitted light was recorded through a glass window.

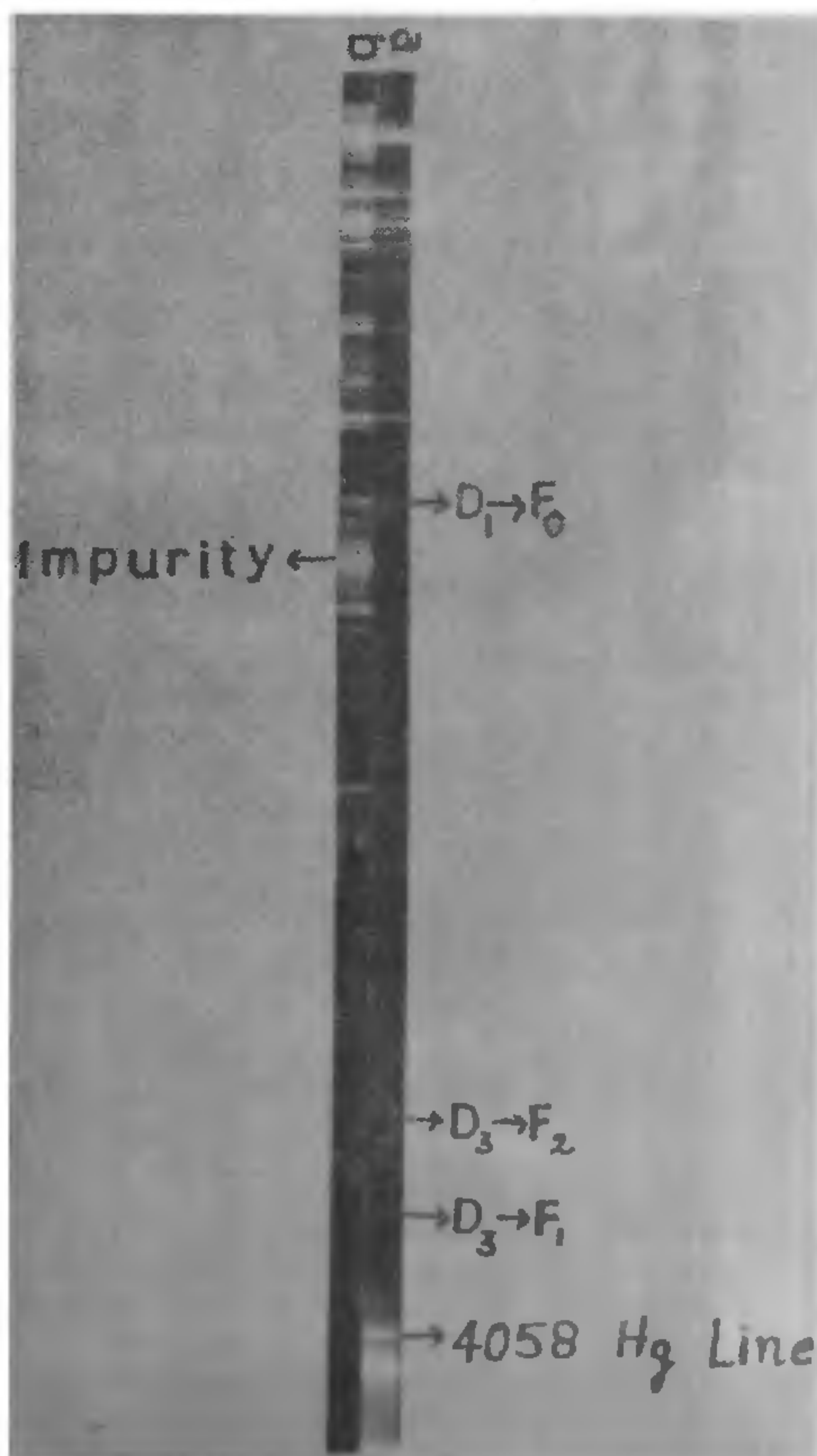


Figure 2. Emission spectra of $\text{LaCl}_3:\text{Eu}^{3+}$ (0.5%) under (a) PE (exposure time one hour), (b) CRT (exposure time 10 minutes).

The phosphor plaque was oriented at 45° to the incident electron beam while the emission passed at 90° to the beam. The emission spectra were photographed with a Fuess prism spectrophotograph. Without disturbing the position of the sample and spectrophotograph, the arrangement for the excitation of the sample by 365 nm radiation was made and the emission spectrum was photographed. The curves from the photographs were scanned with the help of a Zeiss microphotometer.

The emission spectra of Eu^{3+} in LaCl_3 (0.5%) by cathode ray excitation (CRE) and photoexcitation (PE) are given in figure 2. The cathodoluminescence and photoluminescence spectra contain a large number of lines emitted from all the four excited states viz., 5D_0 , 5D_1 , 5D_2 and 5D_3 states. The spectral positions of lines in cathodoluminescence coincide with the photoluminescence peaks[†]. However, the relative intensities of the lines emitted in the two spectra are different. The relative intensities of D_1 and D_3 transitions are given in table 1 for the two excitations. The results are only approximate as the plate has not been calibrated for linearity. However, since the transitions from D_1 , D_2 , and D_3 states are weak and the exposure times were so adjusted that there was no overexposure for these transitions, linearity can be approximately assumed. The D_0 transitions are overexposed and have not been taken into account for relative intensity calculations. It will be observed from the table that the transitions from the D_3 state are less intense in CRE compared to PE.

TABLE 1

Intensity ratio of D_1 and D_3 transitions under photoexcitation and cathode ray excitation

	Intensity ratio (CRE)	Intensity ratio (PE)	CRE/PE
$\frac{D_1 \rightarrow F_0}{D_3 \rightarrow F_2}$	6.0	2.3	2.6
$\frac{D_1 \rightarrow F_0}{D_3 \rightarrow F_1}$	5.0	2.0	2.5

Gavrilenko *et al.*⁶ have reported a similar effect in TB^{3+} emission in silicate glass and have suggested that the decrease in D_3 emission is due to the enhanced temperature in CRE. In the case of $\text{LaCl}_3:\text{Eu}^{3+}$ (0.3%) we carried out the experiments to study the relative fluorescence intensities under PE with temperature. The variations are reported in figure 3. The peak at 240 K is fictitious as it arises on account of change in absorption due to broadening. However, it is clear that D_3 falls more rapidly than D_2 whereas D_1 and D_0

remain substantially unaffected. In fact photoexcitation at the charge transfer band in $\text{Y}_2\text{O}_2\text{SEu}^{3+}$ has been shown by Struck and Fonger⁷ to undergo rapid decrease in intensity with temperature in order of D_3 , D_2 , D_1 , D_0 . The life time measurements which

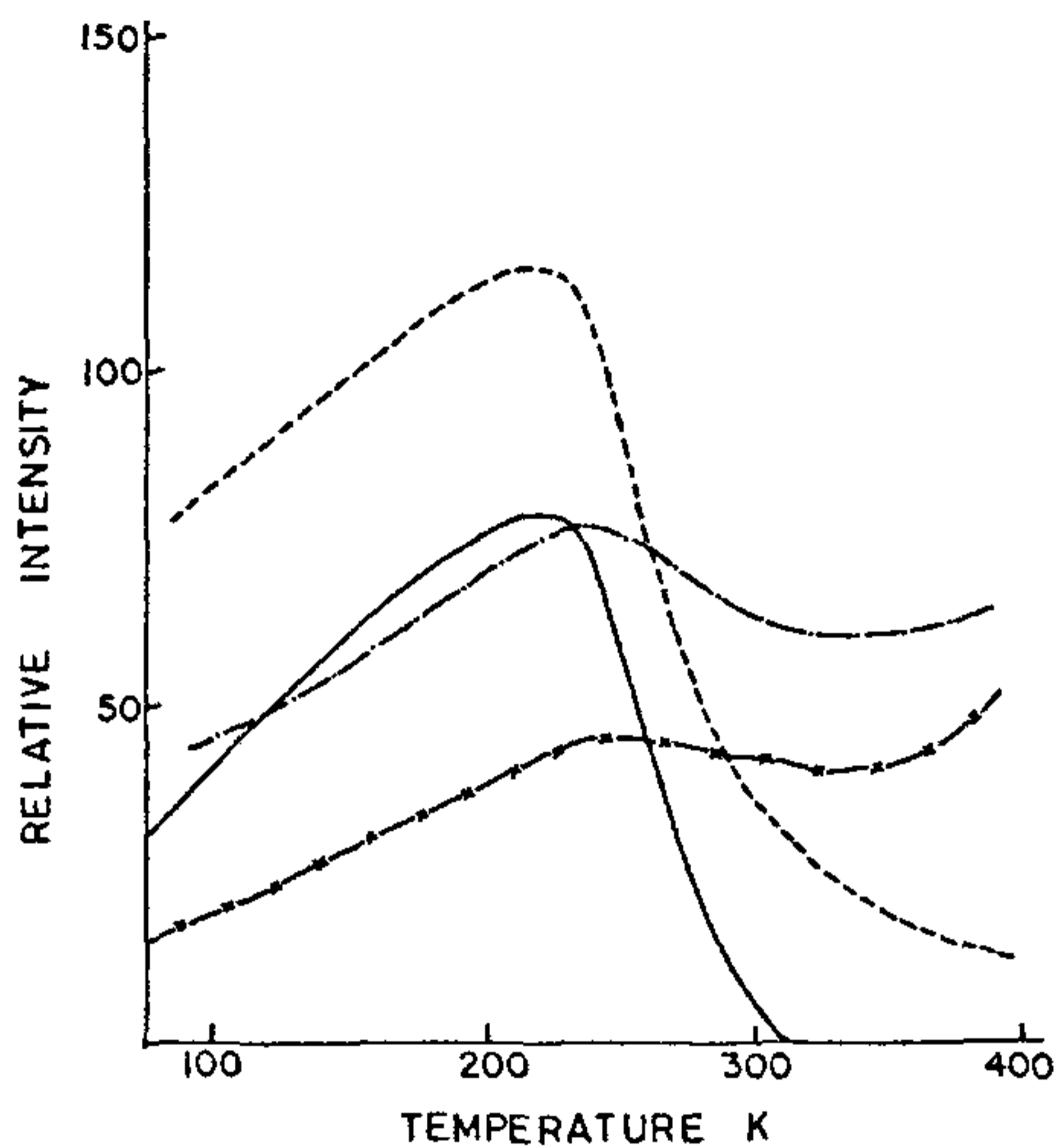


Figure 3. Temperature variation of fluorescence intensity of $\text{LaCl}_3:\text{Eu}^{3+}$ (0.3%) for: — D_0 , - - - D_1 , - · - · D_2 and - x - x - x - D_3 transitions.

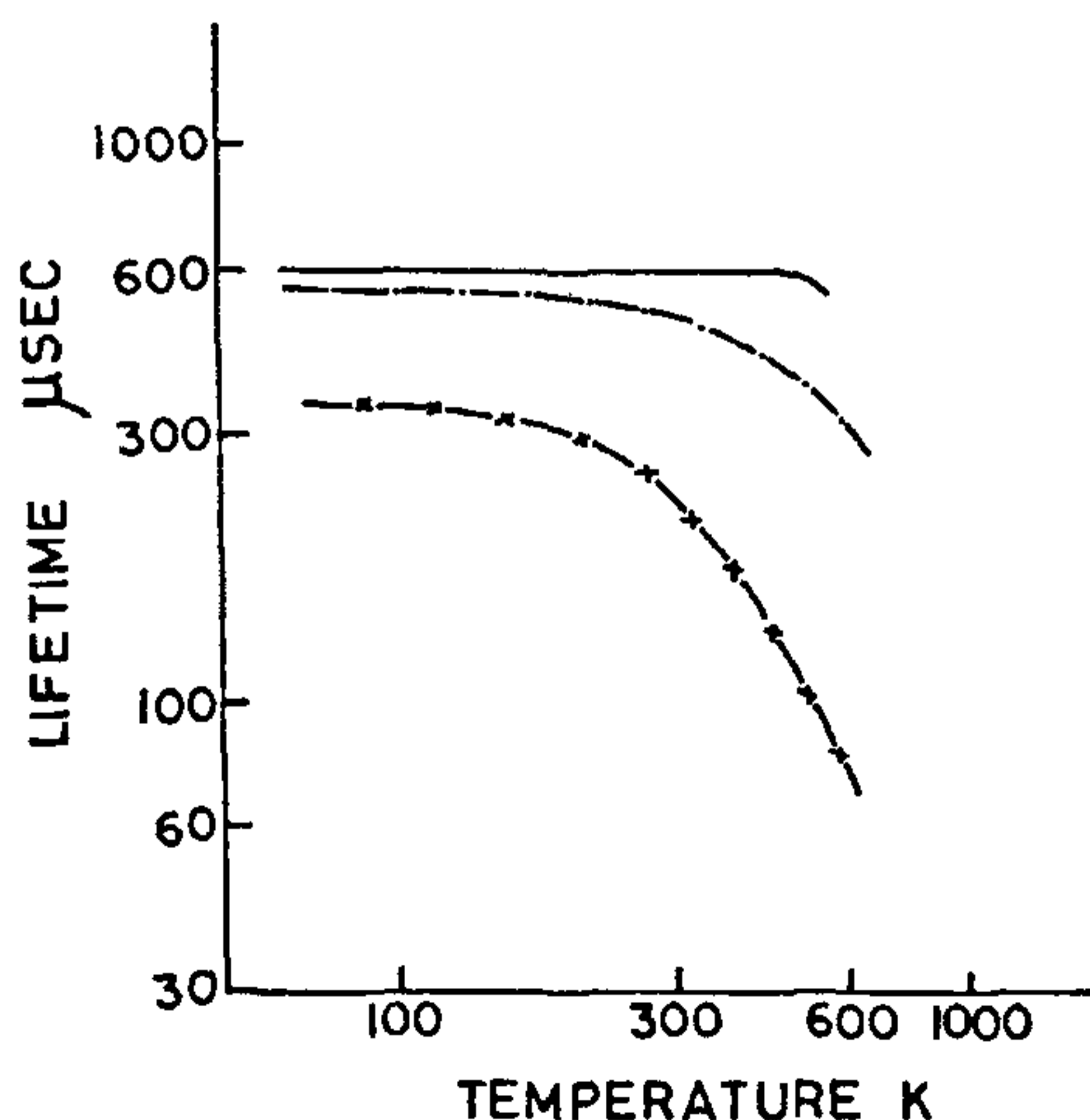


Figure 4. Temperature variation of fluorescence lifetimes of $\text{LaCl}_3:\text{Eu}^{3+}$ (0.3%) for: — D_0 , - - - D_1 and - x - x - x - D_2 excited states.

do not depend on the value of the absorption coefficient are reproduced for $\text{LaCl}_3 : \text{Eu}^{3+}(0.3\%)$ in figure 4 which also show that the nonradiative processes increase in order of $D_2 > D_1 > D_0$ with the temperature.

The most probable explanation of the decrease in relative emission intensities of the 5D_3 state can be the temperature quenching of the higher state emission during electron bombardment. Although both the spectra were recorded at room temperature (290 K), in case of CRE the intensity ratio of D_1 and D_3 transitions correspond to a temperature of 305 K for PE. It seems that some sort of local temperature develops by 15°C approximately during CRE and results in the quenching of the D_3 emission. The other probability is that $D_3 \rightarrow D_j$ ($j = 0, 1, 2$) nonradiative crossing rate may be different in the two excitations.

The authors thank the C.S.I.R. and U.G.C., New Delhi for financial support.

28 July 1981

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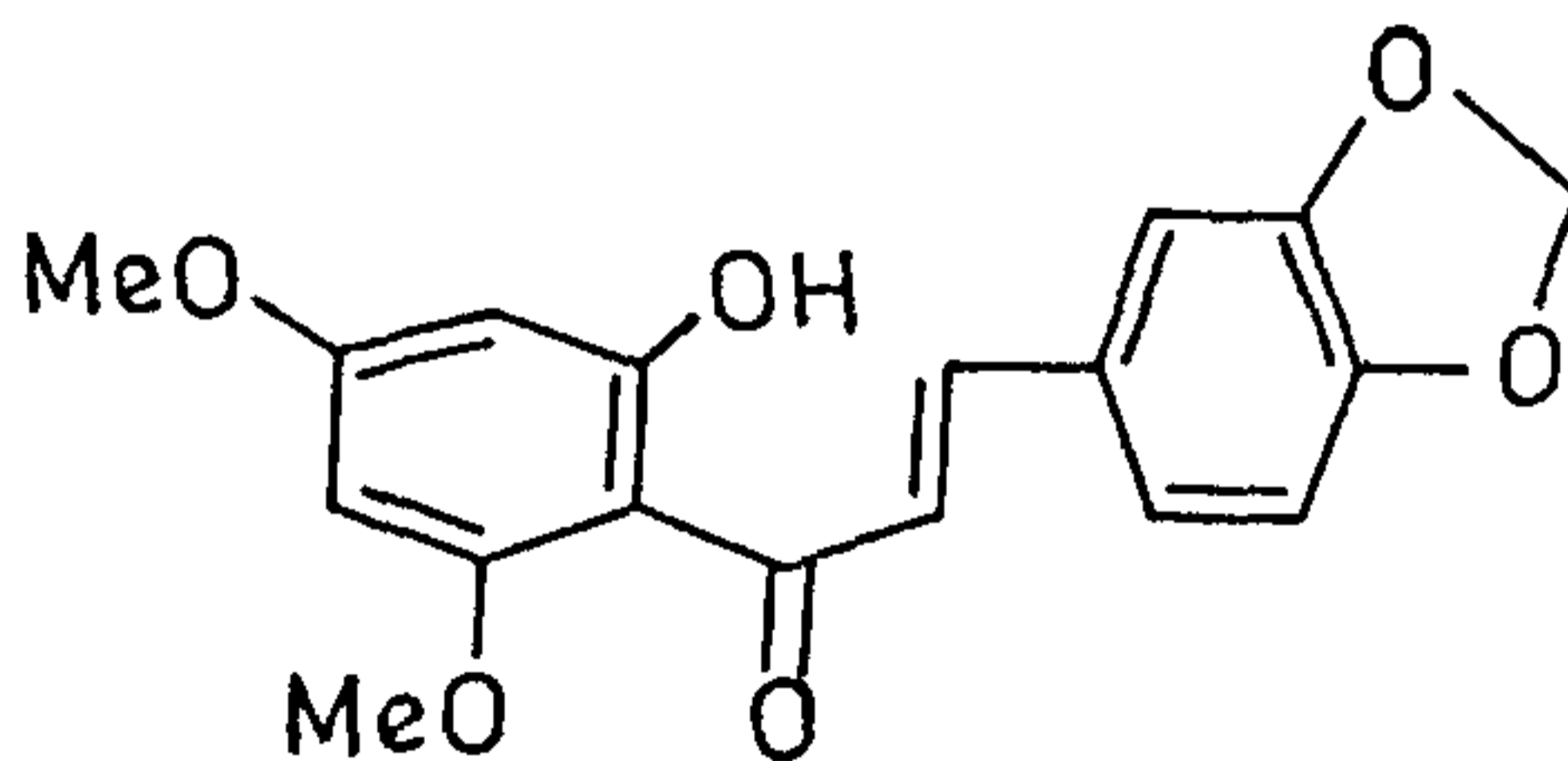
TEPHRONE, A NEW CHALCONE FROM *TEPHROSIA CANDIDA* SEEDS

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IN our earlier work on the chemical constituents of the seeds of *Tephrosia candida*, the isolation and identification of pongachin, candidin and candidol were reported¹⁻³. The present note reports the isolation and characterization of a new chalcone, tephron, from the same source.

The petroleum ether and benzene extracts of the seeds were found to be similar on TLC, hence combined and treated with ether. The ether soluble fraction was subjected to column chromatography over silica

gel. Elution with petroleum ether-benzene (7:13) yielded a yellow crystalline compound (40 mg), m.p. $165-6^\circ$. When analysed for $\text{C}_{18}\text{H}_{16}\text{O}_6$, it did not respond to Shinoda's test, but gave a greenish-brown colour with alcoholic ferric chloride and a green colour with gallic acid- H_2SO_4 , indicating chelated hydroxyl and methylenedioxy group, respectively. The former was further supported by absorptions at 3370 and 1635 cm^{-1} in IR and a singlet at $\delta 14.30$ in the NMR spectrum (CDCl_3) of the compound. The UV spectrum showed λ_{max} $224, 368\text{ nm}$ in methanol which was found to undergo a bathochromic shift of 44 nm with aluminium chloride suggesting a 2'-hydroxychalcone skeleton for the compound. That tephron is a chalcone was confirmed by two doublets ($J = 17\text{ Hz}$) at $\delta 7.44$ and 7.72 (characteristic of H_α and H_β of chalcones)⁴. NMR of the compound also showed two singlets at $\delta 3.78$ and 3.86 , integrating for three protons each, due to two methoxys. A positive Gibb's test and two doublets ($J = 2.5\text{ Hz}$) centred at $\delta 5.90$ and 6.04 , corresponding to $\text{H}-3'$ and $\text{H}-5'$ respectively, established the 2'-Hydroxy-4',6'-dimethoxy substitution pattern for ring A. The presence of the methylenedioxy group was confirmed by bands at 925 and 1040 cm^{-1} in IR⁵ and a two-proton singlet at $\delta 5.95$ in the NMR spectrum. The fact that it must be present in ring B was indicated by an ABX system in NMR in the range $\delta 6.72-7.22$, characteristic of 3,4-substitution in ring B. The piperonyl residue⁶ was established by alkaline degradation of tephron which yielded a compound, m.p. $227-9^\circ$, identified as piperonylic acid. On the basis of the above spectral and chemical data, tephron is assigned the structure 2'-hydroxy-4',6'-dimethoxy-3,4-methylenedioxy-chalcone (I).



(I)

The identity of the compound was finally confirmed by its synthesis⁷ starting from 2-hydroxy-4,6-dimethoxyacetophenone and piperonal. Condensation of the two substances in the presence of 60% potassium hydroxide in aqueous alcohol yielded a yellow solid which agreed with the natural sample (m.p., m.m.p., co-TLC and co-IR).

26 April 1982