CHAPTER III

THERMOLUMINESCENCE AND DECAY STUDIES

A. THERMOLUMINESCENCE

1. INTRODUCTION

Thermoluminescence is one of the most useful and popular techniques for obtaining information about the defect and impurity energy levels of the phosphors, a rough qualitative picture of the distribution of electrons in the various traps and some idea about the reaction kinetics. It consists in filling the traps at low temperature by excitation, followed by immediate cooling, so that the traps retain captured electrons and recording the luminescence intensity as a function of phosphor temperature while it is continuously heated at a uniform rate. Glow curves so obtained are often characterised by one or more peaks, the position of which on temperature scale is a measure of the depth in energy of the trapped electrons.

2. THEORY

The theory of Randall and Wilkins is based on the assumption of monomolecular mechanism as in the case of phosphorescence, and the equation may be written as:

\[ \frac{d\ln}{dt} = - \frac{n}{t} \]

\[ I = \frac{dn}{dt} \]

\( (3.1) \)

\( (3.2) \)
where \( n \) is the number of traps filled at the time \( t \), \( \tau \) is the mean life time of the trapped electrons and \( I \), the thermoluminescence intensity.

If \( \beta \) is the linear rate of heating, then the temperature \( T \) increases with time according to the relation:

\[
\frac{dT}{dt} = \beta \quad \ldots \quad (3.3)
\]

and so \( T \) also varies as

\[
\frac{1}{T} = \frac{1}{T_i} \exp \left( -\frac{E}{kT} \right) \quad \ldots \quad (3.4)
\]

and \( n \) is given by

\[
\begin{align*}
n &= n_0 \exp \left( -\int_{T_i}^T \frac{1}{T(\xi)} \, d\xi \right) \\
&= n_0 \exp \left( -\int_{T_i}^T \exp \left( \frac{E}{kT} \frac{dT}{\beta} \right) \right) \quad \ldots \quad (3.5)
\end{align*}
\]

\( T_i \) being the initial temperature at which the phosphor was excited, \( n_0 \) being the number of filled traps at time \( t = 0 \) (at the beginning of heating).

The glow intensity \( I(T) \) at temperature \( T \) is given by

\[
I(T) = n_0 s \exp \left( -\frac{E}{kT} \right) \exp \left[ -\int_{T_i}^T \exp \left( \frac{E}{kT} \frac{dT}{\beta} \right) \right] \quad \ldots \quad (3.6)
\]

Since direct evaluation of \( s \) and \( E \) from the equation (3.6) is not possible, a number of methods have been proposed to obtain them from glow-curves as summarised below.
(a) **Method of Initial Rise:**

This method is based on the fact that the second exponential in equation 3.6 is almost unity over the initial part of the glow curve. The equation is then representable by:

\[ I = F \exp\left(-\frac{E}{kT}\right) \]

where \( F \) is a constant.

On the basis of theoretical arguments, Hacke (11) has shown that this method may lead to inconsistency and error.

(b) **From Glow Maxima:**

If \( T_m \) be the maximum temperature of thermoluminescence, then with \( \frac{dI}{dT} = 0 \), the equation (3.6) becomes

\[ \frac{E}{kT_m^2} = \frac{8}{\beta} \exp\left(-\frac{E}{kT_m}\right) \quad \cdots \quad (3.7) \]

From numerical calculations, this relation can be obtained with sufficient accuracy, as

\[ E (\text{ev}) = \frac{T_m \left( ^0k \right) - T_0 \left( \frac{\beta}{s} \right)}{k \left( \frac{\beta}{s} \right)} \quad \cdots (3.8) \]

The values of \( T_0 \) and \( K \) being obtained graphically from the following table.
\[ \theta = \frac{\beta}{s} \quad (^\circ K) \quad k (^\circ K/ev) \quad T_o (^\circ K) \]

| \(10^{-4}\) | \(833\) | \(35\) |
|\(10^{-5}\) | \(725\) | \(28\) |
|\(10^{-6}\) | \(642\) | \(22\) |
|\(10^{-7}\) | \(577\) | \(17\) |
|\(10^{-8}\) | \(524\) | \(13\) |
|\(10^{-9}\) | \(490\) | \(10\) |
|\(10^{-10}\) | \(441\) | \(7\) |
|\(10^{-11}\) | \(408\) | \(6\) |
|\(10^{-12}\) | \(379\) | \(6\) |
|\(10^{-13}\) | \(353\) | \(5\) |
|\(10^{-14}\) | \(331\) | \(5\) |
|\(10^{-15}\) | \(312\) | \(4\) |

The relation (3.3) is subject to the accuracy of 
's' value which is of the order of \(10^{-9}, 10^{-10}/sec\).
It is, therefore, usually determined by trial and error method.

(c) **From half width of Glow peak:**

Grosswiiener (1) employs the temperature 'T_m' of 
glow maximum at \(T_1\) on the low temperature side of the peak 
at which, thermoluminescence intensity is half of its maximum value. If
$$\frac{E}{kT} > 20 \quad \text{and} \quad \frac{\theta_0}{\rho} > 10^7$$

then

$$E = 1.51 \left( \frac{kT_m T_2}{T_m - T_1} \right)^n \quad \ldots \quad \ldots \quad (3.9)$$

to a good approximation.

(d) **From symmetry of glow peak:**

Halperin (2) uses a symmetry factor i.e. the ratio between half width \((T_m - T_2)\) towards the fall off side and total half width \((T_1 - T_2)\) of the glow maxima.

The formula for energy is

$$E = \left( \frac{\gamma}{\delta} \right) k T_m (1 - \Delta) \quad \ldots \quad \ldots \quad (3.10)$$

where \(k\) = Boltzman Constant;

\(\delta\) = half width towards fall off;

and \(\Delta = \frac{2kT_m}{E}\).

The factor 'q' depends on the shape of glow peak and kinetics of the process.

(e) **From the shift of glow maxima with different warming rates:**

Number of workers (3-5) have independently shown that, if the thermoluminescence is studied at two different warming rates \(\beta_1\) and \(\beta_2\), the same trap depth gives two different values of \(T_m\) say, \(T_{m_1}\) and \(T_{m_2}\), and if \(\beta_1 > \beta_2\) then \(T_{m_1} > T_{m_2}\). The elimination of 's' from the two equations like (3.7) gives
\[
\frac{E}{k} \left( \frac{1}{T_{m_2}} - \frac{1}{T_{m_1}} \right) = \log \left( \frac{P_1}{P_2} \cdot \frac{T_{m_2}^2}{T_{m_1}^2} \right)
\]

from which \( E \) can be obtained, for \( s \) we get

\[
\log \frac{S}{k} = \frac{T_{m_2} \log \frac{T_{m_2}}{T_{m_1}} - T_{m_1} \log \frac{T_{m_1}}{T_{m_2}}}{T_{m_2} - T_{m_1}}
\]

\[
\cdots \cdots (3.11)
\]

Trap depth can also be evaluated from the area under the glow curve (6).

3. EXPERIMENTAL METHODS:

Various experimental methods, which have been adopted by different workers are as follows:

Randall and Wilkins spread a thin layer of powdered phosphor on the surface of a small copper box smeared slightly with glycerol. A Copper-Constantan thermo-couple is soldered to the surface of the box. Liquid air could be poured into a funnel, attached to the box for obtaining low temperature. The method though convenient, has the disadvantage that the rate of warming varied considerably with temperature.

In an alternative arrangement, the apparatus was so designed that the heat losses from the surface of the box would not affect the warming rate, and so high temperature could be reached. For cooling, the whole system is placed in a flask full of liquid air when the box is cooled with liquid air, the phosphor is excited with a
mercury arc. Then the apparatus is placed in the dark and the phosphor is heated by an electric heater placed inside the box. The glow intensity is measured with a photo-multiplier and galvanometer system. Further modification of the apparatus ensures warming rate upto 50° K/sec.

Thermoluminescence of F⁻ centres in alkali-halides was studied by Bonfiglioli. In this arrangement, an oven is built up of a large plate of copper covered by a layer of evaporated platinum to avoid oxidation. The phosphor is kept inside a small well in the centre of the oven along the axis of the plate. Temperature was recorded by Pt / Pt - Rh thermocouple located at the definite position under the specimen. Detection of the thermoluminescence light was performed through the use of RCA IP 21 or IP 28 photo-multipliers recording directly the light spot of a galvanometer on a rotating drum equipped with a sheet of photographic paper.

Halperin et al (2) mounted an alkali halide crystal in a vacuum crystal which could be heated from liquid air temperature to about 600° K with the help of a heating element. The emission is passed through a quartz window and falls on a detector (RCA IP 28 photomultiplier). The glow curves were recorded by a 50 mv Brown recorder after amplification. Temperature was measured with a calibrated copper-constantan thermocouple. The heating rate could
be varied between $10^0$ K to $20^0$ K/min. High speed of the recorder chart enables temperature determination to an accuracy of 0.2 degree.

4. **PRESENT METHOD**

(a) **Instrumentation**

(i) **Source of excitation:**

The samples were excited by means of an aluminium arc, which was a condensed one. It was energised by a spark coil, capable of supplying voltage of 5 KV. Parallel plate condensers working at this voltage and having a capacity around 120 p.F. were specially prepared in the Solid State Physics Laboratories of M.S. University of Baroda. The condensers were connected across the electrodes to condense the arc. The $\text{Al}_2\text{O}_3$ formed on the electrodes during the arcing, gave emissions with band heads at 259, 302 m and a broad band at 250 m.

(ii) **Phosphor Holder:**

The phosphor powder was held against the flattened surface of a copper rod, 20 cms. long and 2 cms. in diameter, using a thin coat of non-luminescent silicon grease on the flattened surface. One junction of the thermocouple (Copper-Constantan) was fixed to the top of this rod, at a point very near the phosphor. The other junction was immersed in an ice bath. The rod could be heated by a
coil wound round it. Since the coil was heated electrically, a thin layer of non-conducting material like Cotton Wool was placed immediately around the rod, to avoid direct contact between the coil and the rod. A uniform heating rate used in the experiment was adjusted to be $10^5$ /minute.

(iii) Detector:

The luminescence emission of the excited phosphor was detected and measured in arbitrary units, using a photomultiplier of 931-A type. The photo-multiplier was housed in a light proof mount, fitted with a relay-operated camera shutter. The cathode of the photomultiplier tube, was connected, to a highly stabilized negative voltage (w.r.t. earth) variable upto 1200 volts. A bleeder network of resistors maintained the nine dynodes at suitable potentials. The anode was connected to a D.C. amplifier by means of a short shielded cord. The multiplier tube had to be periodically cleaned with absolute alcohol and dried with hot air, in order to keep the dark current at a low level.

The D.C. amplifier, the circuit diagram of which is shown in fig. 3.2 employed an electrometer tube ME 1400, with a single cathode follower circuit. The input resistance of the preamplifier could be varied in 8 steps, with values 100 K, 300 K, 1 Meg, 3 Meg, 10 Meg, 30 Meg, 100 Meg and 300 Meg. The time constant for the system was 3 secs. The casing of the preamplifier was screened separately.
Fig 3.20 Electrometer-Amplifier
**Fig 3.2(b) Power Supply**

For Amplifier
The amplified photo-current was recorded by a mirror galvanometer with a lamp and scale arrangement. The galvanometer coil was critically damped. A compromise between sensitivity and damping was struck by adjusting resistances in parallel and in series with the galvanometer.

The exciting source, the photomultiplier and the rod carrying the phosphor, were arranged, so as to conform to the most advantageous geometry.

(iv) Measurement of phosphor temperature:

A Leeds and Northrup potentiometer was used for the measurement of the temperature of the phosphor in the thermoluminescence recording. Using a Copper-Constantan thermocouple, the temperature could be conveniently noted with an accuracy of 0.1°C. The external galvanometer, chosen as the null detector, had a period almost the same as that of the time constant of the D.C. amplifier.

§b) Method of Operation:

The whole assembly was covered with thick black cloth, which prevented the ambient stray-light from reaching the photomultiplier. The phosphor was then excited by means of the aluminium arc for 5 minutes, which was sufficiently more than the time required for the saturation of the initial phosphorescence intensity.
of the phosphor. In order to maintain, the uniformity for all the recording, a lapse of 30 seconds was allowed between, the cessation of the excitation and the switch on of the heating current for the coil surrounding the rod. This interval served the experimenter to open the photomultiplier shutter (the high tension for the photomultiplier being already on) and choose the proper amplification factor for the photo-current. The intensity of luminescence as recorded in arbitrary units by the photomultiplier galvanometer, was noted for every step of 0.05 mV increase in the thermo e.m.f. which corresponded approximately to 1º rise in temperature of the rod and hence of the phosphor.

The CaS : Sm phosphor was heated from room temperature to 500º K, when majority of the traps providing glow peaks, under optical excitation, were observed to be deactivated. It had been confirmed by preliminary trials, that, there were no peaks in the thermoluminescence of the phosphor examined beyond 500º K, after exciting the phosphor with aluminium arc. Immediately after switching off the heating current, the phosphor was cooled down to the room temperature. The phosphor was either allowed to cool normally, under ordinary conditions or it was cooled rapidly by circulating ice cold water round the rod, holding the phosphor. In the former case, the total time required was about 12 hours, whereas in the later case, it was only 15 minutes.
Fig 3.3 Thermoluminescence or Glow Curves
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Fig 3.3
Thermoluminescence or Glow Curve

Temperature (°K)

Thermoluminescence Intensity (arb. units)
Fig 3.3 Thermoluminescence or Glow Curve
**Fig 3.3** Thermoluminescence or Glow Curve
FIG 3.3 THERMOLUMINESCENCE OR GLOW CURVE
Fig 3-3 Thermoluminescence or Glow Curve
Fig 3-5 Thermoluminescence or Glow Curves
Fig. 3.3  THERMOLUMINESCENCE OR GLOW CURVE
5. RESULTS:

(a) Glow Curves:

Glow Curves for the samples studied are given in fig. No. (A, B, C, D, E, F, & G) corresponding to the series A, B, C, D, E & F corresponding to the different fluxes and G corresponding to the samples without flux. The temperature limits of the study were 300° K to 500° K. For the warming rate of 10°/minute, almost all the samples of series B, D, E, F, & G show good resolution of glow peak giving rise to two peaks, except for the samples of A & C series at the higher concentration of the flux.

(b) Trap depth:

Equation (3.8) have been used to calculate the trap depth.

The trap depth corresponding to the two peaks in glow curves obtained, are given in table No. 3.2. There appears no appreciable change in trap depths with flux concentration. The same results have been reported by earlier workers (7-11).

<table>
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<th>Sample No.</th>
<th>Percentage of flux w.r. to CaS</th>
<th>1st Peak Temp</th>
<th>Trap Depth</th>
<th>2nd Peak Temp</th>
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B. DECAY

1. INTRODUCTION

The decay characteristic of the phosphors have been studied extensively in the field of luminescence, in order to understand, the kinetics and the energy distribution of the trapping levels. The decay characteristics can be derived by simply measuring the decrease in the intensity of the afterglow as a function of time. Urbach (12) studied the decrease in time of the residual light sum by observing the infra-red stimulated extinction. However, the experimental technique adopted depends upon the duration of decay.

2. THEORIES OF DECAY

A better distinction can be made by considering the order of the kinetics rather than the molecularity (13).

(a) Kinetics of decay :

(i) First order Kinetics :

The lifetime of luminescent centre in the excited state depends on the transition probability $'p'$ at time $'t'$ is given by :
\[
I = \frac{dn}{dt} = -pn \quad \cdots \quad (3.13)
\]
which gives
\[
I = I_0 \exp\left(-pt\right) \quad \cdots \quad (3.14)
\]
where \(I_0\) is the emission intensity at the beginning of the decay.

(ii) Second order kinetics:

When the probability of recombination depends both on the number of excited electrons and on the number of available centres, then the intensity is given by the relation:

\[
I = \frac{dn}{dt} = -pn^2 \quad \cdots \quad (3.15)
\]

i.e.,
\[
I = \frac{I_0}{(1 + at)^2} \quad \cdots \quad (3.16)
\]

where \(a = \left(\frac{I_0}{p}\right)^{\frac{1}{2}}\)

(b) Kinetics of Fluorescence:

The kinetics mentioned above do not take into account the intermediate process of trapping and hence applies to the case of fluorescence only. Sometimes in actual practice, the kinetics of fluorescence is more complicated. For example in KCl : Ti, the weak photoconductivity, due to levels other than those of Ti\(^{+}\) ions, perturbs the luminescence kinetics (14, 15). With uranyl salts which generally exhibit a simple exponential decay (on U, V excitation), evidence of electron-hole recombination has been found by Luechin (16) et al.
(c) Kinetics of Phosphorescence in photocconducting phosphors:

In the case of phosphorescence, the kinetics depends upon the spatial location of the traps with respect to the luminescence centres and on the motion of conduction electrons (17). When the traps and centres are separated by a distance of the order of $10^{-6}$ cms or less, only a small movement of electrons is involved and hence they can be considered as single units. In this type of phosphorescence, the number of electrons recombining with centres equals the number arriving from traps and monomolecular kinetics applies.

In the case where the traps and centres are specially independent of each other, the electrons can move over large distances and recombine with any one of the available centres. The emission intensity would depend on the recombination of the electrons and vacant centres, and hence second order kinetics would apply.

Assuming traps of one mean lifetime only and assuming equal electron capture cross-sections for the centres and traps, the phosphorescence decays according to the equation

$$I = \frac{\text{Const}}{(t + t_0)^2}$$

where $t_0$ is the constant of integration equal to the mean life time of the traps for saturation excitation.
Thus the decay tends towards a final form

\[ I \propto t^{-2} \]

a result which is usually not in agreement with experimental observations.

3. METHOD OF MEASURING DECAY:

(a) Fast Decay \( t < 10^{-5} \text{ sec.} \)

Bril and his associates (18) used the oscilloscope method for the measurement of short duration decay of the order of \( 10^{-2} \text{ sec.} \) by transmission of very short pulses through coaxial cables and the use of colour shiftness to convert the ultra-violet luminescence to match closely the spectrol response of the detector. Shutz (19), using pulsed 60 e.v. electronic beam for excitation, photomultiplier counter circuit and time discrimination of about \( 10^{-9} \text{ sec.} \) has determined point to point, the rise and decay curves.

An indirect method involving the measurement of the phase angle between the sinusoidally modulated excitation source and its luminescence counterpart is also suitable for fast decaying phosphors (20-22) and has been used to determine luminescence decay times of \( 10^{-9} \text{ sec.} \) with accuracy.
It is often convenient to measure the luminescence signal relative to the signal from the reflection of the incident radiation by a non-luminescent substance. A better method is that due to Henle et al. (23) in which the phase difference is measured by determining the shift of the fluorescence fringe pattern with respect to the exciting light fringe pattern. Bennett (24) has described a noble method of obtaining the time resolutions of the order of $10^{-9}$ sec. by exciting fluorescence, by \( \text{H}_2 \) flash lamp, observing stroboscopically and gating the photomultiplier.

(b) \textbf{Slow Decay (} \( t > 10^{-5} \) \text{ sec.)}

First mechanical device, for the measurement of decay time, was suggested by Becquerel named as Becquerel's phosphoroscope. It consists of two sectored discs mounted on a common shaft, such that, the phosphor sample can be kept in between and the excitation slit, leads the viewing by a certain angle. With the use of detector, such as photomultiplier and oscilloscope along with it measures the decay time upto $10^{-4}$ sec. (25).

Randall and Wilkins (26) used another form of apparatus developed by R.W.Wood which consists of placing the phosphor in the form of annulus around the circumference of a disc. The excitation takes place at some position, fixed in space. By changing the angular position of the detector with respect to that of the excitation, the phosphorescence is observed at various
times after excitation. This method also permits a direct
observation of colour changes during decay process (27).

Long decay can easily be recorded by using a
photomultiplier having anode characteristics, such that,
when operated at constant current, voltage output is
proportional to the logarithms of illumination and coupled
with C.R.O., having a linear time base (28). A simple
mechanical shutter has been used by Ellickson (29) and
Radley (30) to cut off the exciting light at the desired
interval and afterglow recorded using a photomultiplier
and a galvanometer.

3. Present Method

The experimental technique for the measurement of
phosphorescence decay is essentially the same as used for
the measurement of thermoluminescence after taking out
the heating arrangement of the phosphor from it.

The phosphor was excited to luminescence by
irradiation with ultraviolet light. The measurements
were carried out in the dark with the 931-A type detector
in conjunction with the D.C. amplifier and the mirror
galvanometer. The deflections of the galvanometer,
showing the intensity of the phosphorescent light falling
on the photocathode were recorded at regular intervals
of time.
FIG 3.4

Time (Minutes)
Fig. 36
Log of Time (Seconds)

Log of Phosphorescence Intensity (C.P. units)
4. RESULTS

(a) **Decay Curves**

The afterglow intensity as a function of time was measured for all the phosphors and the plot of the two have a series of decay curves as in fig. 3.4 (a b c d). The curves are similar to those reported by earlier workers for alkaline earth sulphide phosphors. The logarithms of afterglow intensity as function of time is not a straight line, indicating non-exponential nature of the decay. And the graph plotted in logarithms of afterglow intensity against the logarithm of time shows approximately a linear relationship suggesting a hyperbolic decay representable by

\[ I = I_o t^{-b} \quad \ldots \quad \ldots \quad (3.17) \]

where \( b \) is the power to be estimated. To determine the degree of linearity between log \( I \) and log \( t \), correlation coefficient was evaluated.

(b) **Correlation coefficient**

If there is an approximately linear relationship between two variables \( x \) and \( y \) the degree of linearity is given by the relation:

\[
y = \frac{n \sum xy - \sum x \sum y}{\sqrt{n \sum x^2 - (\sum x)^2} \sqrt{n \sum y^2 - (\sum y)^2}} \quad \ldots \quad \ldots (3.18)
\]
where \( n \) is the number of observations and \( Y \) is called the correlation coefficient.

The magnitude of \( Y \) determines the strength of the relationship between the two variables \( x \) and \( y \) and the sign indicates if \( 'y' \) increases or decreases with \( x \). The should satisfy the inequality

\[-1 \leq Y \leq +1\]

In the present case \( y \) represents the logarithm of afterglow intensity and \( 'x' \) represents the logarithm of the time. The value of \( Y \) calculated for all the phosphors are found to be very near unity and negative indicating the linear relationship between \( \log I \) and \( \log t \). The values of \( Y \) are given in the table 3.3.

(c) Decay Constant :-

The decay constant i.e., the power \( 'b' \) of \( t \) in equation (3.13) was calculated by the method of least squares.

If the value of a certain variable to be estimated is given by \( 'y' \) and corresponding curve value of \( 'y' \), the error of estimation is given by \( y - y' \). The error may be positive or negative and might add up to a small value even for a poorly fitting curve. Hence to obtain a good estimate of the parameter, it is necessary that the sum of the squares of this error shall be a minimum. There are number of methods of fitting a curve to a set of points. The method of 'least squares' gives rise to
equations requiring tedious mathematical computations. In the method followed in the present calculations, new variables have been introduced as functions of old variables such that they lead to a more tractable relationship (18).

Taking the log of the equation

\[ I = I_0 \, t^{-b} \]

log \( I \) = log \( I_0 \) - b log \( t \) \( \cdots \) \( \cdots \) (a₁)

If we put \( y = \log I \), \( x = \log t \)

and \( c = \log I_0 \)

the equation (a₁) reduces to

\[ y = -bx + c \quad \cdots \quad \cdots \) (a₂)

Now the problem has been reduced to a problem of fitting a straight line to a set of points in \( xy \) phase, hence is easily solved by the method of least squares. Constants \('b' and 'c' are to be adjusted so that the sum \((y - y')^2\) is a minimum.

Substituting for \( 5 \) and equating to differential of the sum with respect to \('b' and 'c' to zero separately, we obtain two equations from which two constants can be evaluated:

\[ b = \frac{\frac{\sum x}{n} \frac{\sum xy}{n} - \frac{\sum x^2}{n} \frac{\sum xy}{(\sum x)^2}}{n} \quad \cdots \quad \cdots \) (3.19)

and \[ c = \frac{\sum y \frac{\sum x^2}{n} - \frac{\sum x}{n} \frac{\sum xy}{(\sum x)^2}}{n} \quad \cdots \quad \cdots \) (3.20)
The value of 'b' calculated for all the decay curves in the interval from 15 secs. to the time when intensity decayed to the negligibly small value, are given in Table 3.3, along with the correlation coefficients. The value of 'b' comes out to be negative.

**TABLE 3.3**

Correlation coefficients and Decay Constant for CaS : Sm phosphors

<table>
<thead>
<tr>
<th>Sample S. No.</th>
<th>Percentage of flux w.r.t CaS</th>
<th>Decay Const. 'b'</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>0.595</td>
<td>0.82</td>
<td>0.99</td>
</tr>
<tr>
<td>A₂</td>
<td>1.190</td>
<td>0.74</td>
<td>1.00</td>
</tr>
<tr>
<td>A₃</td>
<td>1.780</td>
<td>0.84</td>
<td>1.00</td>
</tr>
<tr>
<td>A₄</td>
<td>2.380</td>
<td>0.76</td>
<td>0.98</td>
</tr>
<tr>
<td>A₅</td>
<td>2.970</td>
<td>0.86</td>
<td>0.99</td>
</tr>
<tr>
<td>B₁</td>
<td>1.190</td>
<td>0.86</td>
<td>1.00</td>
</tr>
<tr>
<td>B₂</td>
<td>1.780</td>
<td>0.86</td>
<td>1.00</td>
</tr>
<tr>
<td>B₃</td>
<td>2.380</td>
<td>0.78</td>
<td>0.99</td>
</tr>
<tr>
<td>B₄</td>
<td>2.970</td>
<td>0.85</td>
<td>1.00</td>
</tr>
<tr>
<td>B₅</td>
<td>3.570</td>
<td>0.82</td>
<td>1.00</td>
</tr>
<tr>
<td>C₁</td>
<td>1.190</td>
<td>0.89</td>
<td>0.99</td>
</tr>
<tr>
<td>C₂</td>
<td>1.780</td>
<td>0.82</td>
<td>0.99</td>
</tr>
<tr>
<td>C₃</td>
<td>2.380</td>
<td>0.90</td>
<td>1.00</td>
</tr>
<tr>
<td>C₄</td>
<td>2.970</td>
<td>0.79</td>
<td>0.99</td>
</tr>
<tr>
<td>C₅</td>
<td>3.570</td>
<td>0.87</td>
<td>0.98</td>
</tr>
</tbody>
</table>
(d) **Variation of Decay Constant with flux:**

Decay constant as a function of flux is given in fig. . The variation of the decay constant is quite unsystematic. The value of the constant varies from 0.72 to 0.90 but for most of the phosphores it lies between 0.82 to 0.87. The average value of the constant may be taken as 0.85. It appears that the value of the decay constant
does not depend upon the flux variation to any marked extent. In general, it is observed that the samples with higher intensity decay more rapidly in the beginning. Also the samples of A, B and C series are of very weak intensity hence they decay in a longer time and gave less number of points to plot.

(e) **Feeling-off of decay curves**:

The probability of the ejection of an electron for a single trap depth 'E' and at temperature T is given by:

\[
p = s \exp \left( -\frac{E}{kT} \right) \quad \text{3(21)}
\]

where \( s \) is the frequency factor, \( k \) = Boltzman constant.

If at any instant \( 'n' \) is the number of traps populated, the rate of ejection will be given by:

\[
\frac{dn}{dt} = -np \quad \text{3(22)}
\]

leading to

\[
n = n_0 \cdot p \cdot \exp \left( -pt \right) \quad \text{3(23)}
\]

\( n_0 \) being the trap population at \( t = 0 \).

Now if the recombination centres are situated to the trapping centres, so that they may be regarded as a single unit and further if retrapping and the radiationless transitions are negligible, the afterglow intensity I at any instant will be given by:

\[
I = \frac{dn}{dt} = n_0 \cdot p \cdot \exp \left( -pt \right) = I_0 \exp \left( -pt \right) \quad \text{3(24)}
\]
Fig. 37 "Peeling off" of decay curves
Fig 3.7 "Peeling off" of Decay Curves
Fig 3.7 Peeling off of Decay Curves
Fig. 4: Peeling off of decay curves
For a distribution of trap depth, Randall and Wilkins have shown a hyperbolic decay. Therefore decay curves were broken into two or more exponentials as has been done by many workers (31-33). The slope of the straight line gives the decay constant for these three exponentials. Then with the help of the equation 3.17, the values of trap depth were evaluated as given in table 3.4. The value of 's' was assumed to be $10^9$/sec. and $T$ as $300^\circ$ K average room temperature during the study.

The trap distribution usually occurs as a collection of approximately "Gaussian group". Each of this group can be assigned a value of trap depth, corresponding to that of its maximum(17). So in the present case the value corresponding to the slowest exponential can be taken as the representative trap depth for this group of traps.

**TABLE 3.4**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percentage of flux w.r.t CaS</th>
<th>TRAP DEPTH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>First exponential</td>
</tr>
<tr>
<td>$A_1$</td>
<td>0.595</td>
<td>0.72</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1.190</td>
<td>0.72</td>
</tr>
<tr>
<td>$A_3$</td>
<td>1.780</td>
<td>0.72</td>
</tr>
<tr>
<td>$A_4$</td>
<td>2.380</td>
<td>0.71</td>
</tr>
<tr>
<td>$A_5$</td>
<td>2.970</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>B₁</td>
<td>B₂</td>
</tr>
<tr>
<td>---</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>1.190</td>
<td>1.780</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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