Chapter 3

Decay of Luminescence
3.1 INTRODUCTION:

In the field of luminescence the decay characteristics of phosphors have been studied extensively in order to understand the kinetics and the energy distribution of the trapping levels. The decay characteristics are determined by measuring the decrease in intensity with time after excitation has ceased. Urbach et al. have determined this by measuring the decrease in time of the residual light sum by observing the infrared stimulation extinction. The decay studies though easy to carry out, are often difficult to interpret since arbitrary assumptions have to be made\(^1\)\(^-\)\(^3\). Saddy\(^4\) has suggested an accurate method for discussing the gaussian shape of the trap distribution curve. Thus, the aim of the study of phosphorescence decay is to obtain information regarding the energy distribution of trap levels and time constant for luminescence process.

3.2 KINETICS OF LUMINESCENCE DECAY:

Becquerel\(^5\) distinguished luminescence decay on the basis of the nature of decay as:

(i) **Exponential decay**: Which is usually attributed to a first order kinetics or monomolecular mechanism.

(ii) **Hyperbolic decay**: Which is attributed to second order kinetics or bimolecular mechanism.

In general, in all cases where the luminescence process is confined to the luminescence centre i.e. the excitation, the trapping and the recombination, all take place in the same centre, a monomolecular
mechanism applies; whereas in the photoconducting phosphors although a bimolecular recombination of electrons and centres may occur the kinetics may be of the first or the second order depending on the particular conditions. Garlick\textsuperscript{6} preferred to divide it on the basis of processes involved in luminescence decay as fluorescence decay and phosphorescence decay.

3.3 FLUORESCENCE DECAY:

In the kinetics of fluorescence, the intermediate process of trapping is not considered.

(i) First Order Kinetics of Fluorescence: In this case, the luminescence is confined to the transition within the luminescence centre only and the monomolecular mechanism applies. Let \( n \) and \( n_0 \) be the number of excited electrons at any instant 't' and \( t = 0 \) (the instant when the excitation source is removed) respectively. Let \( \tau \) be the life time of the excited state. Then the probability of an electron in the excited state to return to the ground state is

\[
P = \frac{1}{\tau}
\]  

...3.1

The decrease in the number of excited electrons is given according to the constant probability law, viz.

\[
dn / n = -Pdt
\]  

...3.2

which gives

\[
n = n_0 \exp (-P t)
\]  

...3.3

Therefore, the luminescence intensity at time 't' is given by

\[
I = -dn / dt = n_0 P \exp (-P t)
\]  

= \( I_0 \exp (-P t) \)  

...3.4

where \( I_0 \) is the intensity at \( t = 0 \). Equation 3.4 represents an
exponential curve and is independent of temperature and excitation conditions and occurs in the systems of quadrupole and multipole character\textsuperscript{7,8}.

(ii) **Second Order Kinetics of Fluorescence** : In the case of photoconducting phosphors an excited electron in the conduction band can recombine with the original centre to give fluorescence. Here the probability of recombination depends not only on excited electron, but also on the available centres. Thus -

\[ \frac{dn}{n} = -Pndt \] \hspace{1cm} \ldots 3.5

On solving, \[ n = n_0 / (1 + n_0 \cdot Pt) \] \hspace{1cm} \ldots 3.6

The luminescence intensity is given by

\[ I = -\frac{dn}{dt} = -Pn^2 \]
\[ = I_0 / (1 + \alpha \cdot t)^2 \] \hspace{1cm} \ldots 3.7

where \( \alpha = (I_0 \cdot P)^\frac{1}{2} = n_0 \cdot P \).

This represents a hyperbolic form of the decay curve which is independent of temperature but depends on the conditions of excitation\textsuperscript{9}.

3.4 **PHOSPHORESCENCE DECAY** :

The order of kinetics involved in phosphorescence decay depend on the spatial location of luminescence centres, electron traps and on the motion of conduction electrons\textsuperscript{3,10}. Accordingly, two different types of kinetics have to be considered.

(i) **First Order Kinetics of Phosphorescence** : In this case, the metastable state is localised very near to the centre (less than \( 10^{-6} \) cm. away).
Only a small movement of electrons occurs between them. Each centre and neighbouring trap can be considered as a single unit giving a constant recombination, constant with time. The trapped electron always recombines with its centre on being released. The resulting decay is governed by an exponential law and thus conforms to the first order kinetics.\(^3\)

In the simplest case, considering the traps of one depth and neglecting retrapping, the probability of the release of an electron from metastable state is given by

\[ P = S \exp\left(-\frac{E}{kT}\right) \quad \text{...3.8} \]

The electrons are released according to the relation,

\[ \frac{dn}{n} = -Pdt = -S \exp\left(-\frac{E}{kT}\right)dt \]

On solving,

\[ n = n_0 \exp\left[-St \exp\left(-\frac{E}{kT}\right)\right] \quad \text{...3.9} \]

where \( n_0 \) is the number of electrons in the metastable state at \( t = 0 \). The resulting luminescence intensity is given by

\[
I = \frac{-dn}{dt} = n_0 \cdot S \exp\left(-\frac{E}{kT}\right) \exp\left[-St \exp\left(-\frac{E}{kT}\right)\right] = I_0 \exp\left[-St \exp\left(-\frac{E}{kT}\right)\right] \quad \text{...3.10}
\]

This equation represents an exponential nature of decay curve and depends on the temperature and the conditions of excitation.

(ii) **Second Order Kinetics of Phosphorescence**: In this case the traps and luminescence centres are spatially independent. The electrons can move over a large distance (\( > 10^{-5} \text{ cm.} \)) and recombine with any of the available centres.\(^3,10\). Thus the decay of luminescence is proportional to the number of empty centres and the number of filled traps. The latter is determined by the rate of emptying of
traps, retrapping and recombination rate. When there is an equilibrium between the conduction electrons and the traps, if we consider the traps of single mean life time, the luminescence intensity as

\[ I = \text{constant} / (t + t_0)^2 \quad \ldots 3.11 \]

where \( t_0 \) is an integration constant equal to the mean life time \( \tau \), of the traps for saturation excitation \(^3\).

This relation also holds good for the distribution of traps if the shallow traps are in equilibrium with deeper ones. Thus, finally the decay law tends towards the inverse square law of the form

\[ I \propto t^2 \quad \ldots 3.12 \]

Deviations from this may be attributed to the simplifying assumptions introduced into calculation\(^2,11\). The result is usually not in agreement with experimental results.

Adirowitch\(^{12}\) suggested a Becquerel type of relation,

\[ I = \text{constant} / (t + t_0)^b \quad \ldots 3.13 \]

where 'b' depends on the ratio '\( \gamma \)' of the capture cross-section of traps and empty centres. The table below gives various values of the index 'b' for different values of the ratio '\( \gamma \)'.

**Table - 3.1**

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>1/3</th>
<th>1/2</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>2.5</td>
<td>2.3</td>
<td>2</td>
<td>1.75</td>
<td>1.63</td>
<td>1.47</td>
<td>1.34</td>
<td>1.01</td>
<td>0.97</td>
<td>0.8</td>
</tr>
</tbody>
</table>

This relation is often a very good description of the decay of a number of phosphors over a considerable range. However, several
objections have been made to Adirowitch's theory, among them being the following:

(a) the values of $\gamma$ are often unacceptable e.g. Coustel, found $b = 0.43$ for ZnS phosphor at liquid air temperature, which necessitates a $\gamma$ value greater than 1000.

(b) in the case of a phosphor containing well separated groups of traps the Becquerel formula is no longer suitable and a 'Kink' is observed in the $\log I$ vs $\log t$ curve. Modifications have been suggested to the bimolecular theory by many workers$^{13,14}$ to develop a general theory of the decay process, taking into account hole migration in the valence band, distribution of trap life time, non-radiative recombination, capture of hole in activator centre and transfer processes.

Medlin$^{15}$ has discussed the phosphorescent decay curves for a number of thermoluminescent crystals including calcite, dolomite, anhydrite, aragonite and magnesite and has pointed out that bimolecular kinetics cannot account for the details of the power law decay as shown in equation 3.13, in luminescent materials except at temperatures well above the thermoluminescent glow-peak.

Fig. 3.1 illustrates the transitions involved in phosphorescent decay of the second order. The constants $\gamma$, $\alpha$ and $\beta$ refer to the rates of emptying filled traps, filling empty traps and recombination with empty luminescent centres respectively. It is reasonable to expect $\alpha$ and $\beta$ to be roughly independent of temperature over the range of a glow peak but $\gamma$ is a strong function of temperature.
FIG. 3.1 ENERGY LEVEL SCHEME FOR SECOND ORDER DECAY (MEDLIN)
\[ Y = S \exp^{-E/kT} \] (equation 3.8) where \( S \) is a frequency factor, \( E \) is the activation energy associated with the trap and \( kT \) is the Boltzmann factor. At temperatures near or below the glow peak \( Y \) is much less than unity for most trapping levels whereas \( \alpha \) and \( \beta \) should be much larger since they are proportional to the probability that an electron will combine with positively charged centres in the crystal. Therefore, at temperatures near the glow peak, the emptying of traps should occur at a much slower rate than either the rate of retrapping or recombination and should thus be the rate determining step for the complete decay process.

Medlin proposed that decay discrepancies can be accounted for by first order kinetics from a gaussian distribution of trapping levels. The specific values of 'b' (which can be unity) was determined by the particulars of the trap distribution and by the experimental conditions.

Alternatively, explanations for the \( t^{-1} \) decay are suggested by studies such as those by Delbecq et al.\(^{16}\) where a temperature dependent \( t^{-1} \) decay law of luminescence from the combination of trapped electrons and holes in KCl:AgCl and KCl:TiCl was ascribed to electron tunneling. A simple model which did not consider the details of the distribution of tunneling centres was used to show that electron-hole recombination through electron tunneling can in principle generate a \( t^{-1} \) decay.\(^{17}\) The approach of using the tunneling phenomenon here is similar to that in other fields such as semiconductor luminescence\(^{18,19}\) and recombination luminescence from irradiated organic molecules in inorganic glasses\(^{20,21}\) where analogous
observations of approximate $t^{-1}$ decays of recombination luminescence have been made and interpreted in terms of electron tunneling.

3.5 SUPERPOSITION THEORIES:

There are two reasons which account for the deviations of the observed decay curves from the theoretical curves, one due to the non-uniform absorption of the exciting and emitting radiation by a finite thickness of the phosphor materials$^{9,22}$ and the other is due to different decay constants which are associated with luminescent centres and traps in the phosphors. The superposition theory is developed on account of the interpretation of distribution of decay constants, according to which only one process (either monomolecular or bimolecular) takes place in a phosphor with more than one value for one of the physical constants$^{23,24}$. The decay is however explained in terms of a superposition of intensities as (i) Monomolecular Superposition theory; and (ii) Bimolecular Superposition theory.

3.5.1 Monomolecular Superposition Theory:

This theory is based on the distribution of traps of different depths which has been supported by many investigators$^{2,25,26}$. The success of this theory is due to Randall and Wilkins$^2$ who have entirely rejected the bimolecular theory to explain complex hyperbolic decay of sulphide phosphors. They obtained the following relation corresponding to different types of distributions.

Absorption of exciting radiation by a luminescence centre raises an electron into the excited state, $F$. It may then either return directly
to the ground state G with emission of luminescence or it may fall into the metastable state M lying just below F as shown in Fig. 3.2. In the latter case a rearrangement of the atoms of the centre takes place and the transition M-G is usually forbidden. Thus electrons in the metastable states can only return to the ground states if they are first raised into the excited states by receiving sufficient thermal energy or by the absorption of long wavelength radiation. For the case of thermal excitation the probability of the transition M-F per unit time is given by

\[ P = S \exp \left( \frac{-E}{kT} \right) \] (equation 3.8) where S is a constant having the dimensions of frequency, E is the energy separation between the levels M and F, k is Boltzmann's constant and T is the absolute temperature. If the transition probability for F-G is high compared with P above, then the phosphorescence emission depends on the rate at which electrons escape from metastable states and will be given as follows.

(i) **Single Trap Depth** :- If 'n' is the number of electrons in traps of depth E, then the intensity I, of phosphorescence due to traps of depth E is given by

\[ I = \frac{dn}{dt} = -n S \exp \left( \frac{-E}{kT} \right) \]  

The solutions of these equations for a fixed temperature gives-

\[ I = n_0 S \exp \left( \frac{-E}{kT} \right) \exp \left[ -St \exp \left( \frac{-E}{kT} \right) \right] \]

or

\[ I_t = I_0 \exp \left[ -St \exp \left( \frac{-E}{kT} \right) \right] \]  

(3.10)

which is the form of the decay of phosphorescence with time, \( n_0 \)

being the number of electrons in M states at the beginning decay. It agrees with that found experimentally for thallium activated KCl by *Bunger* and *Flechsig*.

(ii) **Uniform Distribution of Trap Levels** :- In most phosphors there are trap levels at many different depths. It is required to find
FIG. 3.2 ENERGY STATES FOR FLOURESCENCE AND PHOSPHORESCENCE IN A LUMINESCENCE CENTRE.
the phosphorescence for a phosphor in which there is an equal number of traps of all depths, that is, the trap distribution is uniform. If \( N_E \) is the number of traps between depths \( E \) and \( E + dE \), then the phosphorescence at time \( t \) is given by

\[
I_t = \int_0^\infty N_E S \exp[-E/kT] \exp[-St \exp^{-E/kT}] dE
\]

which on integration gives directly

\[
I_t = nkT/t (1-\exp^{-St})
\]

when \( St \gg 1 \) that is after a microsecond \( \exp^{-St} \) is negligible and

\[
I_t = nkT/t \quad \ldots 3.14
\]

The decay of many phosphors approximates to this law. If there is an equal number of traps at all depths, the phosphorescence is at all times proportional to \( 1/t \).

(iii) Exponential Trap Distribution :- If the electron trap distribution is exponential in form, that is \( N_E = A \exp(-\alpha E) \) as is found for many phosphors, the phosphorescence is given by

\[
I_t = \int_0^\infty A \exp(-\alpha E) S \exp(-E/kT) \exp[-St \exp(-E/kT)]dE
\]

putting \( w = St \exp^{-E/kT} \), the equation then becomes

\[
I_t = (St)^{-kT} \frac{ASkT}{t} \int_0^\infty St \exp{-w} \exp{wkT} dw
\]

As \( St \) is always large (> \( 10^9 \)), the integration may be taken to infinity.

\[
I_t \approx (St)^{-kT} \frac{ASkT}{t} \int_0^\infty \exp{-w} \exp{wkT} dw
\]

\[
I_t \approx \int (S, kT) \beta_t^{-(\alpha kT + 1)}
\]

or \( I_t = \text{constant} \cdot t^{-(\alpha kT + 1)} \)

or \( I_t = \text{constant} / t^{(\alpha kT + 1)} \) \ldots 3.15
(under conditions $St \gg 1$ i.e. $t > 10^{-6}$ second)

It is clear from equations 3.14 and 3.15 that the decay law of phosphorescence for a phosphor with a distribution of trap depths will be little dependent on temperature (V.V. Antonov-Romanovskii: 1935; de Groot: 1939).

Equation 3.15 shows that the phosphorescence decays according to a simple inverse power law. For $\alpha$ zero, the case of a uniform trap distribution, the reciprocal law holds; this result agrees with equation 3.14. When $\alpha kT$ is unity, an inverse square law results.

**The Capture of Electrons by Traps (Retrapping)**

It has been assumed that an electron released from a trap passes immediately to an empty luminescence centre and that retrapping does not occur. The extent of retrapping depends on the relative number of empty traps and empty luminescence centres and the relative probabilities of capture for the two types of centres.

**Growth of Fluorescence with Time**

Consider a phosphor in which all the luminescent centres are filled and all the traps are emptied and let there be more luminescent centres than traps. The phosphor is exposed to a constant exciting radiation. At the first instant of exposure there are no empty luminescence centres and all the excited electrons will be captured by traps. As the traps are filled, the luminescence centres are emptied and are available for capturing electrons, so that fluorescence results. The fluorescence intensity increases with time and reaches an equilibrium value when all
the traps are filled. Garlick and Gibson\textsuperscript{25} have supported Randall and Wilkins\textsuperscript{2} theory by using monomolecular theory and assuming the absence of retrapping. Although, the possibility of these superpositions makes it easier to represent these results, it becomes more difficult to infer the specific mechanism involved in decay\textsuperscript{29}.

3.5.2 Bimolecular Superposition Theory:

This theory is favoured by Antonov-Romanovskii\textsuperscript{30} and Urbach et al.\textsuperscript{1,31}, considering two different superpositions. In one case, if there exists fluctuations in the density of the excited states, the decay is expressed as the sum of terms, each representing a bimolecular decay curve\textsuperscript{24}. In the other case a continuous distribution of traps of different depths is considered and the superposition is represented by a simultaneous system of different equations of bimolecular type each equation representing a particular trap depth.

3.6 METHODS OF MEASUREMENT OF GROWTH & DECAY:

The growth and decay of luminescence intensity after the start and after the end of excitation respectively, offers information about the population and energy distribution of trap levels in addition to the time constants of luminescence processes.

The methods of measurements of luminescence decay at a given temperature, depends on the afterglow intensity as a function of time or the decrease in time of the residual light sum\textsuperscript{1,31}. Methods generally depend on the time involved as follows:
3.6.1 Fast Growth & Decay ($t < 10^{-5}$ sec):

Growth and decay of this order are conveniently measured by (i) phase shift method and (ii) oscillographic method.

(i) **Phase Shift Method**: In the phase shift method, phase angle between a sinusoidally modulated exciting radiation with a frequency of $10^6$ cps or more and the luminescence emission is determined photographically by simple fluorometers or phosphoroscope\textsuperscript{32,33}. The phase of emitted radiation is also sinusoidal and the phase shift with respect to the exciting radiation is given by

$$\tan \psi = \frac{w}{P} \text{ or } \frac{w}{P} (\text{since } P = \frac{1}{\tau})$$

where $\psi$ is the phase shift, $\tau$ is the mean life time of luminescence and $w$ is the angular frequency of modulation. Birks and Little\textsuperscript{34} have measured the decay period using air discharge modulated light source ($\tan \psi = 2 \frac{w}{P} = 2 \frac{w}{\tau}$) and the emission was detected by a photomultiplier tube and the phase shift by electrical circuit techniques\textsuperscript{35}. This method has been used to determine luminescence decay time of $10^{-9}$ sec with high accuracy\textsuperscript{36,37}

(ii) **Oscillographic Method**: The oscillographic method is the most desirable since it provides a direct presentation of the decay curve. Matossi and Nudelman\textsuperscript{38} have further improved the method by using coaxial cables suitable for the transmission of very short pulses and of "color shifters" which convert U.V. luminescence to a spectral region more closely matching the spectral response of the detectors. In this method, the luminescence emission, excited by a pulse source is received by the P.M. tube and the output of the tube is fed to
an oscilloscope in which decay curve is observed or can be photographed.

3.6.2 Slow Decay \((t > 10^{-5} \text{ sec})\):

(i) **Phosphoroscope Technique** :- The first phosphoroscope invented by Becquerel\(^{39}\), has been used extensively with modifications to measure the decay time of the order of \(10^{-4}\) sec. Lenard made some improvements on it and the principle of phosphoroscope was modified by Wood\(^{40}\). This has been further improved by Randall & Wilkins\(^{2}\), in which the phosphor was coated uniformly in the form of an annular along the periphery of a disc rotated by a d.c. motor at constant speed. The exciting source and detector unit can be arranged at any desired position and the intensity of the phosphorescence decay observed at different times after excitation with the help of a photocell. By replacing the photocell with a photographic arrangement the decay may also be studied densitometrically. The main advantage of this method over other methods is that the color change during decay process can be observed directly\(^{41}\).

(ii) **Oscilloscope Technique** :- In this method luminescence excited by a pulse source is received by P.M. tube and its output after proper amplification fed to an oscilloscope or sensitive galvanometer\(^{9,42}\). For recording exponential curves of a long decay an oscilloscope was modified to have a linear base and the logarithm of the measured signal was taken. The experimental decays have also been measured by comparing the decay characteristics of a phosphor with the discharge characteristics of a condenser in an R-C circuit using
appropriate trigerring of the oscilloscope$^{43}$. Similarly using a self recording P.M. tube connected to a galvanometer, the hyperbolic or power law decay of very long duration also can be measured. Another, useful technique$^{44}$ consists of pulsing the P.M. power supply, thus avoiding overloading and at the same time obtaining the zero reference level as part of the oscilloscope trace. For exponentially decaying phosphors, the response of a phosphor to sinusoidal excitation can be used to determine decay times$^{45}$.

3.6.3 Long Period Phosphorescence Technique:

Long period phosphorescence decay measurements are comparatively easier than those of short period. Experimental arrangements used by many workers$^{23,43,46}$ mainly consist of an exciting light source with a mechanical shutter to cut-off excitation. The phosphorescence is measured with a photoelectric multiplier connected to a galvanometer or to an amplifier and pen recorder system.

The longer duration of phosphorescence decay with increased excitation dose is related essentially to a bimolecular kinetics operating in the sample. An increase in excitation time gives a higher initial intensity $I_0^{47}$. If the decay were monomolecular the time required for reaching half of the maximum intensity should be the same.

The decay rate increases with the operating temperature. This is consistent with the theory where it is assumed that the rate of release of trapped electrons is increased$^{48}$. 
3.7 PRESENT METHOD:

(i) **Experimental Arrangement** :- The present arrangement involves the measurement of long period decay of phosphorescence (duration > 2 seconds). The source of excitation was X-rays (X-ray machine type 11074 operated at 32 kV and 12 mA). A photomultiplier Model No. Eu 701-30 was coupled with the phosphor holder assembly. The output of the P.M. tube was connected with the D.C. Microvoltmeter Model No. PP 9004 (Philips).

**Phosphor Holder Assembly** :- It (Fig. 3.3) consists of a brass cylinder \( (P_1, P_2) \). Two metal tubes of lead, were fitted into the openings of the cylinder at right angles to each other \( (O_1, O_2) \). The top of the cylinder consists of an aluminium plate \( (A) \) at the centre of which a sample mounting plate is fixed. The plate is essentially a rectangular brass sheet \( (S) \) and can be raised or lowered and can also be rotated by means of a Knob \( (K) \) and its position is indicated by a pointer \( (l) \). The plate is provided with a circular cavity \( (C) \) in the centre to fit a removable brass sample holder with a fine hole to hold a thermocouple \( (T) \). A heating element of Kanthal strip \( (H) \) was attached behind the sample holder to maintain it at different temperatures. A collimated beam of X-rays through the slit \( (SL) \) is allowed to fall on the sample through the tube \( (A_1, A_2) \) and the emitted luminescence radiation emerges through another tube. \( T_1, T_2 \) and \( T_3, T_4 \) are terminals for heater and thermocouple respectively.

(ii) **Experimental Procedure** :- The phosphor was packed into the cavity of the sample holder and kept inside the assembly and was excited
FIG. 3.3 PHOSPHOR SAMPLE HOLDER
by X-rays for 5 minutes. The saturation time for excitation was
determined by trial, which came out to be 4 minutes. Hence, each
sample was excited for 5 minutes. The excitation was cut-off, the
shutter of the P.M. tube being kept open. The decaying of lumine-
scence intensity was then recorded as a function of time, every
2 seconds, till the intensity reached an undetectable level. The
same amount of phosphor was taken every time. The distance
between the phosphor cavity and X-ray window was kept constant
throughout the experiment. Two sets of observations were taken
for each sample under similar conditions. They were found to be
consistent.

All the measurements were made at room temperature i.e.
at 308 K. Decay measurements were also carried out at a higher
temperature. The temperature chosen was 383 K which was the
average temperature corresponding to the second TL peak.

3.8 RESULTS:

The decay curves were obtained for all the samples. Initially,
the decay of the phosphors was found to be rapid and subsequently it
decays slowly till the intensity becomes negligible (Figs. 3.4-3.6).

Investigation of decay may be done on the basis of a power
law corresponding to the general equation

\[ I = I_0 \cdot t^b \] ...

(neglecting the sign of 'b' for the present)

Taking logarithms on both side, we get

\[ \log I = b \log t + \log I_0 \]
FIG. 3.4 DECAY CURVES (AT 308 K) (Simple graph)
INDEX

a - Ce (10%)

b - Ce (10%)

c - Ce (10%) Tb (10%)

d - Ce (10%) Tb (10%)

FIG. 3.5 DECAY CURVES (AT 308 K) (Simple graph)
FIG. 3.6 DECAY CURVES (AT 383 K) (Simple graph)
which has the form \( y = mx + c \)

The relation between \( \log I \) and \( \log t \) for some of the representative samples are shown in fig. 3.7. The curves were found to be fairly linear suggesting a power law decay.

To study quantitatively, the degree of linearity, the correlation coefficient, \( r \) was calculated by using the relation \(^{49}\)

\[
\begin{align*}
    r &= \frac{n \sum xy - \sum x \sum y}{\sqrt{n \sum x^2 - (\sum x)^2} \sqrt{n \sum y^2 - (\sum y)^2}} \quad (3.19)
\end{align*}
\]

where \( x = \log t; \ y = \log I; \) and \( n \) is the number of observations.

The magnitude of \( r \) came out to be nearly unity showing a linear relationship between \( x \) and \( y \) (Table 3.1). The sign of \( r \) is negative because \( \log I \) decreases as \( \log t \) increases.

The nature of the decay curves was also studied by plotting \( \log I \) as a function of time (Figs. 3.8-3.10). Non-linear curves were obtained for all the samples. Hence, a simple exponential nature of decay may be ruled out.

**Decay Constant:**

According to the monomolecular superposition theory of Randall & Wilkins\(^2\) a power law decay results, if a distribution in trap-depth exists. The form of the decay is then hyperbolic

\[
    l_t = l_0 t^b \quad (3.17)
\]

where \( l_0 \) is the intensity at \( t = t_0 \), and 'b' is the decay constant. The value of this constant given by the slope of the \( \log I \) versus \( \log t \) is calculated by the method of least squares\(^{49,50}\).
FIG. 3.7 DECAY CURVES (AT 308 K)

INDEX
1 - Tb (10\%)
2 - Tb (10^{-2}\%)
3 - Tb (10^{-3}\%)
4 - Tb (10^{-4}\%)

INDEX
1 - Tb (10\%) Ce (10\%)
2 - Tb (10^{-2}\%) Ce (10^{-5}\%)
3 - Tb (10\%) Ce (10^{-4}\%)
4 - Tb (10\%) Ce (10^{-3}\%)

INTENSITY IN ARB. UNITS

TIME IN SECONDS

10^2

10^1

1

10^2

10^1

1

10^{12}

10^1

1

FIG. 3.7 DECAY CURVES (AT 308 K)
FIG. 3.7 DECAY CURVES (AT 308 K)

INDEX
1 - Ce (10%)
2 - Ce (10%) Tb (10%)
3 - Ce (10%) Tb (10%)
4 - Ce (10%) Tb (10%)

INTENSITY IN ARB. UNITS

TIME IN SECONDS

FIG. 3.7 DECAY CURVES (AT 308 K)
FIG. 3.8 "PEELING-OFF" OF THE DECAY CURVES (AT 308K)
FIG. 3.8 "PEELING-OFF" OF THE DECAY CURVES (AT 308 K)
FIG. 3.8 "PEELING-OFF" OF THE DECAY CURVES (AT 308 K)
Fig. 3.9 "Peeling-Off" of the Decay Curves (at 308 K)
FIG. 3.9 "PEELING-OFF" OF THE DECAY CURVES (AT 308 K)
FIG. 3.9 "PEELING-OFF" OF THE DECAY CURVES (AT 308 K)
FIG. 3.10 "PEELING-OFF" OF THE DECAY CURVES (AT 383K)
FIG. 3.10 "PEELING-OFF" OF THE DECAY CURVES (AT 383 K)
FIG. 3.10 "PEELING-OFF" OF THE DECAY CURVES (AT 383 K)
FIG. 3.10 "PEELING-OFF" OF THE DECAY CURVES (AT 383 K)
\[
b = \frac{\varepsilon x \cdot \varepsilon y - n \varepsilon x y}{(\varepsilon x)^2 - n \varepsilon x^2}
\]...

The value of 'b' calculated for all the samples are given in Table 3.1. There is no significant variation in the value of 'b' with activator or with concentration. The value varies from 0.59 to 0.81, the sign of 'b' being negative.

\[l_t = l_0 t^{-b}
\]...

Assuming monomolecular superposition theory of Randall & Wilkins, the decay curves were 'peeled off' according to the procedure suggested by Bube. In every case, the curves could be analysed in terms of three exponentials. For each straight line component using the formula given below, the trap-depths were calculated.

\[E = 2.3026 k T [\log_{10} S + \log_{10} t - \log_{10} \{2.3026 (\log_{10} I_0 - \log 1)\}]
\]...

(derived from equation 3.4 & 3.8)

The value of S was taken to be 10^9 per sec, a value used by earlier workers in the case of silicate phosphors. The trap-depths of different phosphors involved at 308 K lie between 0.57 eV and 0.68 eV and are shown in Table 3.2.

The decay curves obtained at 383 K showed essentially the same nature as the ones at room temperature i.e. at 308 K, although the intensity falls to negligible values much faster. It was possible to analyse these curves also by the 'peeling off' procedure and the trap-depths corresponding to the three components were calculated as before. The trap-depths involved in this case lie between 0.68 eV and 0.86 eV and are shown in Table 3.3.
Table - 3.1
Initial Intensity, Decay Constant and Correlation Coefficient

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc(3^+) of Tb(3^+) mole %</th>
<th>Conc(3^+) of Ce(3^+) mole %</th>
<th>Initial Intensity (Arb.Units)</th>
<th>Decay Constant</th>
<th>Correlation Coefficient *</th>
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<tbody>
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<td></td>
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<td>101.2</td>
<td>0.72</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>((10^{-2}))</td>
<td>-</td>
<td>101.8</td>
<td>0.65</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>((10^{-3}))</td>
<td>-</td>
<td>97.3</td>
<td>0.72</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>((10^{-4}))</td>
<td>-</td>
<td>77.0</td>
<td>0.66</td>
<td>1.00</td>
</tr>
<tr>
<td>RVC Series</td>
<td>-</td>
<td>(1)</td>
<td>98.1</td>
<td>0.59</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>((10^{-1}))</td>
<td>100.8</td>
<td>0.76</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>((10^{-2}))</td>
<td>101.8</td>
<td>0.74</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>((10^{-3}))</td>
<td>98.3</td>
<td>0.66</td>
<td>1.00</td>
</tr>
<tr>
<td>RVTC Series</td>
<td>((10^{-2}))</td>
<td>((10^{-6}))</td>
<td>102.7</td>
<td>0.62</td>
<td>1.00</td>
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<tr>
<td>(Optimum conc.)</td>
<td>((10^{-2}))</td>
<td>((10^{-5}))</td>
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<td>0.70</td>
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<tr>
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<td>((10^{-4}))</td>
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</tr>
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<td>((10^{-3}))</td>
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<td>((10^{-2}))</td>
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<td>1.00</td>
</tr>
<tr>
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<td>((10^{-6}))</td>
<td>((10^{-2}))</td>
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<tr>
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<td>((10^{-2}))</td>
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<tr>
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<td>((10^{-2}))</td>
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<td>((10^{-6}))</td>
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<td>0.73</td>
<td>1.00</td>
</tr>
<tr>
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<td>((10^{-5}))</td>
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</tr>
<tr>
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<td>((10^{-4}))</td>
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<td>1.00</td>
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<td>1.00</td>
</tr>
<tr>
<td></td>
<td>((10^{-4}))</td>
<td>((10^{-3}))</td>
<td>99.1</td>
<td>0.61</td>
<td>1.00</td>
</tr>
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* Results in these columns are with a negative sign.
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<th>Sample No.</th>
<th>Conc. of Tb³⁺ (mole %)</th>
<th>Conc. of Ce³⁺ (mole %)</th>
<th>Slowest exponential E₁ (eV)</th>
<th>Middle exponential E₂ (eV)</th>
<th>Fast exponential E₃ (eV)</th>
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</thead>
<tbody>
<tr>
<td>RVT Series</td>
<td>(1)</td>
<td>-</td>
<td>0.65</td>
<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>(10⁻¹)</td>
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<td>0.64</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>(10⁻²)</td>
<td>-</td>
<td>0.68</td>
<td>0.64</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>(10⁻³)</td>
<td>-</td>
<td>0.65</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>(10⁻⁴)</td>
<td>-</td>
<td>0.65</td>
<td>0.63</td>
<td>0.59</td>
</tr>
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<td>RVC Series</td>
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</tr>
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<td>(10⁻¹)</td>
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<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
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<td>-</td>
<td>(10⁻²)</td>
<td>0.67</td>
<td>0.63</td>
<td>0.59</td>
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<td>(10⁻³)</td>
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<td>0.62</td>
<td>0.59</td>
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<tr>
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<td>0.59</td>
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<tr>
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<td>(10⁻⁴)</td>
<td>0.66</td>
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<tr>
<td></td>
<td>(10⁻²)</td>
<td>(10⁻³)</td>
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<tr>
<td>RVCT Series</td>
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<td>(10⁻⁷)</td>
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<td>0.61</td>
<td>0.58</td>
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<td>(Below opti-</td>
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<td>(10⁻⁶)</td>
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<td>0.63</td>
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<td>RVCT Series</td>
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<td>(10⁻³)</td>
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<td>0.61</td>
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<td>(10⁻³)</td>
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Activation Energies as obtained from the analysis of 'peeling off' of the decay curves (at 383 K).

<table>
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<tr>
<th>Sample No.</th>
<th>Conc. of Tb$^{3+}$ mole %</th>
<th>Conc. of Ce$^{3+}$ mole %</th>
<th>Slowest exponential $E_1$ (eV)</th>
<th>Middle exponential $E_2$ (eV)</th>
<th>Fast exponential $E_3$ (eV)</th>
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</thead>
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<tr>
<td>RVT Series</td>
<td>(1)</td>
<td>-</td>
<td>0.82</td>
<td>0.74</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>$(10^{-1})$</td>
<td>-</td>
<td>0.83</td>
<td>0.77</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>$(10^{-2})$</td>
<td>-</td>
<td>0.83</td>
<td>0.74</td>
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<tr>
<td></td>
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<tr>
<td>RVC Series</td>
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<td>0.73</td>
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<tr>
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<td>$(10^{-4})$</td>
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<td>0.83</td>
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### REFERENCES

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