CHAPTER III

DECAY
CHAPTER III

DECA Y

1. Introduction. One of the aims of studies of the luminescent materials is the identification of the luminescence centers and trapping states and their energy levels. A good deal of information for this purpose can be obtained from measurements of decay characteristics. Most phosphors contain traps with depths distributed over a wide range, and the form of this distribution will determine the overall shape of the decay curve. Therefore, the observed decay characteristics of a particular phosphor may be related to the population and energy distribution of trap levels in that phosphor (1, 2).

Since the time of Becquerel (3), it has been customary to distinguish between exponential decay due to monomolecular mechanism and hyperbolic decay due to bimolecular mechanism. Therefore, to develop theoretical models of decay mechanism, a study of kinetics of recombination of electrons and empty luminescence centers is of considerable importance (4, 5). When the luminescence process is confined to the center itself, then the excitation, the trapping and the recombination all take place in the same center and in all cases there applies a monomolecular mechanism. On the other hand, in photosconducting phosphors there occurs in all cases a bimolecular recombination
of electrons and empty centers, but the kinetics may be of first
or of second order depending on the particular conditions.

2. Kinetics of luminescence. The luminescence decay may
be divided into "Fluorescence
decay" and "Phosphorescence
decay" according to the mechanism involved in the process \( (6) \).

(A) Fluorescence decay. In the kinetics of
fluorescence we do not
consider the intermediate process of trapping.

(a) First order kinetics of fluorescence.

When luminescence is due to the transitions
within the luminescence center, the monomolecular mechanism
applies.

Let the instant at which the exciting source is removed
be noted by \( t = 0 \). Suppose at \( t = 0 \), the number of electrons
in the excited state is \( n_0 \) and at any instant the number is
given by \( n \). Let \( \tau \) be the life time of an excited state.
Then the probability for an electron in the excited state to
return to the ground state is given by

\[
p = \frac{1}{\tau} \quad \text{........... (3.1)}
\]

The number of excited electrons \( n \) decreases according to the
probability law,

\[
\frac{dn}{n} = -p \, dt \quad \text{......... (3.2)}
\]

which gives on solving,

\[
n = n_0 \exp(-pt) \quad \text{......... (3.3)}
\]

the luminescence intensity,

\[
I(t) = -\frac{dn}{dt} = p \, n_0 \exp(-pt) \cdot \frac{dn_0}{dt} = I_0 \exp(-pt) \quad \text{......... (3.4)}
\]

where \( I_0 \) and \( I(t) \) are the intensities at the time when excitation ceases and at time \( t \) afterwards.

The decay curve is thus exponential and is independent of temperature and conditions of excitation.

(b) Second order kinetics of fluorescence.

An electron raised into conduction band in the case of a photoconducting phosphor can recombine with its original center giving fluorescence. In this case second order kinetics apply and the probability of recombination is proportional to the number of available centers as well. Thus,

\[
\frac{dn}{n} = -p \, n_0 \, dt \quad \text{......... (3.5)}
\]

\[
n = \frac{n_0}{1 + n_0 \, pt} \quad \text{......... (3.6)}
\]
The luminescence intensity is given by

\[ I(t) = - \frac{dn}{dt} = \frac{p n_0^2}{(1 + n_0 pt)^2} \]

\[ = \frac{I_0}{(1 + at)^2} \]

\[ ........... (3.7) \]

where \( a = \sqrt{I_0 p} = n_0 p \)

\[ ........... (3.8) \]

The decay curve is thus hyperbolic. The form of the curve is independent of temperature but depends on the conditions of excitation (7, 8).

(8) **Kinetics of Phosphorescence.** The order of kinetics involved in phosphorescence emission depends on the spatial location of luminescence centers and electron traps with respect to each other and also on the motion of conduction electrons (4, 9).

Accordingly, two different types of kinetics have to be considered.

(a) **First order kinetics of Phosphorescence** (1).

Phosphorescence decay mechanism conforms to first order kinetics, if

(1) the trap is a metastable state of the luminescence center at a position \( E \) in energy below the excited state of the center (10);
(ii) the electron after being excited is trapped in a trapping state which is localized very near to the center (less than $10^{-6}$ cm.). The trapped electron after being released always recombines with the same center from which it has been excited. Thus, each trap and its neighboring center is considered as an independent entity giving a constant recombination with time and the process conforms to first order kinetics (4).

In the simplest (1) case let us consider that metastable states or traps (as the case may be) of only one depth exist. When the exciting source is removed at the instant $t = 0$, a certain number of electrons $n_0$ will be in the metastable states or traps. The probability per second for the release of electrons from the metastable state or trap is

$$p = s e^{-\frac{E}{kT}} \quad \ldots \ldots \ldots \ldots (3.9)$$

The terms involved have already been explained in Chapter 1.

Neglecting retrapping, electrons are released according to the relation

$$\frac{dn}{n} = -pd\tau = -s e^{-\frac{E}{kT}} \tau \quad \ldots \ldots \ldots \ldots (3.10)$$

The intensity of luminescence is given by

$$I(t) = -\frac{dn}{dt} = n_0 s e^{-\frac{E}{kT}} \exp \left[-s e^{-\frac{E}{kT}}\right] \ldots \ldots \ldots \ldots (3.11)$$
The decay curve is exponential. The form of the curve depends on temperature and conditions of excitation.

(b) **Effect of retrapping.**

In the above theoretical treatment, retrapping was considered as an ineffective process. However, a number of workers (11 - 16) have found evidences of retrapping. In order to include the possibility of retrapping the rate of trap emptying must be multiplied by the ratio of the capture probability for recombination centers to the sum of capture probabilities for recombination centers and empty traps. Garlick and Gibson (15) have assumed equal probabilities for retrapping and recombination of a conduction electron. They have shown that for traps of one depth, the retrapping causes a fundamental change in the form of decay from exponential to hyperbolic. A more elaborate treatment (considering unequal coefficients for centers and traps) has been given by Klasens and Wise (16).

(c) **Second order kinetics of Phosphorescence.**

The second order kinetics apply to phosphorescence emission if the traps and luminescent centers are separate entities independent of each other. The electron displacement which occur during recombination or trapping is large enough (i.e. $10^{-5}$ cm.) and the free electrons in the conduction band may recombine with any of the available centers (4,9
Thus, the decay of emission for this type of kinetics is proportional to the number of empty luminescence centers and to the number of filled traps, the latter being determined by the rate at which the traps are emptied and retrapping and recombination takes place.

Considering traps of single mean life $\gamma$ and assuming equal electron capture probabilities for empty centers and traps, the phosphorescence emission decays according to the relation (4),

$$ I = \frac{\text{Const.}}{(t + t_0)^2} \quad \cdots \cdots \quad (3.12) $$

where $t_0$ is the integration constant equal to the mean life time of the traps for saturation excitation. This relation also holds good for the distribution of trap depths, provided equilibrium conditions between shallow and deep traps are assumed.

However, considering traps of single mean life time and taking unequal electron capture cross sections for traps and luminescence centers, Adirovitch (17, 18) arrived at an approximate relation of the form

$$ I = \frac{\text{Const.}}{(t + t_0)^b} \quad \cdots \cdots \quad (3.13) $$

where $b$ depends on the ratio $r$ of the capture cross sections of the traps to the centers. However, most of the decay
curves conform to this type of relation, but sometimes it leads to very high values of 'r' which are not acceptable. In addition to this, the equation is not valid where well separated groups of traps exist.

The bimolecular theory of phosphorescence decay has been elaborated by Schon (19), Broser-Warinsky (20) and Urbach (21) who, while approaching the problem have considered the distribution of trap life times, nonradiative recombination, positive hole migration in the valence band, capture of holes in the activator centers and transfer processes.

3. Superposition theories. There are two reasons which account for the deviation of the observed decay curves from the theoretical models. One is the nonuniform absorption of the exciting and emitted radiation by a finite thickness of the phosphor materials (22, 23). The absorption effect changes the bimolecular decay, at least in its large stages, into a curve closely resembling a power law with an exponent smaller than two (24, 26). The other reason is that in many phosphors different decay constants are associated with luminescence centers and traps and the overall decay is interpreted by assuming suitable distribution of decay constants (5, 26).

These viewpoints have led to the development of superposition theories according to which in one phosphor only
one process occurs, either monomolecular or bimolecular, but for
either of the processes the physical constants involved may have
a suitable distribution of values. The observed decay is thus
interpreted in terms of superposition of intensities and each
intensity component varies with time according to monomolecular
or bimolecular law (9).

(A) Bimolecular superposition theory.  Antonov-Romanovsky (27)
and Urbach (2) favoured the bimolecular superposition theory. However, in this
case two different types of superpositions must be considered
(5, 28). In one case, if there exist fluctuations in the
density of excited states, it is appropriate to form a sum of
terms, each representing a bimolecular decay curve. In the other
case, if there occurs distribution of traps of different depths,
the superposition is represented by a simultaneous system of
differential equations of the bimolecular type, each equation
representing a particular trap depth (29).

(B) Monomolecular superposition theory. Several workers in
the field of
luminescence have supported the monomolecular superposition theory
based on the distribution of trap depths (1, 15, 30–33).
Randall and Wilkins (1) have entirely rejected the bimolecular
theory and have applied monomolecular type of phosphorescence decay
to the more complex hyperbolic decay of sulphide phosphors. They
have assumed the thermal release of trapped electrons as the main rate determining process and considering no retrapping of the released electrons, derived the decay laws for several complex distribution of traps.

4. Methods of decay measurement.

(A) Fast decay \( t < 10^{-5} \) sec. \( \text{The measurement of luminescence life times down to microseconds have been performed using the following methods.} \)

(a) Oscilloscope method.

This method may be used to measure luminescence life times of the order of \( 10^{-9} \) seconds \( (34, 35) \). The luminescence emission excited by a pulsed source is received by a photomultiplier tube which is also pulsed to yield a high gain. The voltage output from the tube is fed to an oscilloscope and the resulting decay curve is photographed. The development of coaxial cables for transmitting very short pulses and colour matchers have improved the method to a great extent \( (34) \).

(b) Phase shift methods.

The life time of luminescence is also determined by exciting the luminescent substance with light modulated at high frequency and measuring the phase angle between
the exciting radiation and resulting emission (36). To modulate
the exciting radiation, different workers have used different types
of fluorometers (37–42). The phase angle between excitation
and emission is connected to the mean life time \( \tau \) of luminescence
by an equation (43, 44),

\[
\tan \phi = \omega \tau \tag{3.14}
\]

where \( \omega \) is the angular frequency of modulation. This phase shift
is determined by photographing the exciting radiation and the
luminescence bands separately and measuring the displacement
between the two.

In the method used by Birks and Little (45),
a modulated light source is used. In this case the phase shift is
given by

\[
\tan \phi = 2\omega \tau \tag{3.15}
\]

The emission is detected by a photomultiplier. The integrated
current output from the tube is presented on a recording
galvanometer or potentiometer and the phase shift as such is
determined by electrical circuit techniques (46, 47).

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

(a) \textbf{Becquerel's phosphorescope.}

Luminescence life times of the order of \( 10^{-4} \) seconds could be measured using improved designs of earliest known
Becquerel's phosphorescope in conjunction with photomultipliers and
oscilloscopes (36, 48).

(b) Rotating disc phosphoroscope.

In the rotating disc phosphoroscope (49) due to R.W. Wood, the phosphor is coated uniformly in the form of an annulus ring around the surface of a rotating disc. The excitation source is kept at some fixed position. By changing the angular position of the detector with respect to excitation source, the emission intensity is observed at various time intervals after the excitation. The emission can be measured by photographic recording system and the decay curve can be obtained by measuring the relative intensity of the photographic record of the spectral system with the help of densitometer. The main advantage of this method over other methods is that the colour changes during decay process can be observed directly (50).

(c) Oscilloscope methods.

The luminescence excited by a pulsed source is received by the photomultiplier. The output voltage corresponding to emission after proper amplification is presented to an oscilloscope (9, 51, 52). The sweep speed is adjusted so that the entire decay curve is seen on the scope. For recording exponential curves of long decays, oscillographs with a linear time base and a means for taking the logarithms of the measured
Fig. 3.1 Decay Apparatus.
signal have been used (53).

A rather instructive method for measuring the exponential decay of a phosphor is by comparing its decay characteristics with the discharge characteristics of a condenser in an R.C. circuit using an automatic triggered oscilloscope (54). By suitably adjusting the circuit elements of the R - C circuit its trace can be matched with that produced by the phosphor. The R - C trace and the luminescence trace can also be mixed in opposite phase to produce disappearance of the trace (55). The time constant is then calculated from the circuit components.

(d) Other methods.

The decay time of long persisting phosphors are measured by photomultiplier and galvanometer. The exciting radiation is cut off by means of mechanical shutters (25, 56).

5. Present method.

(A) Decay apparatus. The apparatus used in the present investigation essentially consists of a metal cylinder A whose lower end is fixed on a rigid base C (Fig. 3.1). The cylinder is provided with side openings O1 and O2 with their axes lying on the same horizontal line. Two horizontal metal tubes D and E are mounted against the openings O1 and O2. The source of excitation is mounted inside the tube D and the detector of
emission is fitted to the tube E. A hollow ebonite cylinder B (coaxial to the outer cylinder and just fitting into it) is suspended inside the outer cylinder by means of a circular plate H. The plate H is screwed to the inner cylinder in such a way that the rotation of H is accompanied with the rotation of inner cylinder. The inner cylinder is also provided with a side opening O₃ and the axes of O₁, O₂ and O₃ coincide.

Two pieces of springs S₁ and S₂ are attached to the holder of the plate H. These are stretched horizontally by means of two rigid vertical stands G₁ and G₂ fused to the tubes D and E respectively. The specimen tube P packed with the phosphor under investigation is held vertically downward inside the ebonite cylinder by means of a cork which in turn is attached to the lower surface of the plate H. The tube P also passes through a hollow ebonite cylinder F fitted horizontally against the opening O₃. This helps to keep the experimental phosphor in proper position.

To begin with, the openings O₁ and O₃ are brought to face each other and the phosphor is excited. The apparatus is held in position by means of a trigger (not shown in the figure). On releasing the trigger, the inner cylinder rotates through 180° due to the couple exerted by the springs S₁ and S₂ and the opening O₃ now faces the detector of emission. A stopper S is used to ensure proper alignment. To minimize the displacement of phosphor particles during release,
Fig. 3.2  Ferrand Electron Photomultiplier.

FARRAND ELECTRON PHOTOMULTIPLIER

A: DETECTOR
B: POWER SUPPLY
C: RUBICON GALVANOMETER
the stopper is padded with rubber.

( B ) Source of excitation. The source of excitation was a 18 watt, 6 volts tungsten lamp operated by a 6 volts accumulator. The voltage was stabilized by floating charge arrangement. The current during excitation was maintained constant using an ammeter and a rheostat in the circuit.

( C ) Electron multiplier photometer (Fig. 3.2). The phosphorescence emission intensity was recorded with the help of Ferrand electron multiplier photometer. The essentials of the photometer are,

1. Detector unit,
2. Power supply control and

(a) Detector unit.

The detector was 1P21 photomultiplier tube, the spectral response curve of which is shown in Fig. 3.3. The curve has a peak at about 4720 Å. This is also the approximate region of the luminescence emission in the present phosphors. The current amplification factor of the photometer is $2 \times 10^6$ and the current is a linear function of light intensity up to an out put of 150 microamperes.

(b) Power supply control.

The circuit diagram of the power supply and
Fig. 3.3 Spectral Response Curve of 1P21.
Fig. 3.4  Power Supply Circuit arrangement.
control devices is depicted in Fig. 3.4. It consists of 30 batteries each of 30 volts. A separate battery of 1.5 volts is provided for balancing the dark current of the phototube. To control the sensitivity, coarse and fine sensitivity control devices are also provided.

(c) **Galvanometer.**

The current output corresponding to luminescence emission was passed through a Rubicon galvanometer which has a built-in lamp and scale arrangement. The galvanometer has a resistance of 4830 ohms and sensitivity of the order of 0.0013 amp/mm. Coarse and fine adjusting devices are provided to adjust the position of light spot on the scale. The connecting cable has a 6V in-line transformer.

(D) **Setting up of the photomultiplier.** The phototube was screwed to the tube D of the decay apparatus. The power supply unit and galvanometer were connected to the phototube as shown in Fig. 3.2. By loosening the collar of the phototube the height of the cathode was properly adjusted. Keeping the sensitivity knobs at some convenient position, the phototube was adjusted for peak response. To balance the dark current, the shutter of the phototube was kept at closed position and the sensitivity knobs were turned to read full sensitivity. The zero button at the top of the power supply unit was pressed gently and the galvanometer deflection was recorded.
Releasing the zero button, the coarse and fine dark current knobs were adjusted to produce the same deflection. The photometer was thus balanced for dark current. The sensitivity knobs were then turned to read the zero sensitivity and the light spot on the galvanometer scale was brought to zero position by coarse and fine zero adjusting screws. Dark current was again checked by pressing the zero button. The sensitivity range of the apparatus was then adjusted as required.

(E) Experimental procedure. The phosphor under investigation was packed in a test tube and mounted in the decay apparatus as has been described earlier. The time of excitation to reach equilibrium was determined by varying the excitation time from 30 seconds to 5 minutes in regular steps. During this process all other parameters were kept constant. The optimum time was found to be 2 minutes and to ensure complete saturation, every phosphor was excited for three minutes. The phosphorescence intensity in arbitrary units was measured over a reasonably long time so that the particular traps involved were all emptied. Three sets of observations were taken for each phosphor under identical conditions. These were found to be fairly constant.

6. Results.

(A) Decay curves. The decay measurements were made at room temperature

(T = 308°K). The phosphorescence intensity in arbitrary units
Fig. 3.5 (a) and (b) Decay curves.
was plotted against time on a linear intensity time scale. The curves thus obtained are shown in Figs. 3.5(a) to 3.5 (f).

The general trend of the curves resembles with those obtained by earlier investigators. The area under a decay curve or 'light sum' is a measure of the trap concentration. The form of the decay curve is directly related to the rate of change of the phosphorescence intensity \( I \). If the rate of change of \( I \) with respect to time \( t \) is proportional to \( I \), the decay curve is exponential and may be represented by

\[
I = I_0 e^{bt} \quad \ldots \ldots \ (3.16)
\]

or

\[
\log_e I = \log_e I_0 + bt \quad \ldots \ldots \ (3.17)
\]

Thus in exponential decay, \( \log I \) and \( t \) are linearly related. On the other hand, in the case of powerlaw (hyperbolic) decay, the phosphorescence intensity \( I \) decreases rapidly for small values of \( t \) and slowly for larger values of \( t \) and the rate of change of phosphorescence intensity is proportional to \( t^b \). This type of decay may be represented by

\[
I = I_0 t^b \quad \ldots \ldots \ (3.18)
\]

or

\[
\log I = \log I_0 + b \log t \quad \ldots \ldots \ (3.19)
\]

Thus in hyperbolic decay, logarithm of phosphorescence intensity and logarithm of time are linearly related and straight line will be obtained if \( \log I \) is plotted against \( \log t \) on a log-log graph paper.
Fig. 3.5 (c) and (d) Decay curves.
Fig. 3.5 (e) and (f) Decay curves.
In the present investigation the analysis of decay curves was done by plotting logarithms of phosphorescence intensity as a function of time on a semilogarithmic graph paper. The curves obtained (Fig. 3.9) were not linear, indicating that the decay process does not conform to exponential law. The logarithms of phosphorescence intensity were then plotted against logarithms of time on log-log graph paper. The curves obtained are shown in Figs. 3.6 (a) to 3.6 (c). Here it is evident that approximately linear relationship holds good between \( \log I \) and \( \log t \). This indicates that the decay process conforms to hyperbolic law. This linear relationship between \( \log I \) and \( \log t \) can be confirmed by calculating the correlation coefficient between \( \log I \) and \( \log t \), treating them as related variables.

1. Correlation coefficient. The correlation coefficient offers a criterion for estimating the degree of relationship between two related variables \( X \) and \( Y \). The linear correlation between \( X \) and \( Y \) for a set of paired values is given by

\[
\gamma = \frac{m \Sigma X Y - \Sigma X \Sigma Y}{\sqrt{[m \Sigma X^2 - (\Sigma X)^2][m \Sigma Y^2 - (\Sigma Y)^2]}} \quad \cdots \cdots \cdots \quad (3.20)
\]

The magnitude of \( r \) is taken as a measure of the degree to which the association between the variables \( X \) and \( Y \) approaches a linear functional relationship. The direction of the
Fig. 3.6(a)  Decay curves (log-log plot).
Fig. 3.6(b) Decay curves (log-log plot).
Fig. 3.6(c): Decay curves (log-log plot).
Fig. 3.6(d) Decay curves (log-log plot).
Fig. 3.6(a)  Decay curves (log-log plot).
relation depends upon whether the two variables $X$ and $Y$ vary together in the same direction (positive correlation) or in opposite direction (negative correlation). So the perfect positive correlation is indicated by $+1$ and the perfect inverse correlation is indicated by $-1$. All other values of correlation fall between these two extremes.

In the present investigation logarithms of phosphorescence intensity $I$ and logarithms of time $t$ were considered as two related variables $Y$ and $X$ respectively. The correlation coefficient comes out to be nearly equal to $-1$. This indicates that a negative linear correlation exists between $\log I$ and $\log t$ and $\log I$ decreases as $\log t$ increases. Thus the magnitude of correlation coefficient also favours that the existing decay curves conform to hyperbolic law.

(c) Decay constant. In the present investigation the form of the decay curve is hyperbolic and may be represented by an equation of the form

$$I = I_0 t^{-b}$$

where the power $b$ known as decay constant is to be estimated.

The decay constant can be evaluated from the method of least squares which consists in fitting a mathematical curve to a set of available data. The method depends on the principle
that the best fit is obtained when the sum of squares of the differences between the observed values of some variable \( Y \) and the corresponding calculated values \( Y_1 \) is as small as possible. That is,
\[
\sum_{1}^{m} (Y - Y_1)^2 = \text{minimize} \quad \ldots \quad (3.22)
\]
where \( m \) is the number of observed paired values of \( X, Y \).

Consider the case in which the paired values \( X, Y \) are assumed to be adequately represented by a straight line
\[
Y = c + bx \quad \ldots \quad (3.23)
\]
fitted by means of the method of least squares. The expression for each vertical deviation from this straight line for a fixed value of \( X \) is
\[
Y - c - bx \quad \ldots \quad (3.24)
\]
Hence the expression to be minimized is
\[
\sum_{1}^{m} (Y - c - bx)^2 \quad \ldots \quad (3.25)
\]
The principle of least squares leads to two equations in the two unknowns \( c \) and \( b \) so that a unique solution is obtained. The equations are,
\[
c \sum X + b \sum X^2 = \sum Y \quad \ldots \quad (3.26)
\]
\[
c \sum X + b \sum X^2 = \sum XY \quad \ldots \quad (3.27)
\]
which give,

\[ c = \frac{\sum y \sum x^2 - \sum x \sum xy}{\sum x^2 - (\sum x)^2} \] ........ (3.29)

\[ b = \frac{\sum xy - \sum x \sum y}{\sum x^2 - (\sum x)^2} \] ........ (3.29)

Taking logarithm of both sides, equation (3.21) may be written as

\[ \log I = \log I_0 + b \log t \]

Putting \( Y = \log I, \quad X = \log t \) and \( c = \log I_0 \), the equation reduces to

\[ Y = c + bX \] ........ (3.30)

which is similar in form for which the constants \( c \) and \( b \) have been evaluated by the method of least squares. Hence the decay constant \( b \) for the log-log plot of phosphorescence intensity and the corresponding time was calculated from equation (3.29) by introducing two new variables \( \log I \) and \( \log t \) for \( Y \) and \( X \) respectively.

In the present work, the decay constants for different phosphors were calculated from first 10 seconds of decay to a reasonably long time so that the particular traps involved were nearly all emptied. These values together with correlation coefficients are shown in Table 3.1. The values thus obtained
may differ from those obtained by solving original least squares equations, but the differences are usually very small and may be neglected for most practical purposes.

Since the value of \( b \) comes out to be negative, the equation of the curve becomes

\[ I = I_0 t^{-b} \] .......... (3.31)

(D) Variation of decay constant with Zirconium. The variation of decay constant as a function of zirconium concentration is shown in Fig. 3.7. The logarithm of zirconium concentration was plotted against the decay constant on a semilog graph paper. It appears that the decay constant decreases as the concentration of zirconium is increased. The resultant curve can be broken into two straight lines \( AB \) and \( BC \). This shows that up to \( B \) (\( Zr = 0.02\% \)), the constant decreases linearly with the exponential increase in zirconium concentration. At \( B \) a kink is observed and the curve \( BC \) then again becomes a straight line with different slope.

(E) Variation of decay constant as a function of time. The initial stages of decay correspond to shallower traps, while after sufficiently long time of decay only deep traps contribute to the phosphorescence intensity. However, different decay constants are associated with these different groups of traps. As a result, the overall decay constant might
Fig. 3.7 Decay constant as a function of zirconium concentration.
Fig. 3.3 Decayed constant as a function of time.
vary during the decay period, if traps of different depths contribute to the phosphorescence intensity at the temperature of study.

The decay constants shown in Table 3.1 were calculated after 10 seconds of decay. To do this, only those observations were considered which were taken after 10 seconds of decay. Similarly, the decay constant after a time $t$ can be calculated by considering only those observations which were taken after $t$ seconds of decay. This criterion was used to calculate the decay constants at various times. The curves representing the variation of decay constant with time for some representative phosphors are shown in Fig. 3.3. It is evident that the decay constant increases with time.

(F) 'Peeling off' of the decay curves. For a phosphor which contains traps of different energies and different population, the hyperbolic decay can be explained by the monomolecular superposition theory of Randall and Wilkins. Each group of traps contributes to the phosphorescence intensity separately and gives its own exponential term. The resultant phosphorescence intensity may then be represented as a sum of these different exponentials. Thus,

$$I(t) = I_1 \exp(-p_1 t) + I_2 \exp(-p_2 t) + \ldots + I_n \exp(-p_n t)$$

where $I_n$ is the phosphorescence intensity due to electrons in
Fig. 3.9 (i) *Peeling off* of Decay curve.
traps of energy $E_n^2$, so that

$$E_n = s e^{-E_n / kT} \quad \ldots \ldots \ldots \ldots \ldots \ldots (3.33)$$

The terms involved have already been explained.

Following Stuza and others (4, 33) the various exponentials contributing to the resultant phosphorescence intensity can be distinguished and the separate groups of traps can be determined. For this, the resultant intensity was plotted against time on a semilog graph paper. The curves obtained are shown in Fig. 3.9. The curves are concave upwards because the exponentials of shorter life, which correspond to shallow traps, decay rapidly, eventually leaving the slower components which correspond to deeper traps. After sufficient long time of decay, only the slowest component corresponding to deepest traps remains and this approaches to a straight line. The straight line portion was extrapolated back to $t = 0$, and subtracted from the total curve. The same procedure was adopted for the remaining portion of the curve. It was thus possible to break up each experimental curve into three exponentials. This appears to be the minimum required. The slope of the exponentials thus obtained, give the corresponding $p$ values. The trap depths corresponding to these exponentials were then determined using equation (3.33). Here $s = 1.7 \times 10^9$ sec was evaluated from thermoluminescence studies (Chapter IV) and $T = 303 K$ was the room temperature at which
Fig. 3.9 (iii) 'Peeling off' of Decay curve.
Fig. 3.9 (iv) "Peeling off" of Decay curve.
Fig. 3.9 (v) 'Peeling off' of decay curve.
Fig. 3.9 (vi)  'Peeling off' of Decay curve.
Fig. 3.9 (vii) 'Peeling off' of Decay curve.
Fig. 3.9 (viii) Peeling off of decay curve.
Fig. 3.9 (in)  'Peeling off' of Decay curve.
Fig. 3.9 (x) Peeling off of Decay curve.
Fig. 3.9 (ii)  'Peeling off' of Decay curve.
Fig. 3.9 (xii) 'Peeling off' of Decay curve.
Fig. 3.9 (xii) Peeling off of Decay curve.
Fig. 3.9 (miv)  'Peeling off' of Decay curve.
Fig. 3.9 (xy) 'Peeling off' of decay curve.
Fig. 3.9 (wvi) 'Peeling off' of Decay curve.
the decay study was performed.

The values thus obtained are shown in Table 3.2.

| Variation of intensity with Zirconium | The variation of initial intensity |

(Just after the cessation of excitation) with the growing concentration of zirconium is shown in Fig. 3.10. The concentration was plotted against the intensity on a semilog graph paper. To explain the variation of intensity, the curve can be considered as a sum of three straight lines ab, bc, and cd. The portion ab corresponds to a linear decrease in intensity with the logarithmic increase in activator concentration. At b (Zr = 0.006%) a kink is observed and the intensity then again decreases as before. The slope of straight line bc is greater than that of ab. This indicates that the change from b to c is more rapid than the change from a to b. At c (Zr = 0.065%) the intensity falls to a negligible small value. The portion cd then becomes almost parallel to the concentration axis thereby indicating that from c to d there is no appreciable change in intensity. This portion may be taken as the region where the concentration quenching occurs.
Fig. 3.10 Initial Intensity as a function of Zirconium concentration.


<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percentage of Zr with respect to Gypsum</th>
<th>Correlation Coefficient</th>
<th>Decay Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.0000</td>
<td>0.98</td>
<td>0.79</td>
</tr>
<tr>
<td>P2</td>
<td>0.00004</td>
<td>0.99</td>
<td>0.80</td>
</tr>
<tr>
<td>P3</td>
<td>0.00012</td>
<td>0.98</td>
<td>0.80</td>
</tr>
<tr>
<td>P4</td>
<td>0.00020</td>
<td>0.99</td>
<td>0.78</td>
</tr>
<tr>
<td>P5</td>
<td>0.00028</td>
<td>0.99</td>
<td>0.79</td>
</tr>
<tr>
<td>P6</td>
<td>0.00036</td>
<td>0.98</td>
<td>0.77</td>
</tr>
<tr>
<td>P7</td>
<td>0.00040</td>
<td>0.98</td>
<td>0.78</td>
</tr>
<tr>
<td>P8</td>
<td>0.00040</td>
<td>0.98</td>
<td>0.78</td>
</tr>
<tr>
<td>P9</td>
<td>0.00080</td>
<td>0.93</td>
<td>0.77</td>
</tr>
<tr>
<td>P10</td>
<td>0.0016</td>
<td>0.99</td>
<td>0.76</td>
</tr>
<tr>
<td>P11</td>
<td>0.0024</td>
<td>0.99</td>
<td>0.76</td>
</tr>
<tr>
<td>P12</td>
<td>0.0032</td>
<td>0.98</td>
<td>0.75</td>
</tr>
<tr>
<td>P13</td>
<td>0.0040</td>
<td>0.98</td>
<td>0.75</td>
</tr>
<tr>
<td>P14</td>
<td>0.0080</td>
<td>0.98</td>
<td>0.74</td>
</tr>
<tr>
<td>P15</td>
<td>0.016</td>
<td>1.00</td>
<td>0.74</td>
</tr>
<tr>
<td>P16</td>
<td>0.024</td>
<td>0.98</td>
<td>0.74</td>
</tr>
<tr>
<td>P17</td>
<td>0.032</td>
<td>0.99</td>
<td>0.73</td>
</tr>
<tr>
<td>P18</td>
<td>0.040</td>
<td>0.98</td>
<td>0.73</td>
</tr>
<tr>
<td>P19</td>
<td>0.048</td>
<td>0.99</td>
<td>0.71</td>
</tr>
<tr>
<td>P20</td>
<td>0.056</td>
<td>0.97</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*continued ************
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percentage of Zr with respect to Gypsum</th>
<th>Correlation Coefficient</th>
<th>Decay Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>P21</td>
<td>0.050</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>P22</td>
<td>0.064</td>
<td>0.99</td>
<td>0.60</td>
</tr>
<tr>
<td>P23</td>
<td>0.063</td>
<td>0.99</td>
<td>0.62</td>
</tr>
<tr>
<td>P24</td>
<td>0.072</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>P25</td>
<td>0.076</td>
<td>1.00</td>
<td>0.64</td>
</tr>
<tr>
<td>P26</td>
<td>0.080</td>
<td>0.99</td>
<td>0.64</td>
</tr>
<tr>
<td>P27</td>
<td>0.084</td>
<td>1.00</td>
<td>0.65</td>
</tr>
<tr>
<td>P28</td>
<td>0.088</td>
<td>0.99</td>
<td>0.60</td>
</tr>
<tr>
<td>P29</td>
<td>0.092</td>
<td>0.99</td>
<td>0.65</td>
</tr>
<tr>
<td>P30</td>
<td>0.096</td>
<td>0.99</td>
<td>0.64</td>
</tr>
<tr>
<td>P31</td>
<td>0.10</td>
<td>0.99</td>
<td>0.65</td>
</tr>
<tr>
<td>P32</td>
<td>0.15</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>P33</td>
<td>0.20</td>
<td>-</td>
<td>0.60</td>
</tr>
<tr>
<td>P34</td>
<td>0.25</td>
<td>0.99</td>
<td>0.57</td>
</tr>
<tr>
<td>P35</td>
<td>0.30</td>
<td>0.99</td>
<td>0.55</td>
</tr>
<tr>
<td>P36</td>
<td>0.35</td>
<td>1.00</td>
<td>0.56</td>
</tr>
<tr>
<td>P37</td>
<td>0.40</td>
<td>0.99</td>
<td>0.56</td>
</tr>
<tr>
<td>P38</td>
<td>0.45</td>
<td>0.99</td>
<td>0.58</td>
</tr>
<tr>
<td>P39</td>
<td>0.50</td>
<td>0.99</td>
<td>0.58</td>
</tr>
<tr>
<td>P40</td>
<td>0.55</td>
<td>0.99</td>
<td>0.57</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Percentage of Zr with respect to Gypsum</td>
<td>Trap depth (eV)</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I Exponential.</td>
<td>II Exponential.</td>
<td>III Exponential.</td>
</tr>
<tr>
<td>P₁</td>
<td>0.00000</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>P₃</td>
<td>0.00012</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>P₆</td>
<td>0.00035</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>P₇</td>
<td>0.00040</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>P₈</td>
<td>0.00040</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>P₁₀</td>
<td>0.0016</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>P₁₂</td>
<td>0.0032</td>
<td>0.76</td>
<td>0.71</td>
</tr>
<tr>
<td>P₁₃</td>
<td>0.0040</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>P₁₅</td>
<td>0.0160</td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>P₁₆</td>
<td>0.0240</td>
<td>0.75</td>
<td>0.70</td>
</tr>
<tr>
<td>P₁₇</td>
<td>0.0320</td>
<td>0.75</td>
<td>0.70</td>
</tr>
<tr>
<td>P₁₉</td>
<td>0.0480</td>
<td>0.73</td>
<td>0.68</td>
</tr>
<tr>
<td>P₂₀</td>
<td>0.0560</td>
<td>0.74</td>
<td>0.68</td>
</tr>
<tr>
<td>P₂₂</td>
<td>0.0640</td>
<td>0.73</td>
<td>0.68</td>
</tr>
<tr>
<td>P₂₃</td>
<td>0.0690</td>
<td>0.73</td>
<td>0.67</td>
</tr>
<tr>
<td>P₂₄</td>
<td>0.0720</td>
<td>0.73</td>
<td>0.68</td>
</tr>
</tbody>
</table>
REFERENCES


<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Antonov-Romanovsky, V.V.</td>
<td>J. Phys. USSR 6, 120 (1942).</td>
</tr>
<tr>
<td>No.</td>
<td>Author(s)</td>
<td>Reference</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>37</td>
<td>Naercke, O.</td>
<td>Z. Physik 109, 685 (1939)</td>
</tr>
<tr>
<td>38</td>
<td>Rohde, F.</td>
<td>Z. Naturforsch 8a, 156 (1953)</td>
</tr>
<tr>
<td>39</td>
<td>Scharmann, A.</td>
<td>Z. Naturforsch 11a, 398 (1956)</td>
</tr>
<tr>
<td>41</td>
<td>Hanle, W., Kotschak, O., and Scharmann, A.</td>
<td>Z. Naturforsch 6a, 202 (1951)</td>
</tr>
<tr>
<td>42</td>
<td>Kirchoff, W.</td>
<td>Z. Physik 116, 115 (1940)</td>
</tr>
<tr>
<td>43</td>
<td>Duschinsky</td>
<td>Z. Physik 81, 7 (1933)</td>
</tr>
<tr>
<td>47</td>
<td>Schreklen, A.</td>
<td>Z. Physik 135, 294 (1953)</td>
</tr>
<tr>
<td>51</td>
<td>Schleede, A., and Bartels, B.</td>
<td>Z. Physik 39, 936 (1938)</td>
</tr>
<tr>
<td>56</td>
<td>Stripp, K., and Ward, R.</td>
<td>J. Amer. Chem. Soc. 70, 401 (1948)</td>
</tr>
</tbody>
</table>