CHAPTER II

LUMINESCENCE
(A) **GENERAL THEORY**

(a) **Definitions**

(i) **Luminescence**: 

According to Widemann\(^{12}\) and Garlick\(^{13}\) Luminescence is defined as absorption of energy in matter and its re-emission in or near the visible spectrum. The initial excitation may be by light, particle bombardment, mechanical strain, chemical reaction or heat. It is distinguished from thermal radiation in the sense that it does not follow Kirchoff's law; and on the basis of time delay, it differs from physical processes like Raman effect and Compton effect. In the case of luminescence emission this time delay is greater than \(10^{-9}\) second while Raman and Compton effects are completed in a time of about \(10^{-14}\) second or less.

(ii) **Fluorescence and Phosphorescence**: 

Fluorescence and phosphorescence have been defined in different ways by different workers. Fluorescence is defined as temperature independent part of luminescence emission, as a result of one or more transitions, within a time interval of \(10^{-8}\) second and phosphorescence is defined as the temperature dependent emission occurring after \(10^{-8}\) second, with the intervention of a metastable state.

(iii) **Phosphors**: 

The substances which exhibit the property of luminescence are called phosphors. These can be divided further in
two classes (1) Those showing luminescence in the pure state; and (2) Those showing luminescence in the presence of an activating impurity.

iv) **Activators**:  
Activators are impurity or structure defects that provide localized levels, permitting radiative transitions. Co-activators are other imperfections that are essential to the luminescence of certain classes of inorganic compounds but have little influence on the spectral distribution of emission.

v) **Centres**:  
The localized discrete levels possessing high capture cross-section for excited electrons and much greater probability for radiative transitions are known as luminescence centres. If the probability for nonradiative transitions becomes greater, then they are called "Killer Centres".

vi) **Traps**:  
Traps are metastable levels of luminescence centres or localized levels introduced in the forbidden band gap capable of capturing electrons or holes, and holding them for a significant time before they give rise to emission.

vii) **Categories of Luminescence**:  
1) Characteristic Luminescence: In this case the whole luminescence process takes place within the luminescence centre, energy levels involved being those of the
activator ions, modified sometimes by the host lattice.

2) Non-characteristic Luminescence: In this case the energy transfer process becomes an integral part of the luminescence mechanism, energy levels being those of the host lattice modified by the activator ions.¹⁴

viii) Types of Luminescence:

Prerequisite to luminescent emission is the excitation of the luminescent substance since the energy radiated by a system must be provided in some way. Various types of luminescence are often distinguished by a prefix denoting the nature of the source of energy. Photoluminescence depends on excitation by electromagnetic radiation or photons; cathodoluminescence by energetic electrons or cathode rays; electroluminescence by a voltage (electric field) applied to the luminescent substance; triboluminescence by utilization of mechanical energy such as grinding; chemi-luminescence by utilization of the energy of a chemical reaction; bioluminescence is a biological process; sonoluminescence depends on the ultrasonic irradiation in liquids.

Often this labelling is carried to extremes and it can be misleading too. For example, the term "thermoluminescence" on the face of it, implies a contradiction of our rough definition of luminescence. Thermoluminescence is the phenomenon of luminescent emission under conditions of increasing
temperature and Radiophotoluminescence does not describe a mode of excitation but a sequence of processes which includes the creation of luminescence response in a nonluminescent material.

The features common to all forms of luminescence are (1) the occurrence of some processes whereby an atom, molecule, or "centre" is excited to a higher energy state, and (2) its radiative de-excitation to the ground state i.e. via the emission of a photon of appropriate energy after the lapse of some period of time.

(b) Distinction Between Fluorescence and Phosphorescence:

A further distinction between the types of luminescence is made on the time dependence of emission. Initially the term "fluorescence" was applied to luminescence which persisted only as long as excitation was continued. If the luminescence was observable after the excitation was stopped the phenomenon was called "Phosphorescence". But this is not a meaningful distinction because with instrumental techniques one can readily observe a luminescent after glow ("persistence", "decay time") of the order of $10^{-8} - 10^{-9}$ second. System that would have to be classified as "fluorescent" using a visual criterion of persistence, would therefore have to be called "phosphorescent" based on the instrumental measurement of after-glow.
**FIG. 1** ENERGY LEVEL DIAGRAM SHOWING VARIOUS ELECTRONIC PROCESSES CONNECTED WITH EMISSION IN A CRYSTALLINE SOLID CONTAINING IMPURITIES AND RADIATION INDUCED TRAPS
A more meaningful distinction between fluorescence and phosphorescence is based on the dependence of luminescence decay time $T_{\text{lum}}$ on the temperature, rather than on its absolute magnitude. Thus, if the emission is due to spontaneous transition of the system from the excited energy level $E$ to the ground energy level $E_g$ (Fig. 1), the luminescence will decay exponentially with a decay time determined by the probability of the transition between these states. If this is an allowed electric dipole transition, with emission of a photon in the visible region of the spectrum, the decay time will be in the range of $10^{-8}$ - $10^{-9}$ second. If the transition $E \rightarrow E_g$ is of different type (electric quadrupole, magnetic dipole, etc.), the transition probability is many orders of magnitude lower, with corresponding increase in decay time. The transition probability in all cases is however, an intrinsic characteristic of the luminescent centre; the luminescence decays exponentially with time, and the decay time is independent of temperature in the range of temperature where the luminescence efficiency remains high. All the above cases are properly characterised as fluorescence the "allowed" transitions producing a "fast" fluorescence whereas the "forbidden" transitions produce "slow" fluorescence.

When the luminescence decay time depends on the temperature range where the luminescence efficiency is high,
the term phosphorescence is applied. On an atomic scale this situation can arise when an atom, molecule or centre (Fig. 1) is somehow excited to an energy level $E_M$, from which it cannot return to the ground level with photon emission, the transition $E_M \rightarrow E_G$ is completely forbidden according to the selection rules. Let us suppose that the system can be raised by absorption of energy $\Delta E = (E - E_M)$ to a higher excited level $E$ such that the radiative transition $E \rightarrow E_G$ is an allowed one (Fig. 1, 7'). Hence if the energy $\Delta E_{\text{absorbed}} = (E - E_M)$ is provided to the centre, the energy $\Delta E_{\text{emitted}} = (E - E_G)$ will be emitted. If $\Delta E_{\text{absorbed}}$ can be provided by thermal means at room temperature a continuing luminescence emission (phosphorescence) can be observed even after the removal of excitation source. This emission will continue with diminishing intensity until there are no longer centres in the metastable state.

If the system is raised to a higher temperature the energy $\Delta E_{\text{absorbed}} = (E - E_M)$ will be provided at a more rapid rate, the phosphorescence thus will be brighter and the decay time will be shorter due to faster depopulation of metastable states via the path:

$$E_M + \text{heat} \rightarrow E \rightarrow E_G + h\nu_{\text{emitted}}$$

Consequently with lowering of the temperature there will be a decrease in phosphorescence brightness and in an increase in
the decay time. Thus the important difference between fluorescence and phosphorescence is the temperature dependence of the decay time.

(c) **Theoretical Models for Interpretations of Luminescence Phenomena (Absorption and Emission)**

The configurational co-ordinate model and Energy band Model generally provide all the interpretations of luminescence phenomena. The two models are exclusive, and complement each other in explaining luminescence phenomena and are in no way incompatible. The energy band model neglects the atomic rearrangement that occurs during luminescence, while configurational co-ordinate model ignores the charge transport through the lattice.

i) **Configurational Co-ordinate Model**:

In contrast to the absorption and luminescence spectra of dilute gaseous atomic systems, which consist of sharp lines, the corresponding spectra in solid phosphors generally consist of rather broad bands having widths of a few tenths of an electron volt. In the photoluminescence of solid systems the emitted light generally is of longer wave length than exciting light, a condition first experimentally noted in 1851 by G. Stokes and is known as Stoke's law. These spectral characteristics as well as other properties connected with the temperature dependence of the luminescence efficiency of phosphors may
FIG. II SCHEMATIC
CONFIGURATION CURVES

FIG. III CONFIGURATION
COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE (SEITZ)

FIG. IV CONFIGURATION
COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE AND CONDUCTION FOR LUMINESCENCE (Dexter)

FIG. V
be understood by consideration of "configuration co-ordinate" diagrams.

Fig. II shows the curves representing potential energies of the normal and excited states of the luminescence centres in relation to the variation of one of its configuration co-ordination. A and B represent the ground and excited state of the centre. Absorption of radiation raises the centre from the state A to state B. Electronic transition (energy absorbed) may be represented by vertical line AB according to the Frank-Condon principle, which states that when an electron is excited optically, the nuclei of ions may be considered to remain at rest during the process. The system is not in equilibrium in the state B, somehow trying to adjust itself so as to reach C, giving off the energy difference BC in the form of lattice vibrations or phonons. Further, the centre returns to the ground state by emission of luminescence CD and finally loses more energy DA by vibrational interchange. Seitz (Fig. III) and Dexter et al\(^{15}\) (Fig. IV) proposed a modified model to show how a radiationless transition can take place from the excited state to the ground state by an internal conversion process. This model with few quantum mechanical modifications explains (1) stoke's shift, (2) width of absorption and emission bands at low temperature, (3) monomolecular decay, (4) F-centre luminescence and (5) thermal quenching of luminescence.
Its limitations are: (1) it cannot explain processes occurring between absorption and final emission, e.g. photo-conductivity and (2) in most cases, precise configuration co-ordinate diagrams have not been possible. Some workers also suggested a multi-dimentional model as against the one dimentional one.

ii) Energy Band Model:

The collective electron model by Bloch has been extended by Mott and Gurney and Seitz to explain luminescence mechanism of phosphors. The energy states of an electron in a crystal may be derived from the states of the individual atoms and ions which compose the crystal. The discrete energy levels in atoms and ions are broadened into bands due to interaction with the crystal lattice. These allowed energy bands are separated by "forbidden regions" and they are either unoccupied or filled. Thus instead of the discrete energy states, there are discrete energy bands for the electrons inside the crystal. The upper most completely filled band is called the valence band and the next higher allowed band is called the conduction band. These energy levels in an allowed band are so closely spaced that effectively they form a continuum. The energy level diagram indicating different electronic processes occurring in a crystalline solid is shown in Fig. I.
When an activator atom is incorporated in a crystalline solid, it will give rise to localized energy levels in the normally forbidden energy gap. These localized levels may be classified into two categories:

(a) Level belonging to the host atoms which are under the perturbing influence of activators.

(b) Levels which belong to activator atoms themselves which are under the perturbing influence of the activators.

Suppose G and A are two levels corresponding to say, an activator atom, represented in Fig. V in terms of energy band picture. When activator atom is in the ground state, level G is occupied by an electron and A is empty, while reverse is true in the excited state. The excitation from G to A may be accomplished in at least three following ways.

(1) It is possible that the incident photon of proper frequency is absorbed directly by the electron in level G, where upon it arrives in A (Fig. V,1).

(2) The optical properties of alkali halides indicate that in the band picture of solids, they are to be described as typical insulators with a forbidden gap of the order of 10eV. Liberation of an electron from the valence band into the conduction band could be the result of absorption of light in the far ultraviolet by an alkali halide crystal. Since the valence band arises from valence-electrons of the halide ions, this corresponds to the removal of an electron from a halide ion. This deficiency of electron behaves like an electron with
a positive charge and is referred to as hole. The freed electron and the resulting positive hole are both free to move in the crystal. If the centre G is in the ground state, the level G may capture a hole from the valence band and A may trap an electron from the conduction band. In this way excitation of the centre can be explained (Fig. V).

Absorption of light in the longest wave length ultraviolet bands by an alkali halide crystal on the other hand does not completely separate the electron and the hole because the radiation is not sufficiently energetic. The electron and the hole remain bound to each other by coulomb attraction. This neutral electron-hole entity is an excited state of the crystal and could be viewed as a particle wandering freely through the crystal, which transports energy but no net electrical charge. This mobile particle consisting of an electron bound to a positive hole is called an exciton. The energy states corresponding to such a configuration are called excitation states shown in Fig. V by 3 & 3'. The light absorption transfers an electron from halogen ion to adjacent alkali ion, and the hole on the halogen ion and electron on the alkali ion remain bound to each other by coulombian forces. The bound pair can migrate by the movement of electron and hole to adjacent alkali and halogen ion respectively. During migration, if an electron reaches an activator centre such as AG in Fig. V, it may give off its energy to the centre which would raise the electron of the activator from the ground state to the excited state. Thus the energy can be transferred from the exciting source to the impurity via the host crystal. When the electron returns from
FIGURE VI  SCHEMATIC REPRESENTATION OF THERMOLUMINESCENCE (AND OPTICALLY STIMULATED LUMINESCENCE) PROCESSES IN AN ALKALI HALIDE CONTAINING COLOUR CENTRES.
the excited state to the ground state luminescent emission is observed.

(B) THERMOLUMINESCENCE\textsuperscript{23,24} (TL)

(a) Mechanism of TL:

Thermoluminescence may be defined as the thermally stimulated release (in the form of light) of energy stored in a material from previous excitation. It provides a technique for studying certain types of defects in solids with a directness not usual with other methods. Thermoluminescence can be illustrated in terms of the properties of defects in the alkali halides. When a pure salt is irradiated trapped electron centres (F-centres) and trapped hole centres (V-centres) are formed (Fig.VI). By absorption of a sufficiently energetic light quantum or by acquiring the necessary energy from the thermal vibrations of the surrounding crystal ions, an electron may be completely ejected from the F-centre into the conduction band (Step I). This ejected electron can wander through the crystal (Step 2) and recombines with trapped hole (Step 3), giving away luminescence emission. When Step I is provoked by heat and is accelerated by raising the temperature the phenomenon is called "Thermoluminescence". A symmetrical series of processes can also take place (shown as 1',2',3') wherein a hole is optically or thermally liberated from its trap and migrates to the valence band. 3' is the luminescence process of recombination of the free hole with a trapped electron.
Fig. VII  Thermoluminescence process in an impurity activated alkali halide leading to luminescence characteristic of the impurity [Mn²⁺ or Ag⁺ impurities as examples].
To ensure that step 3 (or 3') is indeed a luminescent process and to control the luminescence emission spectrum, we can dope the salt with known luminescent ions or activators. Fig. VII shows how Mn\(^{++}\) or Ag\(^+\) can serve as activators. When the doped salt is irradiated, electron trapping leads to F-centre formation but the hole is trapped by Mn\(^{++}\)-ion or Ag\(^+\)-ion and after subsequent ejection of electron from F-centre, it recombines with the hole at Mn\(^{++}\) or Ag\(^+\) ion. After this recombination the activator ion is in an excited state and quickly emits its characteristics luminescence (Mn\(^{++}\)-ion = green-orange, Ag\(^+\) ion = ultraviolet-blue).

(b) **Randall and Wilkins Theory of Thermoluminescence**

Electrons in the trap have a Maxwellian distribution of thermal energies\(^{25}\). Therefore, the probability of escape of an electron from a trap of depth \(E\) (activation energy) is of the form \(P = Se^{-E/kT}\) ... (1.1) where \(k\) is Boltzmann constant and \(T\) is the temperature in °K. \(S\) has the unit \((\text{Sec})^{-1}\) and is called frequency factor. Factor \(S\) is constant but some times it is found to be dependent on the initial concentration of trapped electrons in a given type of trap.

The simplest mathematical representation for the luminescence glow peaks without any overlapping, is provided by the basic theory of Thermoluminescence, given by Randall
and Wilkins. The basic assumption they made were that once an electron escapes from a trap there is no significant probability for it to get retrapped (i.e., monomolecular mechanism) and that the luminescence intensity at any temperature is directly proportional to the rate at which the detrapping occurs. The TL intensity \( I \) is proportional to the rate of release of electrons from the trap

\[
I \propto \frac{dn}{dt} = -cPn
\]

\[
I = -cnSe^{-E/kT}
\]

where \( n \) is the number of trapped electrons and \( c \) is a constant

\[
\frac{dn}{n} = -cSe^{-E/kT} \frac{dt}{dT} \cdot dT
\]

\[
= -c \frac{S}{P} e^{-E/kT} \cdot dT
\]

\( P = \frac{dT}{dt} \) is the constant heating rate (°K/Sec). By integrating on both sides and substituting in equation (1.2), equation for TL intensity can be derived as

\[
I = n_0cSe^{-E/kT} \left[ - \left( \int \frac{S}{P} e^{-E/kT'} dT' \right) \right]
\]

\( n_0 \) is the initial number of trapped electrons. At a fixed temperature \( T \), \( cSe^{-E/kT} \) is a constant and is taken as \( A \). Equation (1.2) can thus be written as

\[
\frac{dn}{n} = -Adt \quad \text{which on integration gives}
\]

\[
n = n_0e^{-At}
\]

\[
(1.4)
\]
from (1.2) and (1.4)

\[ I = I_0 e^{-At} \quad (I_0 = A_0) \quad \ldots \quad \ldots \quad (1.5) \]

Thus at a fixed temperature \( T \), TL intensity decays exponentially and the TL process is said to be following the first order kinetics.

(c) Garlic Gibson's Theory:

The above theory given by Randall and Wilkins is based on the assumption that retrapping is a negligible process in the luminescence mechanism of phosphor. However, Garlic and Gibson\(^{26}\) modified the theory. They considered the case, where a free electron has equal probability for going to recombination centres or returning to the same trap (Retrapping). If \( N \) is the total number of traps of which \( n \) are occupied at a time \( t \), the probability that a released electron will go to the recombination centre is

\[ \frac{n}{(N-n)+n} = \frac{n}{N} \]

Therefore

\[ I = C \frac{dn}{dt} \cdot \frac{n}{N} \]

\[ = - cS e^{-E/kT} \cdot \frac{n^2}{N} \quad \ldots \quad \ldots \quad (1.6) \]

By integrating equation (1.6) and rearranging, equation for TL intensity is obtained as
I = \frac{n_0^2 c S' e^{-E/kT}}{\left[1+S' \frac{n_0}{p} \int_0^t \exp(-E/kT')dT'\right]^2} \quad \ldots \quad (1.7)

Where \( S' = S/N \) is called the preexponential constant and has the unit (cm\(^2\) Sec\(^{-1}\)).

At a fixed temperature \( T \), equation for the TL intensity can be derived as

\[ I = \frac{I_0}{(1+A'n_0t)^2} \quad \ldots \quad \ldots \quad (1.8) \]

Where \( A' = cS'e(-E/kT) \)

A straight line graph obtained by plotting \( I^{1/2} \) against time \( (t) \) provides a test for the applicability of second order kinetics in TL process.

(d) May and Partridge's Equation:

In many cases, a process follows neither the first order nor the second order kinetics. May and Partridge\(^{27}\) gave a following equation which is applicable to a process following any non-first order kinetics

\[ I = c \frac{dn}{dt} = - cS'n^1 \exp(-E/kT) \quad \ldots \quad \ldots \quad (1.9) \]
Where \( l \) is the order of kinetics and can have any value not necessarily an integer. Solution to (1.9) gives

\[
I = S' n_0^{l-1} c \exp(-E/kT) \left[ \frac{(1-l)S'(n_0)^{l-1}}{P} \int_0^T \exp(-E/kT')dT' + 1 \right]^{-1/(1-1)}
\]

\( S' n_0^{l-1} \) has unit (Sec)\(^{-1} \) and in this sense it is similar to frequency factor \( S \) of first order case. Thus

\[
I = cS n_0 \exp(-E/kT) \left[ \frac{(1-l)S}{P} \int_0^T \exp(-E/kT')dT' \right]^{-1/(1-1)}
\]

Equation (1.11) is not valid for \( l=1 \) but when \( l \to 1 \) it reduces to the first order equation (1.3) and for \( l=2 \), it reduces to the second order equation (1.7).

From equation (1.9)

\[
\frac{dn}{n^l} = -S'e^{-E/kT} \, dt
= -P'dt (P'=S'e^{-E/kT})
\]

which on integration gives

\[
n = (a+bt)^{1/(1-l)} \quad .... \quad (142)
\]

Where \( a = (n_0)^{1-l} \) and \( b = -P'(1-l) \)

Substituting the value of \( n \) in equation (1.9) we get,
$I = -cP'(a+bt)^{1/(1-l)}$

Or

$$(I)^{(1-l)/l} = (-cP')^{(1/l)-1} (a+bt)$$

$$= A + Bt \quad \ldots \quad \ldots$$ (1.13)

Where

$A = a(-cP')^{(1/l)-1}$

and

$B = b.(-cP')^{(1/l)-1}$

Thus if the TL process is following general order of kinetics, decay of TL intensity is governed by equation (1.13) such that plot of $(I)^{(1/l)-1}$ vs time would give a straight line.

Activation energy is the most important parameter in the TL process. Each trapping site in a crystal represents a defect in the crystal-structure and is characterised by its activation energy ($E$). Most of the methods for determining $E$ require a prior knowledge of order of kinetics. Hence order of kinetics must be determined accurately.

(e) **Order of Kinetics**:

If the process is following first order kinetics, the isothermal decay of the glow peak will be exponential and the graph between log $I$ vs time will be a straight line.
If the process follows second order kinetics the TL intensity will decay according to equation (1.8). A straight line graph obtained by plotting \((I)^{-\frac{1}{2}}\) against time provides a test for the applicability of second order kinetics.

If the decay does not follow either the first or the second order kinetics, then the order of kinetics is determined by plotting \((I)^{(1/1)-1}\) Vs. time for different values of \(I\). The value of \(I\) which gives a straight time plot is the actual order of kinetics.

Order of kinetics can also be determined from the shape of the glow peak. For the first order kinetics, the ratio of high temperature half width \(\delta = T_2 - T_m\) to the total half width \(\delta = T_2 - T_1\) of the glow peak, called the geometrical factor \(\mu g\) has the value 0.42. For the second order kinetics, \(\mu g\) has the value 0.52 according to Chen. \(T_1\) and \(T_2\) are the two temperatures at which TL intensity falls to half its maximum value towards lower and higher temperature side respectively. \(T_m\) is the peak temperature.

(f) Activation Energy:

Activation energy of a TL glow peak can be determined using high temperature half width \(\delta\), low temperature half-width \(T\) and full half-width \(w\) of a glow peak. Chen summed up three methods \(\delta\), \(T\) and \(w\) by the following equation
$E = C_a \left( \frac{kT^2}{a} \right) - b_a \left( 2kT_m \right) \quad \ldots \ldots \quad (1.14)$

Where 'a' represents half-width and $C_a$ and $b_a$ are constant whose values depend on the geometrical factor $\mu g$.

Initial rise method advocated by Garlic and Gibson\textsuperscript{26} is the only method of calculating activation energy, which does not require order of kinetics. Basically, the method assumes that during the initial rising part of the glow peak, population of trapped electrons remains nearly unaffected. Hence the TL intensity is proportional to $e^{-E/kT}$ and hence $I = \text{constant} \cdot \exp(-E/kT) \quad \ldots \ldots \quad (1.15)$. In this method, only the initial portion of the glow peak is measured. A plot of log $I$ Vs $\frac{1}{T}$ called Arrhenius plot gives a straight line, from the slope of which activation energy $E$ is obtained. Care should be taken to make sure that the peak under investigation is not contaminated with any other peak on either side.

Much controversy exists as regards thermal activation energy in general and with reference to alkali halides in particular. Like Randall and Wilkins\textsuperscript{25}, many other investigators\textsuperscript{1,29-32} assumed the activation energies of the various glow peaks in a glow curve to be approximately proportional to the peak temperature of the individual peaks. On the other hand Hill and Schewd\textsuperscript{33} and Bonfiglioli et al\textsuperscript{34-36} claimed that all the glow peaks in the glow curve have the same activation energy. According to them, all the glow
peaks are due to recombination of electrons released from only F-type centres with holes from V-type centres. Thus TL emission may arise from thermal emptying of the same trap. Halparine et al\textsuperscript{2} also made the evaluation of the activation energies from various glow peaks of NaCl and KCl, single crystals. They computed the activation energies on the basis of initial rise\textsuperscript{29} and on the basis of the method developed by them\textsuperscript{1}. Results were in good agreement and they concluded that activation energies are by no means equal for all glow peaks. From their results they suggested that in alkali halides the process is nearly a first order one, with some tendency towards a second order process for peaks at higher temperature. In agreement to these, the results of Luschick\textsuperscript{37} concluded that for alkali halides examined by him, the probability for recombination was found to be large compared to that of retrapping, which is equivalent to a first order process, which is in contradiction to Bonfiglioli\textsuperscript{34-36}, who observed second order process for the TL of NaCl.

(C) PAST WORK ON TL OF ALKALI HALIDES "PURE" AND DIVALENT IMPURITY DOPED:

It has been shown by Stoddard\textsuperscript{38} that the TL can also be obtained at temperatures below the temperature of irradiation after following treatment. A NaCl crystal at say, room temperature, is irradiated with X-rays then cooled down to
darkness to liquid nitrogen temperature and subsequently illuminated with light into the F-absorption band. When the temperature is raised again, glow peaks appear at various characteristics temperature between LNT and RT. Braner et al\textsuperscript{39} gave the model for this and reported the occurrence of TL below irradiation temperature. This in agreement with the TL model presented by Halperin et al. Braner has shown that glow curves obtained by Stoddard were different from those obtained after X-irradiation at temperatures lower than room temperature (LNT).

Many investigators\textsuperscript{40-45} in the past have observed a correlation between the bleaching temperature of some absorption band and the temperature of the maxima of TL glow peaks in several alkali halides. This led them to conclude that, TL studies correlated with measurement of optical and thermal bleaching of colour centres, give some information about the nature of the traps and the process of formation and destruction of colour centres. Absorption studies on thermal stability of F'-Centre in the dark\textsuperscript{46,47} indicated that F'-Centre becomes thermally unstable in the range 300-380 °K in NaCl 120-160 °K in KBr.

A study of TL light output at different stages in colour centres have been investigated by Rao and Sharma\textsuperscript{48} in the case of NaCl crystals coloured at room temperature by
X-rays. Their results indicated that the thermal bleaching of F-band is maximum in the temperature region of 60-100°C and they attributed it to the larger TL output in that range.

Studies of the growth of F-centres in Harshaw KBr and KCl crystal during X-irradiation as a function of temperature have been reported by Comins. These results provide evidence that "late stage" F-centres are of an interstitial nature. Ausin and Alvarez Rivas have studied the TL glow curves of KCl and NaCl with moderate and heavy gamma doses and observed several glow peaks in KCl and one in NaCl. They reported that the interstitials are the mobile units and the glow peak temperatures correspond to the temperatures at which the V-centres become mobile. Further they suggested that holes are trapped deeper in the heavily irradiated samples. The TL and thermal stability of the F-centres in pure KI, KBr, NaCl and NaF single crystals, X- and gamma-irradiated at room temperature have been studied by Rivas et al. From their results they concluded that the observed thermoluminescence is due to the recombination with F-centres of halogen interstitial atoms which are thermally released from traps.

Katz et al. investigated the thermal annealing of point defects induced by X-irradiation in Sr-doped KCl crystal and showed that a correlation exists between annealing steps of various colour centres. They found that a divalent
impurity causes a shift of all glow peaks to lower temperature. In TL studies of KCl: Sr, Rao and Hari Babu indicated that the positions of the glow peaks and their intensity vary with quenching temperature. They also showed that the glow curves are not only influenced by the nature and concentration of the impurity but also by the state of dispersion in the host crystal. Joshi and Kekan from their studies of NaCl: sr concluded that the shape of the glow curve is influenced by the history of the specimen. Jain and Mahendru observed peaks at 135 and 190°C, in highly pure KCl single crystals (divalent impurity 1 PPPm) and attributed them to the bleaching of first stage and second stage coloration. Introduction of 50 PPPm of calcium gave rise to an additional peak at 85°C which they attributed to the presence of calcium impurity. Studies of undoped KCl by Gartia and Ratnam showed peaks around 105, 185 and 245°C. Rubio et al. in the studies of KCl: Eu showed that X-irradiation greatly increases the rate of aggregation of dipoles and Eu$^{2+}$ cation vacancy dipoles act as the dominant traps for the radiation induced halogen interstitials. They also found that the metastable precipitated phase which was tentatively associated with Suzuki phase showed a slightly higher coloring rate than isolated dipoles or the first products of aggregation. F-colouring efficiency decreases as a function of Eu-precipitation into metastable and stable phases possessing EuCl$_2$ structure.
In TL study of KCl:Ba with different barium concentration by Rao and Hari Babu, three glow peaks were observed in the range 88-95, 110-118 and 182-190°C. From their studies they found that with the increase in barium concentration, the intensities of the glow curve in general, increased up to a certain concentration and decreased on a further increase in the dopant concentration. Excepting for the crystal containing highest barium concentration, they found a shift of the glow curve maxima towards lower temperature, with the increase in barium concentration. They also found that the intensity in general, increased due to quenching from high temperature. Also in quenched samples peak in the range 110-118°C was absent and that in the range 88-95°C was present as shoulder. Optical micrographs of the melted cleavage surfaces of the crystals containing highest barium concentration (0.71 mole %) reveal that in as-grown state visible rod like precipitates could be seen oriented along <100> and <110> direction. On the other hand, in annealed and quenched samples large precipitates observed were no longer seen and cleavage steps could be noticed more clearly. On bleaching with F-light the 182-190°C peak was suppressed and hence they concluded it to be due to F-centres, but did not explain whether 180°C peaks was due to first or second stage coloration. They also found that due to quenching from 500°C precipitates dissociated completely with a more or less uniform distribution of impurity. Etching
and microhardness studies also substantiated this. They proposed that I-V dipoles, unassociated (independent) divalent impurity and cation-vacancy play some role. Probably their proximity to F-centres was suggested to be responsible. In TL studies of KCl:Ca Reddy et al. found similar results and reported three peaks around 80, 110 and 180°C. They suggested the shift of 180°C peak towards lower temperature to be due to change in the configuration co-ordinate curve. Increase in intensity was suggested to be due to higher solubility of divalent impurity and consequently increase in dipole concentration as also the increase in the concentration of single cation vacancies which got converted into anion vacancies and then in F-centres. In TL studies of KCl:Ca and KCl:Sr, Rascon and Rivas observed predominant glow peak at 180°C and shoulders at 137, 100 and 65°C in KCl: Sr specimens irradiated at low exposures. TL spectrum of the same specimen showed a band with maximum at about 450 nm. The TL glow peak around 180°C in KCl: Sr (80 PPM) was more prominent than that in KCl: Sr (210 PPM). The light output in the former was about 50 times higher than the latter. In KCl:Ca (84 PPM) also glow peaks near 80, 110, 190°C were observed. In contrast to KCl: Sr, the glow peaks in KCl:Ca below 200°C vanished with the increase of radiation dose, with the appearance of a new glow peak at higher temperature. The model proposed to explain TL of KCl:Ca and KCl: Sr are the F-centres which act as recombination centres for interstitials which are thermally
released from traps. In this recombination an electron hole recombination takes place and light is emitted. This was supported by the experimental result that the emitted light spectrum in these doped samples was very close to that observed in pure KCl.

(D) **CONCENTRATION QUENCHING**

When the concentration of the activator in a single activated phosphor is increased beyond a certain value, it is observed quite generally that luminescence efficiency decreases. This phenomenon is known as concentration quenching. This has been explained on the basis that an activator centre is non-luminescent if there is another centre at the nearest point of the surrounding lattice. Dexter and Schulmann have assumed that degradation of energy takes place at special quenching sites in the crystal. Quenching is assumed to involve the resonance transfer of energy from activator to activator until it arrives at an activator near one of the energy sinks. Activator quencher transfer then occurs and the energy is lost. Dexter and Schulmann also proposed that the absence of luminescence in most unactivated pure crystal is the result of rapid resonant transfer of excitation energy to imperfections and impurity quenchers.