(A) General Theory

(a) Definitions

(i) Luminescence:

Following Wiedmann\textsuperscript{29} and Garlick\textsuperscript{30}, luminescence may be defined as an emission from a substance in or near the visible spectrum excited by previous or simultaneous irradiation with photons or energetic particles. Luminescence is distinguished from thermal radiation since it does not follow Kirchoff's law, and from physical processes such as Raman and Compton scattering, on the basis of time delay. This, in the case of luminescence emission, is greater than $10^{-9}$ second while the 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. The temperature independent part of luminescence emission, as a result of one or more transitions, within a time interval of $10^{-8}$ second is defined as fluorescence and the temperature dependent emission occurring after $10^{-8}$ second, with the intervention of a metastable state is defined as phosphorescence.
(iii) Phosphors:

The substances which exhibit the property of luminescence are called phosphors. These can be further divided into 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. Other imperfections that are essential to the luminescence of certain classes of inorganic solids but have little influence on the spectral distribution of emission are called coactivators.

(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 non-radiative 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) Catagories of Luminescence:

(1) Characteristic Luminescence: The whole luminescence process takes place within the luminescence centre, energy levels involved being those of activator ions modified sometimes by the host-lattice.

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

(viii) Types of Luminescence:

Excitation of the luminescent substance is a prerequisite to luminescent emission. 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. Thus 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
subject; triboluminescence by utilization of mechanical energy such as grinding; chemiluminescence by utilization of the energy of a chemical reaction; bioluminescence is a biological process; sonoluminescence depends on the ultrasonic irradiation in liquids.

Very often this labelling is carried to extremes, and it can even be misleading. For example, the rather ill-chosen term "thermoluminescence" on the face of it, implies a contradiction of our rough definition of luminescence. Thermoluminescence is the phenomenon of luminescent emission after removal of the excitation under conditions of increasing temperature. "Radiophotoluminescence" does not describe a mode of excitation but a sequence of processes which includes the creation of luminescence response in a non-luminescent material. Although they are part of the vocabulary of luminescence, excessive significance should therefore not be attached to terms like the foregoing. 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 various types of luminescence is also frequently made based on the time dependence of emission. Initially the term "fluorescence" was applied to luminescence which persisted only as long as the excitation was continued. If luminescence was observable after the excitation was stopped, the phenomenon was called "phosphorescence". Clearly, a distinction on this basis is not very meaningful, because with instrumental techniques one can readily observe a luminescent "afterglow" ("persistence", "decay time") of the order of $10^{-8} - 10^{-9}$ second. Systems that would have to be classed as "fluorescent" using a visual criterion of persistence, would therefore have to be called "phosphorescent" based on the instrumental measurement of afterglow.

A more meaningful distinction between fluorescence and phosphorescence is based on the temperature-dependence of the luminescence decay time, $T_{\text{lum}}$, rather than on its absolute magnitude. Thus, if the emission is due to a spontaneous transition of the system from the excited energy level $E$ to the ground energy level
Eg (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 $10^{-8} - 10^{-9}$ 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. However, the transition probability in all cases is 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" transition producing a "Fast" fluorescence while the relatively "Forbidden" transitions produce "Slow" fluorescence.

The term "Phosphorescence" is most properly applied when the luminescence decay time depends on the temperature range where the luminescence efficiency is high. On an atomic scale this situation can arise (fig.1) when the atom, molecule, or centre is somehow excited to an
Electron Hole Recombination in the Valence Band
1. Released Hole Combines with Trapped Electron
2. Released Electron Combines with Trapped Hole
3. Electron and Hole Combine at a Recombination Site 'R'
4. Excited Electron Comes Back to Ground State
5. Released Electron from Metastable State 'E_M' Falls Back to Ground State 'E_G'
6. 'Exciton Bands'

**FIGURE**  E-NERGY LEVEL DIAGRAM SHOWING VARIOUS ELECTRONIC PROCESSES CONNECTED WITH EMISSION IN A CRYSTALLINE SOLID CONTAINING IMPURITIES AND RADIATION INDUCED TRAPS
energy level $E_M$, from which it cannot return to the ground level with emission of a photon; i.e., the transition $E_M \rightarrow E_G$ is completely or largely forbidden by the selection rules. Let us suppose that a higher excited level, $E$, exists to which the system can be raised by absorption of the energy $\Delta E = (E - E_M)$, and that the radiative transition $E \rightarrow E_G$ is an allowed one (fig. 1, 7'). Under these circumstances light of the energy $\Delta E_{\text{emitted}} = (E - E_G)$ will be emitted if energy $\Delta E_{\text{absorbed}} = (E - E_M)$ is provided to the centre. If $\Delta E_{\text{absorbed}}$ can be provided by thermal means at room temperature, e.g., by absorption of phonons from the lattice in the case of a crystalline system, a continuing luminescence emission (phosphorescence) can be observed even after the excitation source is removed. This emission will continue with diminishing intensity until there are no longer any 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 consequently. The phosphorescence will be brighter and the decay time will be shorter due to the faster depopulation of the metastable state via the path:

$$E_M + \text{heat} \rightarrow E \rightarrow E_G + h\nu_{\text{emitted}}$$
Conversely, lowering of the temperature will produce the opposite effects — a decrease in phosphorescence brightness and an increase in the decay time. Thus the temperature dependence of the decay time is the important difference between phosphorescence and fluorescence.

From the foregoing description it will be clear that so called "thermoluminescence" — temperature-stimulated light emission following removal of excitation is merely a case of phosphorescence observed under conditions of readily increasing temperature. In the usual thermoluminescence experiment the system is excited at a temperature at which the phosphorescence intensity is low (long decay time); then heated through a temperature range where the phosphorescence is bright (very short decay time), until temperature is reached at which all the centres have been thermally excited out of their metastable level and the luminescence completely disappears.

It will also be apparent that the energy 
\[ \Delta E_{\text{absorbed}} = (E - E_M) \] can sometimes be provided by light absorption, for example by infrared light. In this case the system exhibits the phenomenon of "optically stimulated" luminescence. This terminology is not to be confused with the stimulated emission involved in laser action. In the
optically stimulated emission referred to here the stimulating light is of different frequency

\[ \nu_{\text{stimulated}} = \frac{E - E_M}{h} \]

from that of the emitted light \( \nu_{\text{emitted}} = \frac{E - E_G}{h} \) and the emission is incoherent.

(c) Theoretical Model for Interpretation of Luminescence Phenomena (Absorption and Emission)

Practically all interpretations of luminescence phenomena are based on a configurational coordinate model or on a band theory model. The two models are mutually exclusive, but in no way incompatible, and in fact, complement each other in explaining luminescence phenomena. Both of them have inherent defect however. The configurational coordinate model ignores the charge transport through the lattice while the energy band model neglects the atomic rearrangement that occurs during luminescence.

(1) Configurational Coordinate 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 wavelength (lower energy) than the exciting light, a condition first experimentally noted in 1851 by G. Stokes and 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 be understood by consideration of so-called "Configuration Co-ordinate" diagrams which are generally used to summarize the characteristics of luminescent centres.

Fig. 2 shows the curves representing potential energies of the normal and excited states of the luminescence centre in relation to the variation of one of its configuration coordinates. Absorption of radiation raises the centre from the ground state A to the excited state B. The energy absorbed corresponds to the vertical distance AB (hν) 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. At B, the system is not in equilibrium and
Figure 2: Schematic Configuration Curves

Figure 3: Configuration Coordinate Diagram to Show Absence of Luminescence (Seitz)

Figure 4: Configuration Coordinate Diagram to Show Absence of Luminescence and Condition for Luminescence (Dexter)

Figure 5: Energy band structure
hence tries to adjust itself so as to reach C, giving off the energy difference BC as lattice vibrations or phonons. Finally, the centre returns to ground state by the emission of luminescence CD (\( h\nu \)) and final loss DA of more energy by vibrational interchange. Modification of this model particularly proposed by Seitz (fig. 3) and Dexter et al.\(^{32}\) (fig. 4) shows how a radiationless transition can take place from the excited state to the ground state by an "internal conversion" process. In fact, this model along with its few quantum mechanical modifications successfully explains: (1) stokes shift, (2) width of absorption and emission bands at low temperature, (3) thermal quenching of luminescence and other temperature effects, (4) monomolecular decay, and (5) F-centre luminescence.

Its limitations are: (1) it cannot be applied to the process occurring between absorption and final emission, e.g. photoconductivity, and (2) precise configuration coordinate diagrams on theoretical considerations only have not been possible in most cases\(^{33, 34}\). A multidimensional model as opposed to the one dimensional, one described above has also been suggested by some workers\(^{35,36}\).
An energy band model based on the "Collective electron theory" has been developed by many workers to explain the long durational phosphorescence of photoconducting phosphors. The energy level diagram indicating the different electronic processes occurring in a crystalline solid containing impurities and other related radiation induced trapping is shown in fig. 1. The band theory considers the crystal of the solid as one large unit and the energies of its electrons are treated collectively. According to the theory, qualitatively, when atoms are arranged in an orderly way and in close proximity to each other to form a crystal the energy states for the electron in the atoms are disturbed by mutual interaction. As a result, the discrete electronic states are broadened into bands of allowed energy separated by bands of forbidden energy. Thus, instead of the discrete energy states there are discrete energy bands for the electrons inside the crystal. The uppermost completely filled band is called the valence band and the next higher allowed band is called the conduction band. The energy levels in an allowed band are so closely spaced that effectively they form a continuum.
The incorporation of an activator atom in a crystalline solid will in general give rise to localized energy levels in the normally forbidden energy gap. These localized levels may be classified into two categories:

(a) levels which belong to activator atoms themselves and
(b) levels belonging to host atoms which are under the perturbing influence of the activators.

In terms of the energy band picture of fig. 5 let \( G \) and \( A \) be two levels corresponding to say, an activator atom. In the ground state of the activator atom, level \( G \) is occupied by an electron and \( A \) is empty, in the excited state the reverse is true. The excitation from \( G \) to \( A \) may be accomplished in at least three ways. The corresponding three modes of excitation are discussed below:

1. It is possible that the incident photon of proper frequency is absorbed directly by the electron in level \( G \), whereupon it arrives in \( A \) (fig. 5, 1).

2. In the case of solids like alkali halides, the optical and electrical properties indicate that they are to be described as typical insulators in the band picture of solids with a forbidden band gap of the order of 10 eV. Absorption of light in the far ultraviolet by an alkali halide crystal corresponds to the liberation of an electron from the valence band into the conduction band. Since the
valence band arises from the valence electrons of the halide ions, this corresponds to the removal of an electron from a halide ion. This deficiency of an electron is called a positive hole, and the hole behaves like an electron with a positive charge. The freed electron and the resulting positive hole are both free to move in the crystal. If the centre AG 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 achieved (fig. 5, 2, 2').

(3) Absorption of light in the longest wavelength ultraviolet bands by an alkali halide crystal, on the other hand, does not completely separate the electron and the positive hole, since the radiation is not sufficiently energetic. The electron and the hole remain bound to each other by coulomb attraction. The electrically neutral entity thus formed is an excited state of the crystal and may be viewed as a particle free to wander through the crystal, transporting energy but no net electrical charge. The mobile "particle" consisting of an electron bound to a positive hole is called an "exciton", and the energy states corresponding to such a configuration are called exciton states. These states are shown in
The exciton states can be considered to arise from a process wherein light absorption transfers an electron from a halogen ion to an adjacent alkali ion. The electron on the alkali ion and the positive hole on the halogen ion remain bound to each other by Coulomb forces, and the bound pair can migrate by the movement of the electron and hole to adjacent alkali and halogen ion respectively. During migration, if an electron reaches an activator centre such as AG in fig. 5, 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.

In all the above cases, the return of the electron from the excited state to the ground state gives rise to luminescent emission.

(B) **Thermoluminescence** 37, 38

(a) **Mechanism of Thermoluminescence**

Thermoluminescence provides a technique for studying certain types of defects in solids with a directness not usual with other methods. Experimental studies
of this phenomenon are relatively straightforward and can be used to ascertain the nature of some of the centres produced during irradiation with x-rays or ultraviolet radiation.

Thermoluminescence (and optically stimulated luminescence) can be illustrated in terms of the properties of defects in the alkali halides. Fig. 6 shows trapped electron centre (F-centres) and trapped-hole centres (or V-centres) formed by irradiation of a pure salt. The F-centre is indicated in the energy level diagram farthest to the left. An electron may be completely ejected from the F-centre into the conduction band (step 1) by absorption of a sufficiently energetic light quantum or by acquiring the necessary energy from the thermal vibrations of the surrounding crystal ions. The ejected electron can wander through the crystal (step 2) and recombines with a trapped hole (step 3), giving out the energy of recombination in the form of a light quantum, i.e. luminescence. If step 1 is provoked by light absorption, (generally infrared light), the phenomenon is "Optically (infrared) stimulated luminescence"; if it is provoked by heat, it is called "phosphorescence". When the phosphorescence is accelerated by raising the temperature the phenomenon is called "thermoluminescence". A
FIGURE 6  SCHEMATIC REPRESENTATION OF THERMO-
-LUMINESCENCE (and optically stimulated
luminescence) PROCESSES IN AN ALKALI
HALIDE CONTAINING COLOUR CENTRES
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 via the valence band; the luminescence process 3' is the recombination of the free hole with a trapped electron.

To insure 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. 7 illustrates how Ag⁺ or Mn²⁺ can serve as activators. On irradiation of the doped salt, electron trapping leads to F-centre formation as before, but the hole is trapped by the Ag⁺-ion or Mn²⁺ - ion. When the electron is subsequently ejected from the F-centre, it recombines with the hole at the Ag⁺ or Mn²⁺ ion. After this recombination the activator ion is in an excited state and quickly emits its characteristic luminescence (Ag⁺ - ion = ultraviolet - blue and Mn²⁺ - ion = green - orange).

(b) Randall and Wilkins' Theory of Thermoluminescence

Some of the long afterglow phosphors, which have been excited at low temperature, on warming exhibit an increase in emission intensity which as mentioned earlier is known as
Thermoluminescence process in an impurity-activated alkali halide, leading to luminescence characteristic of the impurity (Mn$^{2+}$ or Ag$^+$ impurities as examples).
thermoluminescence. The luminescence intensity vs
temperature curves are known as "glow curves".
Each group of trap is observed as a separate peak in the
glow curves, thus enabling an estimate of trap depths
and their distribution. This method was first proposed
by Urbach and later by Katz, but became more popular
after the researches of Randall and Wilkins.

Randall and Wilkins' theory of thermoluminescence
assumes a monomolecular mechanism as in the case of phospho-
rescence. The differential equation in this case is given
by,

\[ \frac{dn}{dt} = -ns \exp (-E/kT) \] \hspace{1cm} (1)

or

\[ \frac{dn}{n} = -s \exp (-E/kT) \, dt \] \hspace{1cm} (2)

where \( n \) is the number of traps filled at time \( t \), \( s \) is
frequency factor, \( E \) is the trap depth and \( k \) is Boltzmann's
constant. If a phosphor is heated at a uniform rate of \( \beta \)
deg sec\(^{-1} \) then \( dT = \beta \, dt \). On substituting in equation 2
and integrating, we get,

\[ \log \left( \frac{n}{n_0} \right) = - \int_0^T s \exp (-E/kT) \, dT/\beta \] \hspace{1cm} (3)

or

\[ n = n_0 \exp \left[ - \int_0^T s \exp (-E/kT) \, dT/\beta \right] \] \hspace{1cm} (4)
where \( n_0 \) is the number of traps filled at \( t = 0 \), i.e., at the beginning of heating.

The thermoluminescence intensity at temperature \( T \) is given by:

\[
I = n_0 s \exp \left(-E/kT\right) \exp \left[-\frac{\int_0^T s \exp \left(-E/kT\right) \,dT}{\beta}\right]
\]  
\[\ldots (5)\]

Since this expression represents the glow curve for only a single trap depth, the glow curves of most phosphors would have to be calculated by integration over the distribution of trap depths. However, Randall and Wilkins have shown that the mean life time of the trapped electrons is little different from 1 sec at the temperature of maximum glow, \( T_g \) hence,

\[
s \exp \left[-\frac{E}{kT_g} \left(1 + f(s, \beta)\right)\right] = 1 \quad \ldots (6)
\]

where \( f(s, \beta) \) is nearly constant and has a value small compared with unity. \( T_g \) is a fairly simple function of \( E \) and we can write

\[
E = kT_g \left(1 + f(s, \beta)\right) \log s \quad \ldots (7)
\]

Neglecting \( f(s, \beta) \) in comparison to unity, the equation(7) yields,

\[
E = kT_g \log s \quad \ldots \quad \ldots (8)
\]

from which the trap depth can be calculated.
Much controversy exists as regards thermal activation energy in general and particularly in the case of alkali halides. Like Randall and Wilkins\textsuperscript{39}, many other investigators\textsuperscript{40} assumed the activation energies of the various peaks in a glow curve to be approximately proportional to the peak temperatures of the individual peaks. On the other hand, Hill and Schewd\textsuperscript{11}, Bonfiglioli et al.\textsuperscript{12 - 14} 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-centres with several kinds of V-type centres. Thus thermoluminescence emission of different colours may arise from the thermal emptying of the same trap. Halperin et al.\textsuperscript{9} also made evaluation of thermal activation energies from various glow peaks of NaCl and KCl single crystals. They computed the activation energies on the basis of the method developed by them\textsuperscript{8} and also by the method of initial rise\textsuperscript{40}. They found good agreement between the activation energies as determined by their method and those obtained by initial rise method. From their results Halperin et al. concluded that activation energies are by no means equal for all the glow peaks. The method suggested by Halperin et al. also gave information about the kinetics of the process involved. From the
results of their work they suggested that in alkali halides the process is nearly a first-order one, with some tendency towards a second-order process for the peaks at higher temperatures.

These results are in agreement with the results of Lushchick who concluded that for all 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. It is however, in contradiction to Bonfiglioli et al. who assumed a second-order process for the thermoluminescence of NaCl.

In 1960 Stoddard has reported some results which apparently contradicted the earlier existing model of the thermoluminescence process. It is known that when a crystal is irradiated with x-rays at lower temperature and subsequently warmed to a higher temperature then a number of thermal glow peaks appear. No thermoluminescence is however, detected in the temperature region below the temperature of irradiation if the crystal is cooled down in darkness after x-irradiation. It has been shown by Stoddard that the thermoluminescence can also be obtained at temperature below the temperature of irradiation after the following treatment. A NaCl crystal at say, room
temperature (RT), is irradiated with x-rays, then cooled down in darkness to liquid nitrogen temperature (LNT) and subsequently illuminated with light into the F-absorption band. When the temperature of the crystal is raised again, glow peaks appear at various characteristic temperature between LNT and RT. Braner et al.\textsuperscript{15} gave the explanation for it and reported that the occurrence of thermoluminescence below irradiation temperature is in agreement with the thermoluminescence model presented by Halperin et al. Braner has shown that the glow curves obtained by Stoddard were different from those obtained after x-irradiation at LNT. Appropriate illumination of the cooled sample with F-light was found to produce only part of the glow peaks. The missing glow peaks were obtained by illumination with light absorbed in $V_2$- and $V_3$-bands. It was suggested that this method has been useful in distinguishing between hole and electron processes at temperature higher than room temperature.

Many investigators\textsuperscript{24, 43 - 47} in the past, have observed a correlation between the bleaching temperature of some absorption band and the temperature of the maxima of thermoluminescence glow peaks in several alkali halides. This led them to conclude that thermoluminescence 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{48, 49} indicated that F' - centre becomes thermally unstable in the range 300 - 380 K in NaCl and 120 - 160 K in KBr. Gudden and Pohl\textsuperscript{50} suggested that the glow peak at 360 K in NaCl crystal is due to thermal release of F' - electrons. Dutton and Maurer\textsuperscript{51} and Teegarden and Maurer\textsuperscript{52} studied the thermoluminescence and electrical glow peaks that accompany the thermal bleaching of absorption bands formed by low temperature irradiation of KCl and KBr. According to them the peak at 143 K in KBr and 210 K in KCl is due to thermal bleaching of F' - centres.

A study of thermoluminescence light output at different stages of thermal bleaching and the corresponding changes in colour centres have been investigated by Rao and Sharma\textsuperscript{53} 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 this to the larger thermoluminescence output in that range. Parfianovich\textsuperscript{54},
Katz, Lushchick, and Zeitov have observed several thermal glow peaks in both pure and activated NaCl crystals excited by ionizing radiation at room temperature. They have observed correlation between these peaks and different species of colour centres.

Studies of the growth of F-centres in Harshaw KBr and KCl crystals 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 have studied the thermoluminescence glow curves of KCl and NaCl with moderate and heavy doses of γ-rays and observed several glow peaks in KCl and one glow peak in heavily irradiated NaCl. They reported that the interstitials are the mobile units and the glow peak temperatures correspond to the temperature at which the V-centres become mobile. Further, they suggested that the holes are trapped deeper in the heavily irradiated samples.

Survey of the literature shows that the results obtained during thermoluminescent studies of pure and doped KBr show variations in the positions of the peaks reported by different workers. This can be a consequence of the differences in the type of samples, the
type of irradiation and the warming rates employed.
Mehendru and Radhakrishna\textsuperscript{25} have reported two glow peaks at 363 and 423 K in highly pure KBr crystals and they have interpreted the two peaks in terms of the first and second stage F-centres in analogy with the work done by Jain and Mehendru\textsuperscript{68} for KCl. They have observed that no additional impurity peak is obtained for KBr crystals doped with Cd and Zn. Murti et al\textsuperscript{26} have reported four glow peaks for KBr and KBr:Cu crystals at 359, 377, 392 and 409 K. They have attempted to fit the observed glow peaks to first order kinetics. Gartia and Ratnam\textsuperscript{66} observed two glow peaks at 425 and 453 K in KBr single crystals irradiated with x-rays at a high temperature (in the range 30 - 160°C). Thermal activation energies of these peaks, calculated by using Chen's formulae for general order kinetics are found to be 0.75 and 1.17 eV respectively. They showed that both the peaks follow first order kinetics.

Hageseth\textsuperscript{27} has observed only a peak at 425 K in spectroscopically pure KBr. He has attributed this peak to the F-centres. Thermoluminescence measurements on KBr crystals carried out by Levinson et al\textsuperscript{28} give much narrower glow peaks and higher activation energies for the 425 K peak. In addition they show that not only the 425 K
peak but the total complex of peaks in the glow curve above room temperature is associated with the F-centres.

The thermoluminescence and the 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 recently by Mariani and Alvarez Rivas\textsuperscript{67}. 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.

(C) 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 the 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\textsuperscript{69-71}. Dexter and Schulman\textsuperscript{72} have assumed that the 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 Schulman also proposed that the absence of luminescence in most unactivated pure crystals is the result of rapid resonant transfer of excitation energy to imperfections and impurity quenchers.