CHAPTER I

LUMINESCENCE - A GENERAL REVIEW
1.1 INTRODUCTION

Solid State Physics is mainly concerned with the physical properties of solids, particularly those exhibited by the atoms, molecules and ions, on account of their association to form a solid phase. It is a very vast field with a wide variety of complexities. Out of these, the study of solid state luminescence provides one with a powerful tool in understanding the properties of electronically active solids. The electronic structure is described either in terms of the zone theory or the band theory. The zone theory is more useful in elucidating properties of metals whereas the band theory is perhaps most useful for discussing the semiconductors and insulators. The band theory describes the discrete energy levels of electrons in a single atom, which are broadened into a series of allowed energy bands separated by the forbidden band. The highest occupied band is known as the valence
band and the lowest unoccupied band is known as conduction band, which are separated by the forbidden energy gap. The presence of imperfections or defects in the perfect crystal gives rise to localized energy levels in the forbidden gap due to perturbation of the periodic potential in the crystal. These imperfections and defects play a very important role in giving rise to several important phenomena in the domain of Solid State Physics (1,2). The phenomenon of luminescence is one of the structure sensitive optical properties of matter which not only contributes towards the understanding of the effect of traces of alien impurities and the defects in the regular crystal structure, but also sheds light on the related phenomena such as photoconduction, dielectric behaviour, colour centers, semiconduction etc. Luminescence is most commonly known through its applications in the cathode ray tubes for radar and television, fluorescent lighting, paints, scintillation counters and the recently developed solid state lasers. In recent years significant progress has been made both in the experimental and the theoretical aspects. However, the theoretical understanding of the mechanism of luminescence is far from satisfactory and it is hoped that further investigations of the physical nature of luminescence may elicit fresh facts to account for the known properties in terms of a single unified theory.

1.2 THE ELEMENTARY CONCEPT OF LUMINESCENCE:

(a) Definitions of luminescence:

The term luminescence has been defined as a process
by which matter generates non-thermal radiations in the visible
and the near visible which are characteristic of the particular
luminescent materials (3-5).

The luminescence emission is not due to incandescence,
and so is often called 'cold light' to distinguish it from
radiation due to heating such as occurs in an electric light
bulb. This phenomenon is not included in the emission of black
body radiation, which obeys Kirchoff’s or Wien’s Law. It is
also distinguished from Raman and Cherenkov effects in that
the time delay in luminescence emission after excitation ceases
is longer than $10^{-9}$ seconds, while Raman, Compton, Rayleigh
effects and Cherenkov radiations are completed in a time of
$10^{-14}$ seconds as pointed out by Adirowitsch (6, 7, 8).

(b) **Fluorescence and phosphorescence**:

Luminescence is sub-classified into fluorescence
and phosphorescence on the basis of the duration of the pheno-
menon after cessation of excitation; and are distinguished as
follows:--

(i) **The physical conditions of the experiment**: Garlick (4)
defines fluorescence as the luminescence emitted during excita-
tion while phosphorescence as that emitted after the cessation
of excitation. Some authors (9 - 11) consider fluorescence as
that part of emission where decay is independent of excitation
intensity and of temperature, while phosphorescence is the
temperature dependent emission.
(ii) On the basis of physical process: Perrin (11) defines fluorescence as the emission that takes place by one or more spontaneous transitions and phosphorescence as that which occurs with the intervention of a metastable state followed by return to the excited state due to addition of energy. This definition is preferred by many workers (12 - 14).

(c) Phosphors:

Phosphors are structure and impurity sensitive solid crystalline materials capable of absorbing energy from various sources at a certain frequency and re-emitting it as visible or near visible radiation of other frequency during or after cessation of excitation (5). These are strongly influenced by chemical composition, crystal structure, impurity present in relatively small amounts and physical conditions (e.g. temperature and type of excitation) under which they are made to luminescence.

(d) Host materials:

These form the vehicles for carrying imperfections. They are normally colourless or light coloured and consist of high melting point compounds which have high solubility for foreign atoms. The sulphides, selenides, phosphates, tungstates, oxides, molybdates and silicates mainly of Zn, Cd and the alkaline earths are used as host materials (15).

(e) Activators and Killers:

Activators are impurities in small amounts or structural defects present in most phosphors which provide
localized levels in the forbidden gap of the solid and give rise to radiative transitions. Generally transition and post transition metals like Cu, Mn, Bi, Pb and Eu, Sm, Di act as activators. Yet there are impurities such as Fe, Co, Ni (transition metals) which give rise to non-radiative transitions in phosphors of sulphide class and are known as Killers or poisons (16,17).

(f) **Fluxes:**

These are readily fusible inorganic salts acting as a recrystallizing medium. With the use of flux the firing temperature is lowered and the efficiency of phosphors is increased. The most popular fluxes are alkali and alkaline earth halides, borates and sulphates. The precise role of flux in phosphors is still not completely understood (18).

(g) **Centers:**

These are two types:

(i) **Luminescence centers:** are the localized discrete levels which have a high capture cross-section for excited electrons and a much greater probability for radiative transitions than for non-radiative transitions (19,20). The nature of the luminescence center determines the luminescence spectrum.

(ii) **Killer centers:** are also discrete localized energy levels of impurity atoms which have a small capture cross-section for excited electron and a much greater probability for non-radiative transitions (20).
(h) **Traps** :

Trapping is a fundamental process for energy storage in almost all electronically active solids. These are the regions or metastable states in the forbidden gap capable of capturing electrons or holes and detaining them in a restricted volume for a significant time between excitation and luminescence (21-23). A vacant energy level close to the bottom of the conduction band can act as an electron trap and an occupied electron trap is called a donor level. A filled localized energy level close to the valence band may act as a hole trap and the normally occupied hole trap is known as 'acceptor level'.

1.3 **CLASSIFICATION OF LUMINESCENCE** :

(a) Luminescence may be divided into two types (21):

(i) **Characteristic luminescence** : In this case, all the phenomena, i.e. the excitation, the trapping and recombination take place within the same activator ion. The energy levels are, therefore of the activator atoms modified by the host lattice. Under usual condition of excitation the electrons are not raised to the conduction band and hence photoconductivity is negligible. Luminescence in KCl as host lattice and Ag, Tl, Cu, Mn etc. as activators are the examples of this class.

(ii) **Non-characteristic luminescence** : In this class of luminescence process the energy transfer through the lattice becomes essential and the energy levels involved are those of the host lattice modified by the activator atom. ZnS as host lattice
and Ag, Au, Cu etc. as activators are examples of this type. Photoconductivity is possible in this case since the trapping does not occur at the same site at which light emission occurs and the emptying of the traps give rise to free electrons in the conduction band.

(b) According to Modes of Excitation:

Excitation of luminescent materials is pre-requisite to luminescence emission. Wiedemann (3) gave its classifications according to mode of excitation sources as follows:

(i) Photoluminescence: it refers specifically to luminescence excited by optical radiation and that produced by absorption of electromagnetic radiation or photons of energies from few to several electron volts.

(ii) Radio-luminescence: that produced by bombardment with high energy particles or radiation e.g. x-ray, γ-ray or fission fragments. Roentgeno-luminescence, Cathode-luminescence and Anodo-luminescence are the specific cases and produced when excited by x-rays, cathode rays and canal rays respectively.

(iii) Chemiluminescence: emission produced during chemical reactions. Galvano-luminescence and Bio-luminescence are also specific cases and produced by electrochemical and biological reactions respectively.

(iv) Electro-luminescence: that produced by the application of an electric field.

(v) Tribo-luminescence: emission resulting from mechanical strain i.e. during grinding or pulverising.
1.4 LUMINESCENCE EFFICIENCY

This term is defined in several ways (24) as follows:

(i) Energy efficiency (\(\eta_e\)): It is defined as a ratio of the luminescent output energy to corresponding radiant energy absorbed. This is given by

\[
\eta_e = \int E_{em} \cdot d\lambda / \int E_{abs} \cdot d\lambda
\]  

(1.1)

(ii) Luminous efficiency (\(\eta_l\)): defined as the luminous flux emitted by phosphor (in Lumens) to absorbed power (in watts). This takes into account the spectral sensitivity of the human eye. The energy spectrum has to be weighted by multiplication through the spectrum by the luminosity function \(v_{\lambda}\) of the eye. This gives

\[
\eta_l = \int E_{em} \cdot v_{\lambda} \cdot d\lambda / \int E_{abs} \cdot d\lambda
\]  

(1.2)

(iii) Quantum efficiency (\(\eta_{qu}\)): defined as the ratio of the number of emitted to absorbed quanta. It can be calculated from the energy efficiency (\(\eta_e\)) by the relation.

\[
\eta_{qu} = \eta_e \lambda_{em} / \lambda_{abs}
\]  

(1.3)

or \(\eta_{qu} = \int E_{em} \cdot \lambda_{em} \cdot d\lambda / \int E_{abs} \cdot \lambda \cdot d\lambda\)

where \(\lambda_{em}\) and \(\lambda_{abs}\) represent average wavelengths of the emission and absorption spectrum.

The luminescence efficiency depends on two main factors:

(a) Concentration of activator: The plot of the efficiency (\(\eta\)) versus atomic activator concentration exhibits a maximum luminescence efficiency at a certain activator concentration. Johnson and Williams (25) have studied systematically the mechanism in the case
of inorganic phosphors and showed that more than one activator with a certain nearest distance causes a decrease in luminescence efficiency or the luminescence is quenched due to the interaction of the two giving rise to non-radiative transitions. Some workers (26-28) have explained concentration quenching on the assumption of proximity of a given activator to another activator or certain types of lattice defects or two activator ions are present in lattice as nearest neighbours. Dexter and Schulman (29) have assumed that the degradation of energy occurs at optical quenching sites in the crystal due to transfer of charge.

(b) Effect of temperature: The decrease in luminescence efficiency at higher temperature results generally from competing non-radiative transitions through a thermally activated process. Above absolute zero temperature the centre will not be in its minimum potential energy.

1.5 THEORIES OF LUMINESCENCE:

Centers have specific states which may often be described using the notations of atomic spectroscopy. Absorption and luminescence emission occur due to transitions between these states. Several features of luminescence centers and luminescence emission are explained by the two theoretical models, the configurational coordinate model and the energy band model. Practically all interpretations of luminescence phenomena have been either implicitly or explicitly based on some modification of them. The former neglects energy transport and is best suited for characteristic luminescence while the latter neglects atomic rearrangement and is best suited for non-characteristic luminescence.
(A) Configurational Coordinate Model:

This scheme first introduced by Von Hippel (30) was applied to the problem of luminescence by Seitz (31) and others (32,33).

As shown in Fig. 1.1 the configurational coordinate model is a plot of the total potential energy of the system for the ground and excited states of the centers including both ionic and electronic terms as function of a configuration coordinate which specifies the configuration of the ions around the center.

When the center absorbs a quantum of energy $\hbar \omega$ it is raised from the equilibrium position of the ground state (A) to the excited state (B). Transition (A B) is vertical in accordance with the Franck-Condor principle. After the center has reached the excited state the ions of the system adjust until a new equilibrium position is reached at (C) in a time of the order of $10^{-11}$ sec., the energy difference between (B) and (C) is given off as lattice vibrations. From the new equilibrium position, in about $10^{-8}$ sec., transition (C) to (D) may occur, emitting a smaller quantum $\hbar \omega'$. The center again relaxes from (D) to (A) by giving up energy to the lattice. The energy of emitted photons is smaller than that of absorbed photon because of the energy transferred to the lattice vibrations. This is called Stoke's Shift and depends on the interaction of the center with its neighbouring ions.

Mott and Gurney (32) pointed out that given sufficient thermal energy to a center in the excited state at (C) may
Fig. 1.1 CONFIGURATIONAL COORDINATE MODEL.
be at the same height as E, where the two curves cross or approach very near and non-radiative transitions take place to the ground state. This explains the thermal quenching at elevated temperatures.

Two other mechanisms have been suggested by which radiationless transitions may take place from an excited state to the ground state.

(i) The model shown in fig. 1.2 was proposed by Seitz (34) for the case of excitons. After absorption of light the system relaxes to such an extent that its minimum is outside the ground state curve. In approaching the minimum, possibilities for radiationless transitions exist at a point such as (A).

(ii) The other mechanism suggested by Dexter et al. (35) shown in fig. 1.3, requires less lattice relaxation around a center than that of Seitz. Excitation is to a point (B) on the excited state curve which is higher in energy than the point of closest approach of the curves at (C), the center before reaching its new equilibrium, the radiationless transitions to the ground state can occur at (C).

In practice it is so easy to determine the energy configurational diagrams for luminescence centers. However, some successful attempts have been made by different workers (36-40). Experimental determinations to construct configuration curves include the measurement of absorption and emission spectra, decay constant, luminescence efficiencies and their dependence on temperature over a wide range (38, 41-43). Maeda (44) has
FIG. 12: SEITZ'S MODEL
FIG. 13: DEXTER KLIČK & RUSSELL MODEL
suggested a multidimensional model on the basis of disagreement between the calculated and the observed values of the activation energy for non-radiative transitions.

(B) Continuous Dielectric Model:

In the configurational coordinate model the center is well localized and both the ground and excited states are confined to the nearest neighbours of the center. Huang and Rhys (45) have developed an almost diametrically opposite approach, considering the idea of long range interaction of a center with the phonon field of the lattice. The interactions which come into play were considered electrical in behaviour and the lattice was treated as a continuous dielectric in which the center is imbedded. In the process of absorption the center experiences a difference in charge distribution when the system jumps from the ground state to the excited state which in turn induces a change in lattice polarization accompanied by creation of lattice phonons. Further refinements and extensions of this work have been made by a number of workers (46-49).

(C) Energy Band Model:

The band theory model is based on the quantum mechanical treatment of the interaction of valance electrons with the three dimensional periodic potential of the crystal lattice. This theoretical model put forward by Riehl and Schon (50), Johnson (51) and others (52-55) to explain the characteristics of a phosphor, is a development of Bloch's collective electron model(56).
The formation of bands can be understood on the basis of the tight binding approximation, a method which superposes individual electron wave functions as atoms are brought from infinity to the close spacings of the lattice, the discrete levels of electrons in isolated atoms are broadened into bands of allowed energy separated by bands of forbidden energy gap, as shown in fig. (1.4). The wave functions corresponding to these bands represent a charge density which is spread throughout the crystal so that electrons or holes can move through the crystal without any activation energy. Activator introduces discrete localized levels in the forbidden gap to produce emission centers for luminescence. \(L\) represents the ground state of the center above the filled band \(F\) and \(L'\) is its excited state. Other impurities, lattice perturbations due to activator or defects and the presence of vacant lattice sites produce unoccupied levels \(T\) at various depths in the forbidden gap below the conduction band, in which excited electrons can be trapped. These levels are known as electron traps. Absorption and emission processes in phosphors may be explained only on basis of this model. The excitation of luminescence by photon absorption in the matrix lattice or luminescent center involves raising of an electron from valance band or from the ground state of luminescence center to the conduction band, or from a filled activator ground level to some higher activator level as shown fig. 1.4 by transitions \(A, B\) and \(D\) respectively. Luminescence emission occurs when an excited electron return to an empty ground state of luminescence center. Electrons in the conduction band can return to luminescence center or may be
FIG. 1.4 ENERGY BAND MODEL

C — CONDUCTION BAND
F — FILLED BAND
L — LUMINESCENCE CENTRE
T — TRAPS
captured by the traps (T) and phosphorescence is then determined by their activation (thermal, optical or electrical) from traps and subsequent return to the empty luminescence center.

1.6 **PROCESSES IN CRYSTALLINE PHOSPHORS**:

The luminescence process has been divided into three states — (a) Absorption and excitation (b) Transfer and storage of energy and (c) Conversion of stored energy as light i.e. emission.

(a) **Absorption and Excitation**: The absorption and excitation characteristics of phosphors are primarily functions of the nature of the host lattice and activator combination (10). These mechanisms have been found very useful in the understanding of the fundamental processes occurring in luminescence (4, 5).

Some of the possible modes of excitation (22, 57, 58) are shown in fig. 1.5 and may be described as follows:

(i) **Excitation of the lattice absorption produces a free electron in the conduction band and a free hole in the valence band for the absorption of each photon**.

(ii) **Excitation of the normal valence electrons produces a bound electron hole pair called exciton. In this case no free electrons or holes are produced and the energy is transferred by the diffusion of exciton.**

(iii) **Excitation of luminescent center produces a free electron in the conduction band and a free hole in the neighbourhood of the center.**

(iv) **Excitation of valence electron raises an electron to an unoccupied center and a free hole in the valence band.**
Fig. 1-5 Energy band model for absorption & excitation

1. Occupied state of luminescence centre
2. Unoccupied state of luminescence centre
3. Ground state of luminescence centre
4. Excited state of luminescence centre
5. Trapping state
(v) Excitation of the valence electron creates a mobile hole in the valence band and the electron into the traps.

(vi) Excitation within a luminescence center raises an electron to the excited state of the center. In this case no free electrons or holes are produced and the luminescence is determined only by the center configuration.

Corresponding to these transitions the absorption characteristics may be described as follows:

(I) Any radiation energy greater than the separation between conduction band and valence band raises electrons from valence band to conduction band and the band due to this is known as fundamental absorption band. The wavelength corresponding to minimum energy required for the above transition is known as the fundamental absorption edge. For light of greater energy than the minimum required, the absorption is continuous and fairly constant up to a certain maximum energy (Transition (i)).

(II) In (ii) process of excitation where the energy is lower than the band gap energy, the absorption by the lattice creates excitons, which are thermally dissociated at room temperature (59-61). These electron-hole pairs move in one another's field in the crystal with no net charge and are manifested by a series of narrow absorption lines on the low energy side of the absorption edge.

(III) Other absorption bands due to longer wavelength than the absorption edge will be present corresponding to the electronic transitions (iii), (iv) and (v), which are dependent in the matrix and the activators or both (10). These transitions give
some structure in the tail of the absorption spectrum lying outside the absorption edge.

(IV) Corresponding to the electronic transition (vi), the absorption band occurs at still longer wavelength and which is due to the electronic transition confined to the luminescent center, or the impurity centers.

(V) The trapped electrons may be raised by optical stimulation into the conduction band giving rise to a further set of absorption bands in the long wavelength region. These have been observed in materials in the powder form (62). In addition, electron\(^\hbar\) in excited phosphors may be raised into emptied centers, thus giving long wavelength absorption bands similar to trapped electrons. Defects and impurities present also give new absorption bands usually on the long wavelength side of the characteristic absorption.

In general, the absorption spectrum of a crystalline phosphor may be divided into a short wavelength absorption region associated with the matrix crystal lattice, culminating in the fundamental absorption edge and a longer wavelength region associated with the activators or other impurities.

(b) Transfer and Storage of Energy: When a luminescence center absorbs energy it becomes ionised. This energy is not immediately converted into phonons or photons and may be stored in localized metastable states, first proposed by Jablonski (63) and later adopted by Johnson (51) to explain long decay phosphorescence. As shown in fig. 1.6, absorption of exciting radiation by a luminescence center raises an electron into the excited state(F).
Fig. 1.6 JABLONSKI's MODEL FOR ENERGY STATES IN A LUMINESCENCE CENTER.

G - Ground State.
M - Metastable State.
F - Excited State.
E - Activation Energy.
It may then directly return to the ground state \((G)\) with the emission of fluorescence or it may fall into the metastable state \((M)\), lying just below \((F)\). The transition \((M \leftrightarrow G)\) is usually forbidden. The electron in metastable state requires some activation energy to return to the ground state via \((F)\). The energy is supplied by thermal activation. The resulting delayed emission is phosphorescence. The probability per unit time of an electron being liberated by thermal activation, is proportional to \(e^{-E/kT}\) and is given by:

\[
p = S e^{-E/kT}
\]

where \(S\) is a constant called the escape frequency, \(E\) is the activation energy, \(k\) is Boltzmann's constant and \(T\) is the absolute temperature.

(c) Emission: Luminescence emission takes place when an excited electron in the conduction band or in the excited state of a center, returns to the ground state of the luminescence center. The probability of direct transition from the conduction band to the valence band is low and generally not observable (64). The temporary storage of energy, by trapping of excited quasi or free electrons, positive holes or excitons in metastable state makes the luminescence emission complicated. The excited electrons may fall into these levels releasing energy as lattice vibrations or phonons. The nature of trapping centers is a major factor in determining the behaviour of phosphorescence (65).

The 'Anti-Stokes' luminescence, the emission of shorter wavelength than the exciting one, has been observed in the case of ZnS and CdS phosphors by many workers (66, 67). This
has been explained on the basis of a two stage excitation process (68). The first infrared photon ionizes the impurity level into the conduction band and a second one raises a valence electron into the empty level, thus creating an electron-hole pair followed by luminescence emission of short wave-length.

1.7 TRANSPORT OF ENERGY IN LUMINESCENCE SYSTEMS:

Luminescence systems have been divided into three categories:

(A) Systems in which absorption and emission of energy takes place in the same center—localized center. This has been elaborated in the previous section.

(B) Systems in which absorption is in one center and emission is in another center and the transfer of energy takes place without movement of charge carriers.

(C) Systems in which transport of energy is predominantly affected by charge carriers with subsequent emission.

(B) Luminescence systems in which energy transport is without movement of charge carriers:

The energy transfer without movement of charge during absorption and emission plays an important role in phosphors. A notable example is the phenomenon of 'sensitization', that is, when the exciting energy is absorbed in the host solid or in a center and if the emission of energy takes place in a different center, the first center is called the sensitizer and the latter is called activator. This has been studied by many workers (69 - 72).
There are three different mechanisms of such transfer as follows:-

(i) **Cascade or radiative mechanism**: In this mechanism the emitted radiation from the excited center excites another center by a radiative transition and then a secondary fluorescence will occur. This mechanism is most effective in those cases where the first center must be an efficient activator, the emission spectra of this must overlap the absorption spectra of the other and the absorption band of the second must be sufficiently strong. However, as theory predicts, it is affected by the shape and size of the specimen and exciting source. This mechanism is not common in inorganic phosphors, where often the activator transition is forbidden (73).

(ii) **Resonance or non-radiative mechanism**: According to this mechanism a quantum mechanical resonance process takes place between sensitizer and activator by dipole-dipole or dipole-quadrupole or exchange interaction (71, 74 - 76). On the assumption of random distribution of the sensitizer and the activator ions the distance over which the energy can be transferred has been calculated to be of the order of $10^4$, $10^2$ and 40 lattice sites for dipole-dipole, dipole-quadrupole and exchange interactions respectively. Transitions from sensitizer to sensitizer have also been observed by some workers (71, 74). This process depends on: (a) the distance over which the energy is transferred, and (b) the optical transition at each center. Shafter and Williams (77) have studied the resonance energy transfer between donor-acceptor pairs and deeplying states.

(iii) **Exciton migration**: Energy transfer has also been postulated in terms of 'exciton migration' through the lattice.
(71, 78, 79). Broser and Broser-Warminsky (80) have experimentally shown the probability of excitons at large distances from their point of creation. However, exciton migration is particularly sensitive to presence of surface states and is only possible over large distances in the case of pure and defect free crystals.

(C) Luminescence Systems Involving Transfer of Charge Carriers:

Energy can also be transferred from one point to another by the movement of excited electrons and holes. Many characteristics of photoconducting phosphors have been explained by the storage action of electron traps. Three different models have been advanced for describing energy levels of the luminescence centers:

(I) Schön - Klasen's Model: This model was proposed by Schön (81) and elaborated by Klasens and his co-workers (54,82) for the case of a single luminescence center which is normally occupied and is situated close to the valence band. As shown in fig. 1.7, the sequence of events in considered as follows:

(a) Absorption of light in the valence band produces a free electron in the conduction band and a free hole in the valence band.

(b) The hole may migrate towards the impurity center through the valence band.

(c) The hole may be captured by the impurity center giving off a small amount of energy as infrared radiation or vibrational quanta.

(d) The electron moves through the conduction band until it finally reaches the center.
FIG. (17) SCHON-KLASSENS MODEL

A. ABSORPTION
B. HOLE MIGRATION
C. HOLE CAPTURE (SCHON-KLASSENS)
D. ELECTRON MIGRATION
E. ELECTRON CAPTURE RESULT
(e) The electron is captured by the center.

The recombination of the electron with the bound hole gives off the excess of energy as luminescence emission. The cycle is now complete and the process may again be repeated. This model has been extended to explain many related phenomena such as doubly activated phosphors, storage of energy in traps, temperature quenching of phosphorescence and effect of poisons (54, 83). However, it fails to explain the difference observed for decay times of photoconductivity and luminescence (84).

(II) Lambe - Klick's Model: This model suggested by Lambe and Klick (85 - 87) shown in fig. 1.8, which involves a luminescence center close to the bottom of the conduction band and the luminescence is attributed to a hole transition from valence band to the localized level. The sequence of events in this case is as follows:

(a) When a phosphor is irradiated in the fundamental absorption region, an electron and hole are created.

(b) The hole migrates near the luminescence center.

(c) The hole is captured by the luminescence center and luminescence emission occurs leaving the center now neutral in charge.

(d) The free electron wanders through the conduction band until it comes near the center.

(e) The electron is finally captured by the center. In the capture a small amount of energy is given off non-radiatively or to the lattice vibrations.

The center is now returned to its original condition. In this model the luminescence transition and the capture of the free electron occur in different parts of the cycle so that
FIG: (1-6) LAMBE-KLICK MODEL
A - ABSORPTION
B - HOLE MIGRATION
C - HOLE CAPTURE RESULTING IN
D - ELECTRON MIGRATION
E - ELECTRON CAPTURE
different time constants of decay arise for emission and photoconductivity. This has been observed in the case of sulphide phosphors by Bube (84) and Lambe (88).

(III) **Williams - Prener's Model**: This model proposed by Williams and Prener (89-92), assumes the simultaneous inclusion of activator and co-activator in a phosphor, giving rise to associated donor-acceptor pairs of levels in which an electron has been transferred from the donor to the acceptor level. In this model, centers having a ground state I near the valence band and an excited state II near to the conduction band are involved as shown in fig. 1.9. These states I & II have high capture probability for hole and electron respectively. The sequence of events in this case is as follows:

(a) Absorption raises the electron into the conduction band and leaves a hole in the valence band.
(b)&(d) Hole and electron captures now occur respectively in state I and II with the release of relatively small amounts of energy either as infrared radiation or phonons.
(c) Transition of electron from state II to state I occurs giving rise to luminescence emission.

At low temperature the probability of radiative transition in this model is much greater than that in the above two models. At high temperature the electrons from the level II are raised to the conduction band and so the emission is quenched (93). The model has been useful in explaining temperature dependence of fluorescence and photoconductivity (94) and steady state luminescence for ZnS phosphors (95).
FIG. (19) WILLIAMS AND PIEMER'S MODEL
1.8 SOME METHODS OF STUDYING LUMINESCENCE AND ALLIED PROPERTIES:

(A) Absorption: Absorption spectra help in determining the different radiative transitions responsible for emission. Absorption spectra are usually obtained by observing reflected radiation as a function of the energy of the incident photons. This reveals information about the band width and development of levels on the top of the valence band due to the incorporation of impurities (10).

(B) Excitation: The excitation spectrum is determined by observing the luminescence emission intensities at a particular wavelength as a function of equal number of exciting photons of different wavelengths. The excitation spectrum does not necessarily coincide with the absorption spectrum. It has intimate connection with the absorption (5,10).

(C) Emission: The emission spectra are obtained by exciting the phosphors by a suitable, preferably monochromatic radiations and determining the emission intensity as a function of wavelength. Emission spectra depend on a number of preparative parameters. The fluorescence emission spectra gives information regarding the energy levels of the activator while phosphorescence spectra yield information about the trapping state.

(D) Decay: The rate of decrease of emitted luminescent intensity after excitation of the phosphor is the decay. The decay of luminescence can be measured by directly determining the after glow intensity as a function of time, or the decrease in time of the residual light sum. The measurement of decay gives information about luminescence centers, energy distribution of population of trapping levels and time constant of luminescence processes.
(E) **Thermoluminescence**: Thermoluminescence is the phenomenon of luminescence emission after cessation of excitation under conditions of increasing the temperature. This is also called stimulation. Thermoluminescence study is probably the most elegant technique for studying electron traps and elucidating the mechanism of decay. The glow curves show a number of groups of traps present and the peak temperatures/emission are correlated to the thermal activation energies of the trapping states.

(F) **Paramagnetic Susceptibility and Resonance**: With sufficient sensitivity in the experimental arrangements trapped electrons should be detected because of their unpaired spin. In these experiments the transitions observed are produced between the magnetic microwave field and electron magnetic moment. This phenomenon is a powerful tool for detecting and characterising the defects and impurities in phosphors and much information can be obtained from this study e.g. kinetics and fluorescence and phosphorescence processes, the valence state of paramagnetic ions and localized electrons at trapping states at a particular temperatures (96, 97) etc.

(G) **Electroluminescence**: The phenomenon is defined as the emission of luminescence on applying electric field when the phosphor is placed between the electrodes. In this case the electrical energy is directly converted into luminescence light. A number of workers have made quantitative measurements of ejection of trapped electrons. This method of estimating trap distribution at a given temperature does not give useful information since field up to breakdown values will affect only a very small range of traps (98).

(H) **Photoconductivity**: It is an increase in the electrical conductivity of insulators and semiconductors when they are excited
by light. The photocurrent is due to the excitation of electrons to the conduction band which then move under the action of electric field. Gudden and Pohl (99) showed that the photoconduction is produced by the liberation of charge carriers during luminescence and photocurrent behaviour was indicative of the reaction kinetics involved. Herman and Mayer (100) have attempted to establish relations between conductivity changes and thermoluminescence. This phenomenon is a powerful tool for understanding solids, and mechanism of recombination kinetics and the study of its different aspects helps in the determination of life time of the charge carriers and distribution and density of trapping states (101).

1) **Photodielectric Effect**: Dielectric changes are observed when photoconducting phosphors such as ZnS are excited in the presence of small electric field. The dielectric changes are due to the production of conduction electrons by excitation. Garlick and Gibson (102) correlated photodielectric loss effect with phosphorescence and thermoluminescence and concluded that these changes are due to the polarization of the filled electron traps. This effect can be considered as another manifestation of photoconductivity and adds new information particularly about the deeper traps.

1.9 **PRESENT INVESTIGATION**:

Luminescence of most inorganic solids involves impurities or structural defects and is particularly useful in clarifying our ideas of solids. The alkaline earth sulphide phosphors, which were first investigated extensively by Lenard and his coworkers (103) lapsed in oblivion because of the instability under excitation or atmospheric conditions like humidity, for its
practical and commercial use and the discovery of other phosphors with better luminescence characteristics. However, interest in this class of phosphors seems to have been revived with the discovery of infrared stimulation, sensitization, magnetic properties and electro-luminescence. From various investigations it appears that further precise studies of alkaline earth sulphide phosphors could be fruitful in understanding the basic principles involved. With these things in view, a systematic study of these phosphors in the crystalline form has been undertaken for the last few years in our laboratory.

In the present investigation CaS was taken as the host material which was obtained by reducing purified crystalline gypsum. Two rare earth elements, Cerium and Didymium, were used as activators and sodium sulphate as a flux. Didymium is a mixture of two rare earth elements - Praseodymium and Neodymium, most probably in the ratio of 1:4 (104). The use of more than one activator of the Lanthanide series is of interest from many points of view e.g.:-

(i) The physical and chemical conditions following the formation of efficient phosphors.

(ii) Sensitization.

(iii) Co-activation.

(iv) Structure and ionic state of the activator centers.

(v) Information regarding excited energy states.

(vi) Possible use in solid state lasers: - The spectral studies of rare earth elements in different bases are important because they have proved to be potential laser material (105). and

(vii) Infrared stimulability - Praseodymium shows infrared response in CaS host lattice (106).
Samples were prepared by the method developed in our laboratory (107). Test samples were prepared to find the duration and temperature of firing, the amount of flux and the amount of Ce and Di for the maximum intensity separately. Two series of samples were prepared; in one series the amount of Ce (optimum) was kept constant while that of Di was varied systematically and in the second series the optimum concentration of Di was kept constant and that of Ce was varied.

The following studies were performed:

(I) **Decay of phosphorescence**: The study of phosphorescence decay of these aforesaid phosphors was undertaken at room temperature. Then the values of decay constant, correlation coefficient and trap depths were evaluated from the curves. The decay constant was also evaluated after the phosphor was allowed to decay for specific periods.

(II) **Thermoluminescence**: The study of thermoluminescence was undertaken to check the information obtained from the decay study. Thermoluminescence was studied at three warming rates and the values of trap depths were evaluated from the peak temperature of the glow curves. These trap depths obtained were compared with those obtained from decay studies.

(III) **Emission Spectra**: The emission spectra both, fluorescence and phosphorescence, of these phosphors were recorded photographically at room temperature on a "Steinheil Spectrograph" after exciting the phosphors with ultraviolet light.
The intensity of band and lines at different wavelength were measured with the help of a Rapid microphotometer and attempts were made to identify the energy levels involved.

An attempt has been made to investigate the effect of activators on the distribution of the trapping states and to determine the nature of traps. The results from aforesaid studies have been correlated and examined in the light of the existing theories.

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