CHAPTER :: I

INTRODUCTION
1.1 GENERAL:

Solid state physics is mainly concerned with physical properties of solids, particularly the special properties exhibited by its atoms and molecules, because of their association in the solid phase.

One of the most important problems of solid state physics is luminescence, the description of processes following the absorption of radiation by a substance. Its history reveals the dominant role imperfections and small traces of impurities play in determining a specimen's behaviour with respect to electrical and optical properties. Imperfection or deviation from the general regular pattern of composition and structure of the solids is an essential requisite for the ability of materials to luminescence. The problem of imperfections is one of the extensively studied problems in solid state physics. This has led to the development of laboratory prepared specimens, far superior to those occurring in natural form, in purity and controlled addition of known impurities. Special attention should be given to the problem of reducing unwanted impurities to the minimum possible and controlled addition of desired 'impurities' in a particular sample perhaps in a particular position.
The practical use of the luminescence phenomenon, now a days, is very wide. It is commercially used in fluorescent lighting, cathode-ray tubes for radar and television, advertising paints, scintillation counters, solid state lasers, and image intensifiers.

1.2 DEFINITIONS:

(a) **Luminescence**:

Luminescence is a process by which, under the influence of an exciting agent, matter generates nonthermal radiation characteristic of a particular luminescent material. Following Wiedmann\(^1\) and Garlick\(^2\), 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.

(b) **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\(^{(2-8)}\).

(c) **Phosphors:**

Phosphors are generally structure and impurity sensitive
inorganic materials belonging to the general class of
electronically active nonmetallic solids. These can be further
divided into two classes:

(i) Those showing luminescence in the 'pure' state, and
(ii) Those showing luminescence in the presence of an
activating impurity.

Some workers prefer to classify them according to their
mode of decay and also on the basis of whether they are
photoconducting or nonphotoconducting\(^{(4,6,7,9)}\).

(d) **Activators:**

Activators are impurity or structure defects that provide
localized levels, permitting radiative transitions\(^{(10,11)}\).
(e) **Fluxes:**

Fluxes are readily fusible inorganic salts which melt below the firing temperature and provide a recrystallizing medium effecting the incorporation and homogenous distribution of activator in the host lattice\(^{(12-14)}\).

(f) **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\(^{(15-18)}\).

(g) **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\(^{(15,18-22)}\).

We may now classify luminescence into two categories, viz. (i) Characteristic Luminescence and (ii) Non-characteristic Luminescence:-

**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.

**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 \(^{(19)}\).

### 1.3 THEORETICAL MODEL FOR INTERPRETATION OF LUMINESCENCE PHENOMENA (ABSORPTION AND EMISSION):

Practically all interpretations of luminescence phenomena are based on a configuration 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 configuration coordinate model ignores the charge transport through the lattice while the energy band model neglects the atomic rearrangement that occurs during luminescence.

(a) **Configuration Coordinate Model:**

It was originally proposed by Von Hippel\(^{(23)}\), but Seitz\(^{(24)}\) applied this model for the explanation of characteristic luminescence process and since then it has been extensively used by Schon\(^{(25)}\), Maeda\(^{(26, 27)}\) and others\(^{(28, 29)}\).
Figure 1.1 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 (hγ) 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 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 (hγ') and final loss DA of more energy by vibrational interchange. Modification of this model, particularly proposed by Seitz (loc. cit.) and Dexter et al. (30) helps to explain the radiationless transition as well. In fact, this model along with its few quantum mechanical modifications successfully explains: (i) Stokes' shift, (ii) width of absorption and emission bands at low temperature, (iii) thermal quenching of luminescence and other temperature effects, (iv) monomolecular decay, (v) F-Centre luminescence and (vi) sensitization processes in doubly activated solids (25, 28, 31-37).

Its limitations are: (i) it cannot be applied to the processes occurring between absorption and final emission, e.g. photoconductivity, and (ii) precise configuration coordinate
diagrams on theoretical considerations only have not been possible in most cases\(^{(38,39)}\). A multidimensional model as opposed to the one dimensional one described above has also been suggested by some workers\(^{(27,40)}\).

(b) **Continuous Dielectric Model:**

In the configuration coordinate model the interaction between the centre and the lattice is restricted to the first and second nearest neighbours. An almost diametrically opposite approach was introduced by Huang and Rhys\(^{(41)}\) in considering the centre lattice interaction. They ignored the short range forces and computed the interaction of a centre with the total phonon field of the lattice. The interaction is an electrical one, and the development treats the centre as a static charge distribution embedded in a continuous dielectric. In absorption, the centre experiences a difference in charge distribution when the system jumps from the ground state to the excited state. This rearrangement in charge distribution induces, in turn, a change in lattice polarization which is accompanied by the creation of lattice phonons.

Huang and Rhys applied the method to the case of F centre absorption and non-radiative transitions. They assumed that the most important interaction is the long range longitudinal optical modes of vibrations. Lax\(^{(42)}\) further generalized their procedure by taking into consideration a more complex
centre and all modes of lattice vibration. The edge luminescence, as it is called, is associated with optical transitions in which the lines correspond to the simultaneous emission of 0, 1, 2, ... long wavelength optical phonons. Further refinements and extensions of this model have been made by a number of workers (43-45).

(c) **Energy Band Model:**

An energy band model based on the 'collective electron theory' of Bloch (46) has been developed by many workers to explain the long durational phosphorescence of photoconducting phosphors, mainly of sulphides and silicates (28, 36, 47-52).

Due to interactions with the crystal lattice, the discrete energy states of individual ions and atoms constituting the crystal are broadened into quasi-continuous bands separated by gaps of forbidden energies. Impurities introduced to produce luminescence give rise to discrete localized levels \( L \) in the forbidden gap, the ground state of each centre being occupied. Other impurities and lattice defects provide unoccupied levels \( T \) in which the excited electrons can be trapped.

Excitation may take place by photon absorption in the matrix lattice resulting in transition \( A \) (Fig. 1.2), i.e. an electron is raised to the conduction band leaving a hole
behind. The electron and hole, both being mobile and free to migrate, can give a current when an electric field is applied. In most cases, the probability of direct recombination of the conduction electron and the valence band hole is much less, and holes migrate to luminescence centres \( L \) and capture the ground state electrons, thus emptying the centres, and rendering them available for capture and recombination with conduction electrons. Thus, although the absorption is in the fundamental band of the host lattice, subsequent emission is characteristic of luminescence centres. In some cases, the lattice absorption produces electron-hole bound pairs (Transition B), i.e. excitons and no photoconductivity is observed under the action of an electric field. Radiation of less energy may be absorbed by the impurity centres and the resulting transition may then be to an excited state \( L' \) of the centre or to the conduction levels (Transitions C & D). Emission then takes place due to the return of the centre from the excited state to the ground state or to the recombination of the conduction electron and the hole left at the centre. Some electrons in the conduction band will be 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 centres. Transition \( E \) of electrons from the filled band directly into the trapping state may also take place due to absorption, holes then
Fig. 1.2 - Jablonski's Diagram Illustrating Fluorescence and Phosphorescence Mechanisms

Fig. 1.2 - Energy Band Model and Various Transitions in Absorption and Emission
migrating to the luminescence centres and emptying them. Trapped electrons may be raised to the conduction band (Transition F) due to absorption of radiation giving rise to an absorption band in the long wavelength region. Similarly, electrons may be raised into emission centres (Transition G) from the valence band with the absorption of energy. Such centres are then no longer available for recombination with conduction electrons and lead to the quenching of luminescence (53-59).

1.4 TYPES OF LUMINESCENT SYSTEM:

Luminescent systems have been divided into following categories:

(a) Systems in which absorption and emission of energy take place in the same centre.

(b) Systems in which absorption and emission of energy take place in different centres, the transfer of energy from absorbing to the emitting centre taking place without the movement of charge carriers.

(c) Systems in which transfer of energy is predominantly by the movement of charge carriers.

(A) Such systems are best treated by the configuration coordination model and the continuous dielectric model. The centres involved are localized ones and the emission process
is best represented by the simple diagram (Fig. 1.3) in which F, G and M are excited, ground the metastable states respectively of the luminescence centre. Fluorescence is given by the transition $F \rightarrow G$ but the excited centre may relax to the metastable state M. Transition $M \rightarrow G$ being forbidden; return to the ground state G is conditioned in rate by the thermal process $M \rightarrow F$ and probability of this transition is

$$p = s \exp(-E/kT)$$

where, $s$ is the frequency constant, $E$ is the thermal activation energy, $k$ Boltzmann's constant and $T$ the absolute temperature (60).

(B) There are three different mechanisms of such transfer:

(i) **Cascade mechanism:**

It is a radiative transfer of energy through the emission and reabsorption of photons. The necessary and sufficient conditions for this mechanism are: (1) If $X$ and $Y$ are two luminescence centres, then the absorbing centre $X$ shall transfer part of the absorbed energy to the second centre $Y$; (2) The spectral distribution of $X$ must overlap significantly with the absorption spectrum of $Y$; and (3) The absorption band associated with $Y$ must be of appreciable intensity.
We then call \( X \) and \( Y \) as the sensitizer (S) and the activator (A) respectively. If \( X \) is an impurity, we speak of impurity sensitization and if it is the host lattice itself, we speak of host sensitization. Absorption in the sensitizer \( X \) gives rise to the emission characteristic of \( Y \) and the transfer efficiency of this process depends on the size and shape of the specimen as well as on the type of exciting radiation.

In inorganic solids, one frequently deals with the activators having forbidden transitions where condition (3) is not usually satisfied. We then have to consider another mechanism, called resonance transfer.

(ii) **Resonance transfer:**

In contrast to the conditions necessary for cascade mechanism, the species \( X \) need not be an activator even in the absence of \( Y \). Further, the absorption constants in the absorption of \( Y \) may be small because the optical transitions involved are forbidden ones. Nevertheless the luminescence spectrum of \( Y \) is efficiently excited by the radiations absorbed by \( X \).

Alkaline earth sulphides containing heavy metals and rare earths were the first known examples of impurity sensitized phosphors among the inorganic phosphors\(^{61,62} \). However, more detailed experimental study of energy transfer
has centred around the Mn-activated phosphors (63-69).

The efficiency of energy transfer from sensitizers to activators is not strongly dependent upon temperature, in general. The dependence of transfer efficiency on sensitiser-activator separation and on the relationship between the energies involved in the optical transitions in both impurities have been investigated to understand this process in detail (67,69,70). Dexter (71) generalized the earlier transfer theories and extended them to cases involving forbidden transitions. The approach is a classical one but makes use of the quantum condition $\varepsilon = h \gamma$. He derived different formulae for the sensitiser-activator transfer probability, $p_{sa}$, for dd, dq and exchange interactions.

(iii) **Exciton migration:**

Energy transfer has also been explained in terms of the propagation of an excitation through the lattice. This process being sensitive to presence of surface states, transfer over large distances is possible only in the case of pure and defect-free crystals at low temperatures (71-74).

Host-sensitized luminescence has received very little attention in inorganic systems, despite the insight it gives into energy transfer processes. To some degree, this situation is due to the difficulty of selecting suitable systems for study. Sm-activated tungstates and molybdates of the alkaline
earths, zinc and cadmium, and the recently studied alkali halides are the only inorganic systems in which host-sensitization has been demonstrated and studied extensively. The theory of impurity sensitized luminescence is likewise applicable to host sensitization with the obvious difference that sensitizer-sensitizer transfer is an important process and the high sensitizer concentration allows one to achieve an appreciable absorption coefficient even if the transition in sensitizer is of the magnetic dipole type. Host-sensitization can also be considered from the point of view of the propagation of an exciton through the lattice\(^{(69,71,75-77)}\).

The theory of resonance transfer also explains the concentration quenching and the absence of luminescence in pure crystals\(^{(78)}\).

When the activator concentration in a singly activated phosphor increases beyond a certain value, luminescence efficiency generally decreases. This phenomenon is known as concentration quenching. It can be explained by assuming that the proximity of a given activator or to certain types of lattice defects increases the probability of a radiationless transition in the activator by lowering the activation energy for such a transfer\(^{(79-81)}\). Dexter and Schulman\(^{(78)}\), however, assume the resonance transfer of energy from activator to activator until it arrives at an activator near one of the energy sinks. Activator-quenching transfer then occurs and
the energy is lost. It is further proposed that the absence of luminescence in most unactivated 'pure' crystals is the result of rapid resonance transfer of excitation energy to the imperfections. For crystals like tungstates, in which transfer occurs by exchange, 'self-trapping' of the exciton can occur (78).

(C) Energy can also be transferred from one point to another by the movement of excited electrons and holes. The most intensively studied zinc-cadmium-sulpho-selenide system belongs to this class, and luminescence in such systems is determined more by the host lattice than by the activators. Many characteristics of such photoconducting phosphors have been explained by the storage action of electron traps. Three different models have been proposed for such systems.

(i) Schon-Klasens' Model; (Fig. 1.4)

It assumes the luminescence centre to be normally occupied and situated close to the valence band. Absorption in the matrix produces a free electron in the conduction band and a hole in the valence band: (1) of which the latter diffuses to the centre; (2) and captures the electron located there; (3) the conduction electron then diffuses to the centre giving off luminescence (4).

This model successfully explains various related phenomena such as doubly activated phosphors, traps, temperature
SCHON AND KLASFNS MODEL:

1. Excitation.
2. Hole migration.
3. Hole capture (non-radiative)
4. Electron migration.
5. Electron capture resulting in Luminescence.

FIG. 1.2.
quenching of phosphorescence and effect of poisons \((48, 50, 82)\).

(ii) **Lambe-Klick Model**: (Fig. 1.5)

Schon-Klasens' Model fails to account for the difference in decay constants of phosphorescence and photoconductivity. To overcome this difficulty, Lambe and Klick proposed this model in which the occupied luminescence centre lies slightly below the conduction band. Fundamental absorption produces an electron and a hole \((1)\). The hole then diffuses to the centre \((2)\) and captures the electron \((3)\) giving rise to luminescence. The conduction electron then diffuses to the centre and is captured \((4)\). Increase in photoconductivity by infra-red radiation as well as stimulation of activator emission by irradiation in the quenching band are also explained by this model \((83-87)\).

(iii) **Williams-Freener Model**: (Fig. 1.6)

The impurities involved in luminescence produce acceptor and donor levels which have high hole and electron capture probabilities respectively (levels I & II). Absorption produces a free electron and a hole which are captured by the appropriate levels \((A, B)\) and emission then takes place due to the transition from level II to I \((C)\). This model successfully explains the temperature dependence of fluorescence and photoconductivity and also the steady state luminescence \((88-94)\).
LAMPE AND KLICK'S MODEL.

1. Excitation.
2. Hole migration.
3. Hole capture resulting in Luminescence.
4. Electron migration.
5. Electron Capture (non radiative)

FIG. 1.5.
WILLIAMS AND PRENER’S MODEL.

A- Hole Capture.
B- Electron capture.
C- Transition of Electron from level II to level I giving emission.
1.5 METHODS OF STUDYING LUMINESCENCE:

The luminescence phenomenon being complicated in nature, its various properties and aspects have to be studied together to understand the different mechanisms involved in a phosphor system. A brief account of some of these is given below:

(a) **Absorption**: Absorption spectrum helps in determining the different radiative transitions responsible for emission\(^{(5)}\).

(b) **Excitation**: It is intimately connected with absorption. The excitation spectra though qualitative in nature, provide an understanding of the fundamental processes involved in luminescence\(^{(5,6)}\).

(c) **Emission**: Emission spectra depend on a number of preparative parameters and are useful from theoretical as well as practical points of view. Whereas fluorescence spectra yield information regarding the energy levels of the activators, phosphorescence spectra yield information about the trapping states.

(d) **Stimulation and quenching**: These are most useful when dominant and auxiliary activator systems, such as Sr\(_3\) (Eu, Sm) are used and provide valuable clues regarding the nature of traps\(^{(59,95)}\).

(e) **Decay and Thermoluminescence**: These characteristics are most useful and the two together provide useful information
regarding the kinetics involved, nature of traps, trap-depths and their distribution, retrapping, size of traps and the position of activator ions in the host lattice.

(f) **Slow build-up curves**: These are useful for identifying the deep traps\(^{(96)}\).

(g) **Photoconductivity**: These measurements help in determining the electron and hole trap-depths as well as the life-time of charge carriers\(^{(97,98)}\).

(h) **Photodielectric effect**: This effect can be considered as another manifestation of photoconductivity and adds new information to our knowledge of trapping states, particularly the deeper ones\(^{(99,103)}\).

(i) **Electron emission from phosphors**: This phenomenon is closely related to thermoluminescence and provides information about the trapping states when parallel measurements are made with luminescence\(^{(104-107)}\).

(j) **Electrophotoluminescence**: With the recent developments in crystal growing techniques, electrophotoluminescence has provided a more precise means of studying the release of trapped electrons\(^{(108-113)}\).

(k) **Magnetic properties**: Paramagnetic resonance helps in detecting and characterizing the defects and impurities present in phosphors, exploring the band character of single
crystals and provides information regarding the valence state of paramagnetic ions, localized electrons at trapping states and kinetics of fluorescence and phosphorescence (20,114-118). Susceptibility measurements throw light on the ionization state of the activator and can be used to elucidate the role of flux used in the preparation of phosphors and to verify Kroger's theory of charge compensation (119-125).

(1) X-ray studies: These are helpful for characterizing the commercial phosphors and give insight into the structural differences and the dependence of emission characteristics on them (126,127).

(m) Polarization: Spectral studies carried out with polarized light and measurement of the polarization of emitted light give information about the symmetry of lattice defects comprising the centre (128).

1.6 THE PROBLEM UNDERTAKEN:

Alkaline earth sulfide phosphors are one of the earliest known luminescent materials. Though deceptively simple in structure, which have since been found as having all kinds of hidden possibilities, this class of phosphor lapsed into oblivion because of the marked decline of practical or commercial interest in them, occasioned mainly by their instability under excitation and atmospheric conditions.
However, with the discovery of infrared stimulation and sensitization, interest in these phosphors has been revived and more and more investigations are being undertaken in an attempt to understand their luminescence fully.

Investigations of these phosphors in the form of microcrystalline powders have been undertaken for the last few years in this laboratory. The present work forms a part of this general programme.

Much work has not been undertaken on mixed host phosphors. It is well known that by changing the activator in a given host, the fluorescence emission shifts from one end of the visible spectrum to the other. There is a possibility of emission control by having a particular activator in a graded mixture of two hosts. This will be possible only if a solid solution of the two hosts is formed. The fluorescence emission from lattices containing two cations for example Zinc-Cadmium, Calcium-Barium is continuously displaced as the concentration of one cation increases relative to the other. Smith(129) has investigated manganese activated Zinc-Cadmium phosphates. The results have been explained in terms of structure change by Fonda(130). CaS-SrS (Sm) phosphors have been studied by Rumpf, Travnicek and others(131-135). They find evidence of solid solution with corresponding changes in the lattice constants.

In the present investigation, mixed phosphors of Calcium
sulphide and Strontium sulphide with copper as activator are studied. The phosphors with Calcium sulphide and Strontium sulphide mixed in ten different (varying) ratios as base material and copper as activator (concentration 0.1%) were therefore prepared for the present study. The following properties were studied:

(i) Decay and Thermoluminescence
(ii) X-ray and Solid Solution Study
(iii) Emission

(i) To study the effect of graded mixture of hosts on trap distribution in these phosphors, the decay and thermoluminescence characteristics of these phosphors were investigated. By using Chen's formula, (in T₁) 's' values were computed. Also the trap depths were estimated using Chen's formulae and also that of Randall and Wilkins.

(ii) X-ray studies were undertaken to investigate the possibility of solid solution formation and also to study the changes in lattice constants, if any.

(iii) The emission spectra of phosphors were obtained by photographic-photometric method. From the emission spectra, an energy level scheme of the copper centre in the mixed base containing CaS and SrS, is inferred.

Attempts have been made to correlate and explain all the results so obtained and to suggest a plausible model for the luminescent system.
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